

Structure and properties of states containing strongly-correlated disorder



Alistair R. Overy

Jesus College, Oxford

A thesis submitted to the University of Oxford for the degree of Doctor of Philosophy

Inorganic Chemistry Laboratory

Trinity Term 2018

The work presented in this thesis was carried out between October 2014 and June 2018 in the Inorganic Chemistry Laboratory, University of Oxford and Diamond Light Source. This research was supervised by Prof. Andrew Goodwin, Dr. Philip Chater and Dr. Matthew Tucker. All of the work presented here is my own unless explicitly stated otherwise and has not been submitted previously for any degree at this or any other university.

Alistair Richard Overy

June 2018

Structure and properties of states containing strongly-correlated disorder

Alistair R. Overy, Jesus College

D.Phil., Trinity Term 2018

Understanding of material properties has traditionally emerged from an appreciation of the ordered atomic structure. As such, the development of functional materials has focussed on crystalline systems. Correspondingly, structural disorder is often considered as a motif to avoid, as any desired physical response is believed to be diminished by its presence. The work presented in this thesis aims to challenge this paradigm by showing that, in the presence of particular types of strongly-correlated disorder, useful characteristics are accessible that are not possible in their ordered counterparts.

Here, a new class of disorder, the procrySTALLine state, is introduced. These disordered phases are derived from a generalisation of ice-rules, wherein a combination of a high-symmetry topological template and low-symmetry building unit produces aperiodic configurations. Indeed, there are numerous types of procrySTALLine phases—*i.e.* where different topological templates and building units have been considered. Subsequently, many well-known examples of disordered systems from a wide-variety of scientific fields, beyond those associated with ice, are shown to map onto procrySTALLine configurations including dimer states, polyhedral tilings, the triangular Ising antiferromagnet and the inaugural ferroelectric, BaTiO₃. Furthermore, it is demonstrated that procrySTALLine disorder can be characterised using common experimental methods such as microscopy, pair distribution function data and diffuse scattering signatures in powder and single crystal diffraction patterns.

Initially, the work in this thesis is focussed on understanding the changes in the vibrational spectra due to procrySTALLine disorder. These systems lack the translational symmetry that is axiomatic to conventional lattice dynamical methods, so here, the supercell lattice dynamical (SCLD) method is developed. This approach enables the explicit effect of disorder on the phonon dispersion curves to be determined. Subsequently, the SCLD method is applied to a variety of procrySTALLine models, revealing that in the presence of certain types of correlated disorder, phononic band gaps emerge. Importantly, these features are not present in the vibrational spectra of either a randomly disordered state, or the associated average structure (virtual crystal approximation). Moreover, procrySTALLine models are also shown to ‘break the rules’ of conventional lattice dynamical theory, as a disordered decoration with an average structure containing a single atom in the parent unit cell generates an unconventional and unexpected band gap. Analogous effects are also demonstrated to occur in both the electronic and photonic band structure of procrySTALLine states, where the opening of band gaps is directly correlated with the electronic conductivity and optical properties of these materials. Finally, the effect of disorder on the mechanical properties of one-dimensional fibre packings is investigated, which somewhat surprisingly concludes that the introduction of topological disorder has the potential to increase the swelling response of these structures.

Acknowledgements

I would like to begin by thanking my three supervisors—Prof. Andrew Goodwin, Dr. Philip Chater and Dr. Matthew Tucker. Their guidance, enthusiasm and inspiration over the past few years has been invaluable. I am particularly appreciative of how well-matched they are as a supervisory unit, both in their collective patience and the independence they have given me. The work presented in this thesis would not have been possible without their support. I am especially thankful to Andrew for offering this opportunity to me (a synthetic organic chemist) in the first place without which, this DPhil never would have even started.

If there could possibly have been a fourth supervisory role, it would surely have been filled by Arkadiy. I am extremely grateful for the time and effort he put in on my behalf, especially during my first encounters with lattice dynamics, photonics, Python and Blender. In this respect I would also like to thank Emma and Phil M in particular for the numerous mind-bending discussions on lattice dynamics and the inner workings of GULP.

For specific portions of the work presented in this thesis I would like to thank: Alison Martin for helpful discussions of her weaving topologies (Chapter 1); Matt Cliffe and Andrew Cairns for originally devising the procrystal project (Chapter 3); Prof. Peter Slater for involving me in the oxyfluoride work (Chapter 3); Philip Chater and Andrew Cairns for conducting the oxyfluoride and $\text{Pd}(\text{CN})_2/\text{Pt}(\text{CN})_2$ refinements, respectively (Chapter 3); Carl Romao for performing DFT calculations (Chapter 5); Emma Wolpert for her assistance in generating the disordered α -Po supercells (Chapter 5); Raj Pandya for all his preliminary work in determining the swelling ratio of fibre entanglements (Chapter 6) and Arkadiy Simonov for his help in developing the SCLD method (Chapter 4), determining swelling ratios and tackling Blender for the disordered spaghetti figures (Chapter 6). I am also extremely grateful to Harry Geddes, Emma Wolpert, Chloe Coates and Carl Romao who kindly gave up their time to proof-read this thesis.

I would like to acknowledge the Diamond Light Source, Jesus College, IUCr, Keith Prout fund and the ERC for financial support throughout this DPhil. A huge thanks also goes to the ARC and their staff for access to, and support in using, the supercomputing service at Oxford.

I realise that I have been immensely lucky to have been surrounded by such an amazing set of people during my eight years in Oxford. First and foremost, I am grateful for the Goodwin, Tucker and Chater group members both past and present who have been instrumental in supporting me throughout this DPhil. I would particularly like to thank Phil M, Arkadiy, Carl, Phil W and Emily for collectively answering thousands of stupid questions over the years, who along with Harry, Emma and Peter have kept me (moderately) sane both throughout the research and the writing up process. Additionally, to those out at ISIS and Diamond especially Clare, Dean, Dom, Phoebe, Simone, Michael, Matt, Beth, Lewis and Giles for all their advice, cups of tea and pub lunches. I am also indebted to those who have inspired me and provided important advice to me during this DPhil including Robin Perutz, Julia Dshemuchadse, Charlotte Williams and especially Martin Jones and Grandpa who encouraged me to apply for a DPhil with Andrew four years ago.

To my friends outside of work, thanks for all your support and the much needed distractions. Gemma and Minh, who have been amazing company all the way through my time at Oxford since our first days as undergrads. Will and Jon for taking me on a trip round Europe while I wrote this thesis. Dylan, Julie, Thomas, Jack, Stefan and Chris for all the good times we had living in Cowley. The Trinity and St. Peters students for being such a fun group to teach that it barely felt like work. And of course, Nick, Will, Mike, Preid and Tsgabu for the constant distraction of cycling chat, board games and pub quizzes—long may it continue.

Finally, I have been incredibly fortunate to have been accompanied throughout this process by Alison. Thank you for all your love and support, for encouraging me, caring about my research and always listening to my ramblings. You have been so caring and accommodating, especially when I was writing up. I only hope I can do the same for you.

Dedicated to Prof. Evelyn Ebsworth

Contents

1	Introduction	1
1.1	The structure-property paradigm	2
1.1.1	Reciprocal space	3
1.1.2	Dynamics	7
1.1.3	Electrical conductivity	19
1.1.4	Magnetic properties	23
1.1.5	Photonic properties	24
1.2	Aperiodicity	28
1.2.1	Ordered aperiodicity	31
1.2.2	Disordered aperiodicity	37
1.3	Motivation and aims of this thesis	59
2	Methodology	62
2.1	Scattering theory	62
2.1.1	Bragg scattering	63
2.1.2	Diffuse scattering	64
2.2	The Monte Carlo algorithm	69
2.2.1	Optimisation processes	71
2.3	Lattice dynamical theory	72
2.3.1	Derivation of the dynamical matrix	72
2.3.2	Properties of the dynamical matrix	75
2.4	General Utility Lattice Program	77

2.4.1	Structural optimisation	77
2.4.2	Lattice dynamical simulations	78
2.5	Photonic theory	79
2.6	MIT Photonic Bands	83
3	The procrySTALLine state	85
3.1	Generalisation of ice rules	86
3.1.1	Square ice	86
3.1.2	Square ice analogues	86
3.1.3	Generalisation of ice-like disorder	88
3.1.4	Methodology for generating ice-like states	90
3.2	The procrySTALLine state	93
3.2.1	Definition of procrySTALLinity	93
3.2.2	Nomenclature	97
3.2.3	Entropy	97
3.3	Realisations of procrySTALLine phases	100
3.3.1	Ices	100
3.3.2	KH_2PO_4	101
3.3.3	Loops and dimers	102
3.3.4	Self-assembly of TPTC molecules	104
3.3.5	Oxyfluoride phases	107
3.3.6	$\text{Pd}(\text{CN})_2$ and $\text{Pt}(\text{CN})_2$	110
3.3.7	BaTiO_3 and KNbO_3	112
3.3.8	The phase behaviour of BaTiO_3 and KNbO_3	115
3.4	Discussion	118
4	Supercell lattice dynamics	120
4.1	Introduction	120
4.2	The SCLD method	124

4.2.1	Unit cell lattice dynamical and SCLD approaches	127
4.3	Case study 1: Random disorder	129
4.3.1	Mass disorder	129
4.3.2	Bond strength disorder	131
4.4	Case study 2: Correlated disorder	132
4.5	Discussion	139
5	Structure-property relationships in the procrySTALLine state	141
5.1	Introduction	142
5.2	Methodology	146
5.2.1	Description of models	146
5.2.2	Generation of models of correlated disordered states	147
5.2.3	The VCA model	150
5.2.4	Supercell lattice dynamical calculations	151
5.3	Phononic behaviour	152
5.3.1	ReO ₃ decoration	152
5.3.2	α -Po decoration	158
5.4	Electronic behaviour	162
5.5	Photonic behaviour	164
5.6	Dimer decorations	167
5.6.1	Vibrational behaviour	168
5.6.2	Photonic behaviour	169
5.7	Discussion	173
6	Extreme mechanical responses in disordered fibre entanglements	174
6.1	Rod packings	175
6.1.1	1D bundles	176
6.1.2	2D layered arrangements	176
6.1.3	3D interlaced packings	178

6.2	Swelling	180
6.2.1	Swelling of ordered topologies	181
6.3	Mechanical responses of disordered structures	182
6.4	Generation of fibre entanglements	185
6.4.1	Parent structure	185
6.4.2	Topological continuum of states	185
6.4.3	Consideration of local structure	187
6.4.4	Creating disordered entanglements	187
6.5	Identification of swelling behaviour	188
6.5.1	Initial structure relaxation	189
6.5.2	Determination of the most porous structure	189
6.5.3	Determination of the densest arrangement	190
6.5.4	Calculation of the swelling capacity	193
6.5.5	Topological stability	193
6.6	Results	195
6.6.1	Swelling ratio of ordered end members	195
6.6.2	Swelling ratio of disordered intermediate states	195
6.6.3	Robustness of the structural relaxation method	197
6.7	Discussion	201
7	Conclusions and future work	207
	Bibliography	210
	Appendices	227
A	Summary of procrySTALLINE states	228
A.1	Single crystal diffraction	228
A.2	ProcrySTALLINE notation, point symmetry and entropy	229
A.3	Known realisations and diffraction behaviour of procrySTALLINE phases	232

B	Supporting information for procrystalline refinements	271
B.1	BaFeO ₂ F	271
B.2	Pd(CN) ₂ and Pt(CN) ₂	271
C	Simulation details for electronic density of states calculations	276
D	The nomenclature of rod packings	277
E	Publications	279
F	Contents of the CD Appendix	329

Abbreviations

2θ	scattering angle (diffraction)
Γ , X, M, R	high symmetry reciprocal lattice points
$\text{\AA}$	Angstrom ($= 10^{-10}$ m)
a , b , c	reciprocal lattice vectors
ANNNI	axial next nearest neighbour Ising model
BCC	body-centred cubic
BP	blue phase (liquid crystals)
BZ	Brillouin zone
CCP	cubic close packed
CDW	charge density wave
CRN	continuous random network
DFT	density functional theory
DOS	density of states
EXAFS	extended X-ray absorption fine structure
FCC	face-centred cubic
GULP	General Utility Lattice Program
HCP	hexagonal close packed
HEA	high entropy alloy
INS	inelastic neutron scattering
IR	infrared
k	wave-vector

LCD	liquid crystal display
LO	longitudinal optic
MC	Monte Carlo
MCM	Mobil Composition of Matter
MOF	metal–organic framework
MPB	MIT Photonic Bands
NMR	nuclear magnetic resonance
NTE	negative thermal expansion
OIPC	organic ionic plastic crystal
PDF	pair distribution function
RCP	random close packing
RUM	rigid unit mode
RVB	resonant valence bond
SCLD	supercell lattice dynamics
SDW	spin density wave
SPB	supercell photonic bands
STM	scanning tunneling microscopy
TE	transverse electric
TM	transverse magnetic
TO	transverse optic
TPTC	<i>p</i> -terphenyl-3,5,3',5'-tetracarboxylic acid
VCA	virtual crystal approximation
XANES	X-ray absorption near edge structure
XDW	chiral density wave
ZIF	zeolitic imidozolate framework

Chapter 1

Introduction

Traditional crystallographic methods were established upon the ordered arrangement of atoms, where each three-dimensional crystal structure can be classified into one of the 230 possible space groups [1]. These classifications are used to predict physical properties—*e.g.* piezoelectricity and ferroelectricity [2]—and, as a result, the design of functional materials has often focussed on the optimisation of ordered structures [3, 4]. Disordered materials, however, contain aperiodic features which are unable to be fully encapsulated by conventional crystallographic descriptions [5, 6]. Furthermore, the relationship between the type/correlations of disorder and the resulting effect on physical properties can be subtle and particularly difficult to ascertain [7, 8]. Nevertheless, it is clear that disorder is crucial for certain functional properties, notable examples include dipolar disorder in ferroelectrics and thermoelectrics [9, 10], disordered metasurfaces in photonic devices [11] and the resonant valence bond (RVB) description of cuprate superconductors [12, 13]. As such, it is important to develop our understanding of the relationship between the form and correlations of disorder and its subsequent effects on material properties with a view to aid the design of advanced functionalities. Indeed, it is with this aim in mind that the work in this thesis is presented.

This introduction begins by detailing the link between crystalline order and physical characteristics, with a particular focus on collective properties such as the phononic, electronic and photonic band structures. Subsequently, the concept of aperiodicity is introduced, with the various categories and classifications of aperiodicity discussed together along with their interrelationships. Sections 1.2.1 and 1.2.2 expand on particular families of ordered and disordered aperiodicity, providing details such as their definition, their known influence on physical properties, and realisations that

have been identified both in synthetic and natural systems. Finally the motivation and aims of the thesis are presented in the context of the previous work discussed throughout this introduction.

1.1 The structure-property paradigm

The structure of materials is governed by a multitude of factors including size effects, stoichiometry, molecular shape, electronic effects (*e.g.* ligand-field stabilisation energy and Jahn-Teller distortions) and directional interactions (*e.g.* hydrogen bonding) [14–20]. As such, structure prediction is often very complicated, involving the competition of multiple low-energy phases [21, 22]. However, in simple cases there are clear correlations between, for instance, the local building unit and the three-dimensional structure formed. By way of example, the packing of weakly interacting spherical objects commonly form the face-centred cubic structure, and as such, chemical and physical analogues from the atomic to the macro-scale adopt the same arrangements including the solid phases of the noble gases [23–25], C₆₀ [26] and the human adenovirus [27].

These ordered structures are conventionally decomposed into a combination of a lattice, an infinite periodic array of points, and a basis—*i.e.* the atoms and molecules that decorate the lattice sites. Indeed, the combination of these two components determines the space group of the material—*i.e.* the collection of symmetry elements exhibited by the structure. The underlying lattice and associated space group of a given material has important implications for its collective physical properties. It is this paradigm which makes up the focus of this section—a discussion of the link between order, structure and properties such as vibrational spectra, electronic states, photonic behaviour (in meso-scale systems) and magnetic structure.

1.1.1 Reciprocal space

Each of the collective properties mentioned above involves waves made up of, for example, atomic motion or atomic orbitals. The calculation of waves within crystals, irrespective of their origin, makes use of the reciprocal lattice and the Brillouin zone. As such, before any discussion of collective properties can take place, it is necessary to first have an appreciation of reciprocal space and its associated terminology.

The reciprocal lattice

The periodic and infinite array of points that make up a lattice can be generated by discrete translations along the lattice vectors— $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$ —of any cell containing lattice points on the vertices. Or more simply, any lattice can be recreated through the combination of a unit cell containing lattice points, and the vector $\mathbf{R}$, where

$$\mathbf{R} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}, \quad (1.1)$$

and n_1 , n_2 and n_3 are integers. There are fourteen possible Bravais lattices in three-dimensional space, arising from a combination of the seven lattice systems with the possible centring types—*e.g.* a cubic lattice can be primitive, body-centred or face-centred [28]. The Fourier transform of these real space lattices gives another lattice in reciprocal space; however, the centring of the reciprocal lattice can be different than that of the real-space lattice. For instance, while a primitive cubic lattice in real space gives a primitive cubic reciprocal lattice, the Fourier transform of a body-centred cubic lattice generates a face-centred cubic counterpart, and vice-versa. Nevertheless, irrespective of centring, the reciprocal lattice can be treated in much the same way as for the real space lattice, where discrete translations of a cell make up the infinite array of lattice points:

$$\mathbf{R}^* = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*. \quad (1.2)$$

Here h , k and l are again integers but $\mathbf{a}^*$, $\mathbf{b}^*$ and $\mathbf{c}^*$ are the *reciprocal* lattice vectors, where

$$\mathbf{a}^* = 2\pi \times \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}, \quad \mathbf{b}^* = 2\pi \times \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{b} \cdot \mathbf{c} \times \mathbf{a}}, \quad \mathbf{c}^* = 2\pi \times \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{c} \cdot \mathbf{a} \times \mathbf{b}}. \quad (1.3)$$

Every reciprocal lattice vector is therefore perpendicular to a specific set of planes of real space lattice points. Moreover, the magnitude of the reciprocal lattice vectors are related to the inverse spacing between planes of lattice points in real space. This is particularly important as it is the reciprocal lattice that is observable in the diffraction patterns of crystal structures, evident in the Bragg scattering. As such, the Bragg peaks give information of the real space structure, such as the lattice parameters and the space group symmetry.

Bloch Theory

The relationship between periodicity and periodic properties is best understood through a reciprocal space approach, wherein an appreciation of Bloch theory is key [29]. Here, a periodic array of species (often considered to be electrons) is defined as a Bloch wave with a wavefunction of the form

$$\Phi(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r})u(\mathbf{r}), \quad (1.4)$$

where $\mathbf{r}$ is a position vector and $\mathbf{k}$ is the wave-vector, which encompasses both the direction and the wavelength of the Bloch wave as

$$|\mathbf{k}| = \frac{2\pi}{\lambda}. \quad (1.5)$$

In Equation 1.4, $u(\mathbf{r})$ is a function with the same periodicity as the crystal, often in the form of a periodic travelling wave

$$\mathbf{u}(\mathbf{r}, t) = \tilde{u} \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)], \quad (1.6)$$

where, $\tilde{u}$ and ω represent the amplitude and angular frequency of the wave. This approach is particularly powerful as it is applicable beyond the electronic states generated by periodic arrays of electrons but also to atomic vibrations (phononic states) [30], variations in spin orientations (magnetic states) [31], and the interaction of light with constructions of dielectric media on the mesoscale (photonic states) [32].

The Brillouin zone

Bloch theory and the concept of the Brillouin zone go hand-in-hand, as any two Bloch waves related by a combination of reciprocal lattice vectors have an identical effect on the crystal lattice in real space. So for a one-dimensional crystal a generalised wave-vector in reciprocal space, $\mathbf{k}(\mathbf{x})$:

$$\mathbf{k}(\mathbf{x}) = \mathbf{k}(\mathbf{x} + \mathbf{a}^*) . \quad (1.7)$$

As such, all travelling waves in real space can be described by the set of wave-vectors contained within the reciprocal unit cell, commonly known as the first Brillouin zone. In contrast to the common formalism in real space, the reciprocal lattice point in the first Brillouin zone is at the centre of the cell. The first Brillouin zone is then defined as the Voronoi-Dirichlet cell [33, 34] surrounding the central lattice point. The Brillouin zone therefore represents the volume enclosed by the planes which bisecting the region between the central lattice point and its neighbours [Fig. 1.1]. Correspondingly, the first Brillouin zone simplifies our understanding of generalised wave-vectors further, as $\mathbf{k}$ and $-\mathbf{k}$ give waves that are merely complex conjugates of each other. So only a subsection of the cell needs be considered to evaluate all independent wave-vectors.

Within the first Brillouin zone there are points and directions that are highly significant as they denote pathways of high symmetry. The most important point lies at the centre of the reciprocal unit cell, $\mathbf{k} = 0$. This point is commonly known as Γ

in Bradley-Cracknell notation, which in real space represents waves in which each unit cell is in-phase. For a primitive square reciprocal lattice there are two further high symmetry points of interest: (i) X, which represents the centre of the Brillouin zone edge and has two-fold rotational symmetry

$$\mathbf{k} = \left[0, \frac{1}{2}\right], \left[\frac{1}{2}, 0\right], \left[0, -\frac{1}{2}\right], \left[-\frac{1}{2}, 0\right], \quad (1.8)$$

and (ii) M which denotes the corner of the Brillouin zone with four-fold rotational symmetry

$$\mathbf{k} = \left[\frac{1}{2}, \frac{1}{2}\right], \left[-\frac{1}{2}, \frac{1}{2}\right], \left[\frac{1}{2}, -\frac{1}{2}\right], \left[-\frac{1}{2}, -\frac{1}{2}\right]. \quad (1.9)$$

Yet, each reciprocal lattice type has a different Brillouin zone, and so contains a unique set of high symmetry points and directions, and as such requires Bradley-Cracknell notation specific to it. The Brillouin zones and notation for the primitive, body-centred and face-centred cubic cells in real space (hence primitive, face-centred and body-centred in reciprocal space) are shown in Figure 1.2. The Brillouin zones and associated notation for all reciprocal lattices can be found in Refs. [35, 36].

Often the relationship between $\mathbf{k}$ and, for instance, the energy of atomic vibration is only shown and calculated along the high symmetry directions *e.g.* $\Gamma \rightarrow X \rightarrow M \rightarrow \Gamma$ for the two-dimensional square lattice. As such, the shape of the Brillouin zone will alter the allowed $\mathbf{k}$ -vectors and hence, how a wave is able to behave. It is this relationship that is key to this section: the underlying lattice of the ordered

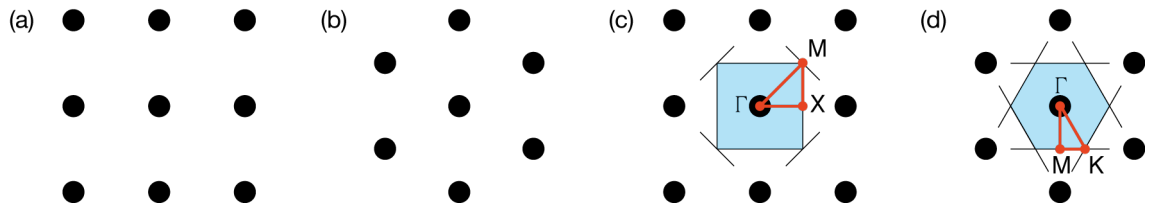


Figure 1.1: Construction of the first Brillouin zone. (a–b) The square and hexagonal lattices. (c–d) The corresponding first Brillouin zone (blue) can be determined through consideration of the Voronoi-Dirichlet cell around a given lattice point. The highly symmetrical directions and point are shown in red with their appropriate labels.

structure effects the lattice in reciprocal space, which in turn changes the Brillouin zone and so has consequences for the associated wave-like properties.

1.1.2 Dynamics

Perhaps the most obvious example of waves in crystal structures is that of atomic vibration. Viewing a crystal as a static arrangement of atoms is sufficient for explaining many physical characteristics of crystals such as chemical, electronic and optical properties [15, 37] as well as the neutron, electron and X-ray Bragg scattering [38]. Nevertheless, the static model is not able to account for all the properties of crystals, with thermal conductivity, phase transitions, thermal expansion and heat capacities remaining unaccounted for. So here, the dynamics of the lattice must be considered as well. The vibrational behaviour of structures is a key focus of this thesis and this section provides an overview of lattice dynamics and the impact it can have on the physical properties of materials.

Measuring phonons

Collective atomic vibrations in crystals are quantised into phonons, which are typically measured using inelastic neutron scattering. Here, the energies of neutron

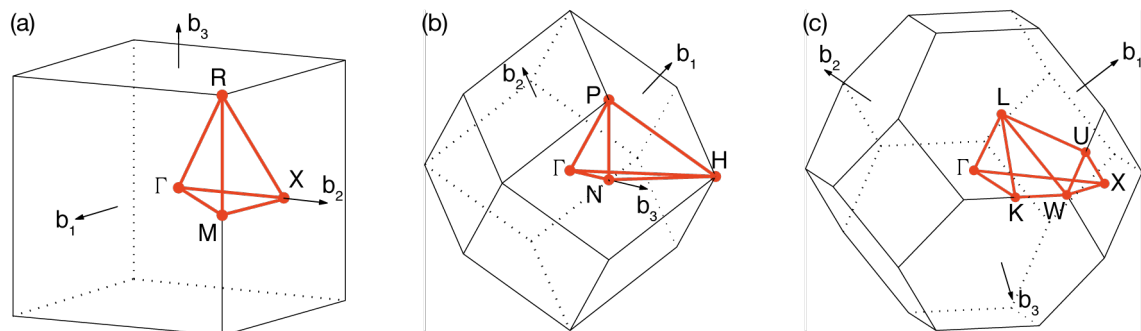


Figure 1.2: The Brillouin zones of the cubic lattices. The Brillouin zones of the (a) primitive, (b) body-centred and (c) face-centred cubic lattices in real space—so primitive, face-centred and body-centred lattices in reciprocal space. Highly symmetrical points and directions are highlighted in red. Reprinted from *Comp. Mater. Sci.*, **49**, W. Setyawan and S. Curtarolo, High-throughput electronic band structure calculations: Challenges and tools, 299–312, copyright 2010, with permission from Elsevier [35].

beams lie in the range of phonon frequencies—the modal energy of neutrons at 298 K is 0.025 eV—and the wavelength of the neutrons are of the order of atomic separation. Neutrons are particularly favoured for this type of measurement as they alone are able to determine the frequencies of all phonon bands throughout Brillouin zone, and hence a full phonon dispersion curve or phonon density of states [39].

The energy of selective lattice vibrations can be determined through other methods including the infrared absorption or Raman scattering—*i.e.* the interaction of the sample with an incident beam of light. However, in both cases only a subset of phonon frequencies at the zone-centre (Γ) is observable. In the case of infrared absorption the excited vibration must involve a change in dipole moment in the crystal whereas the complementary selection rule in Raman scattering requires the atomic displacements to change the crystal polarisability [39].

Phonon dispersion curves

Typically, the dynamical behaviour of a crystal is summarised in a phonon dispersion curve, where the phonon frequency, ω , is plotted against the wave-vector, $\mathbf{k}$, along the unique high symmetry directions of the Brillouin zone. The interpretation of dynamical data is greatly simplified by a few simple concepts that are true to all phonon dispersion curves [30]. Firstly, a structure containing Z atoms in a unit cell of κ dimensionality contains κZ vibrational modes at each wave vector—*i.e.* in a three-dimensional crystal each atom in the unit cell contributes three degrees of freedom, in keeping with classical mechanics. Within each phonon dispersion curve there are κ phonon branches for which $\omega \rightarrow 0$ as $\mathbf{k} \rightarrow 0$; these are known as the acoustic branches as the atoms in a unit cell move in-phase during the vibration. This leaves $\kappa Z - \kappa$ branches for which ω does not approach 0 as $\mathbf{k} \rightarrow 0$, which are known as the optical branches. Here, the atomic motion within a single unit cell is out of phase, and so the vibration is often of significantly higher energy, as bond lengths and angles are severely stretched and compressed [Fig. 1.3]. This is well

illustrated by simple examples: (i) a cubic crystal with one atom in the unit cell (*e.g.* α -Po) has no optical branches as a single atom in a unit cell can exhibit no phase within the unit cell itself but (ii) in the CsI structure—a primitive cubic unit cell containing Cs^+ at $(0, 0, 0)$ and I^- at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ —there are three optic branches as the two atoms in the unit cell can move out of phase relative to each other. Indeed, branches close to the limit of $\mathbf{k} = 0$ can be separated into two further classes by comparing the direction of $\mathbf{k}$ to the atomic motion. Here, waves with displacements parallel to the wave propagation vector are labelled longitudinal whereas waves with vibrations that are perpendicular are transverse modes.

A crucial result of lattice dynamics is that the frequency of a vibration is dependent on $\mathbf{k}$, leading to the construction of phonon dispersion curves. So how might the frequency and form of the phonon branches be affected? In the most general form

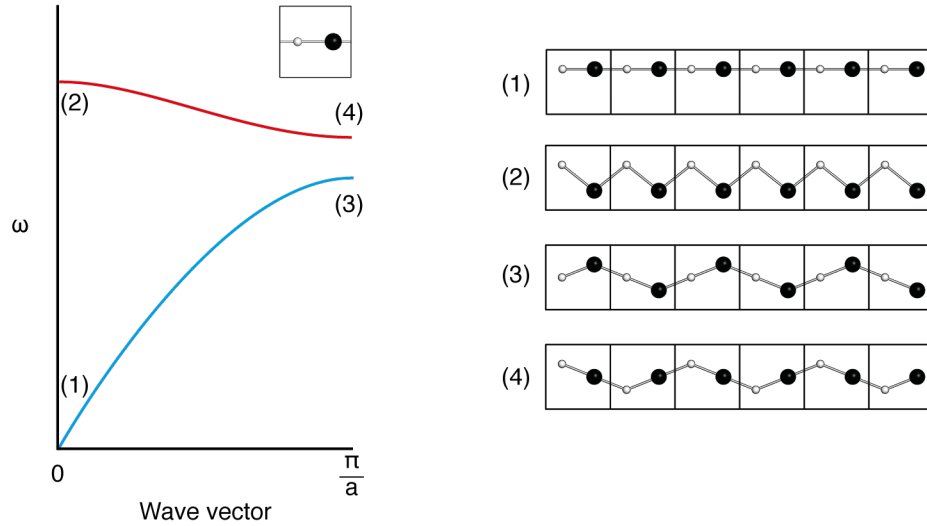


Figure 1.3: The phonon dispersion of a linear diatomic chain. A one-dimensional crystal with two atoms in each unit cell and displacement only in one axis must necessarily exhibit two phonon branches, one acoustic (blue) and one optic (red). Each point on the phonon dispersion curve (left) is associated with the energy and wavelength of an individual vibration. The form of some selected vibrations are shown (right).

there are three factors to consider: (i) the strength and form of the interatomic potentials; (ii) the atomic masses; (iii) the crystal structure. In general, the interatomic potentials and atomic masses are responsible for the energy scale; stiffer bonds and lighter atoms produce higher frequency phonon modes and steeper gradients, $dE/d\mathbf{k}$, for an acoustic mode approaching the zone-centre. However, the crystal structure itself changes the shape and form of the dispersion curves. As alluded to earlier, a different underlying lattice will necessarily change the associated Brillouin zone and so the respective shape of the phonon dispersion curves. Furthermore, the crystal structure is key in controlling the interactions of atoms. By way of example, factors such as the coordination number and local stereochemistry will be entirely dependent on the atomic arrangement.

All of these effects are nicely demonstrated by the phonon dispersion curves measured for the alkali metals (Li, Na, K, Rb) [Fig. 1.4] [40–44] and the solid phases of the noble gases (Ne, Ar, Kr, Xe) [Fig. 1.5] [45–48] or more appropriately: the noble solids. The reason for selecting these sets is twofold. Firstly, the sets adopt different structures—the unit cell of the former is body-centred cubic whereas the latter has a face-centred cubic structure—so within a given group the shape of the phonon dispersion will be the constant, but the two sets will appear different as reciprocal space is traversed in different directions and the coordinations spheres of atoms changes. Secondly, down the group the mass of the atoms increases (although not linearly) and the interatomic potentials such as Van der Waals forces will necessarily change as the atoms become generally softer down the group, resulting in a change in energy for a given phonon mode, $\omega(\nu)$.

Phonons and physical properties

The collective vibrations of atoms are responsible for many properties of solids. One of the best-known applications of lattice dynamical theory involves the heat capacities of solids. The room temperature values of the molar heat capacity, C ,

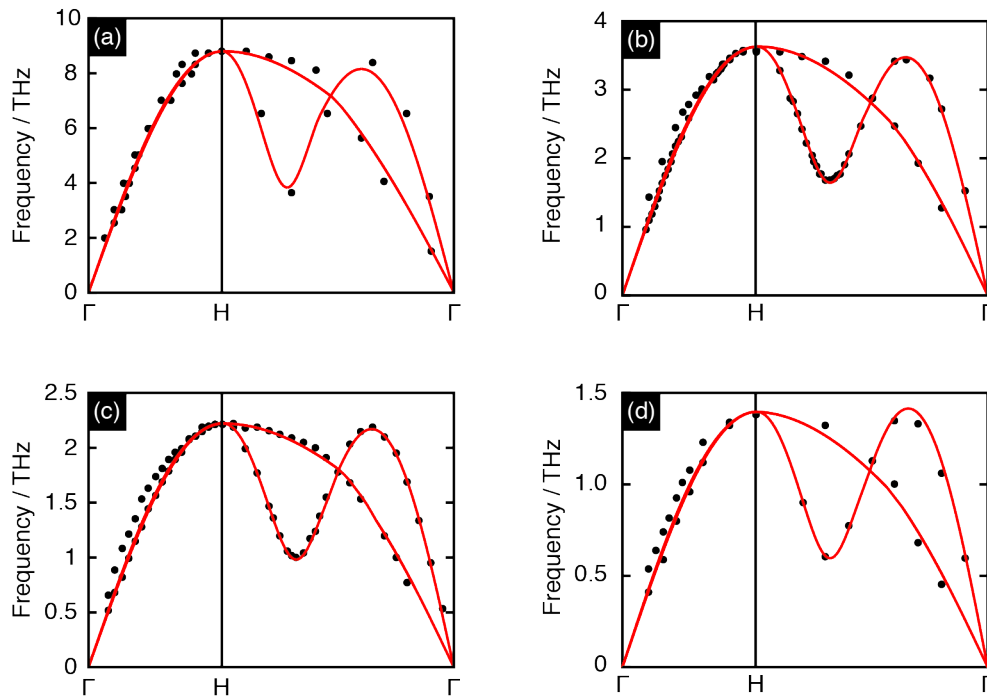


Figure 1.4: The phonon spectra of the alkali metals. The phonon dispersion curves of (a) lithium, (b) sodium, (c) potassium and (d) rubidium share the same form, albeit on different energy scales, as they all adopt the same BCC atomic structure but with different masses and interaction strengths. Experimental data (black points) is adapted from Refs. [40–44] with red lines included to highlight the similarities in the vibrational behaviour.

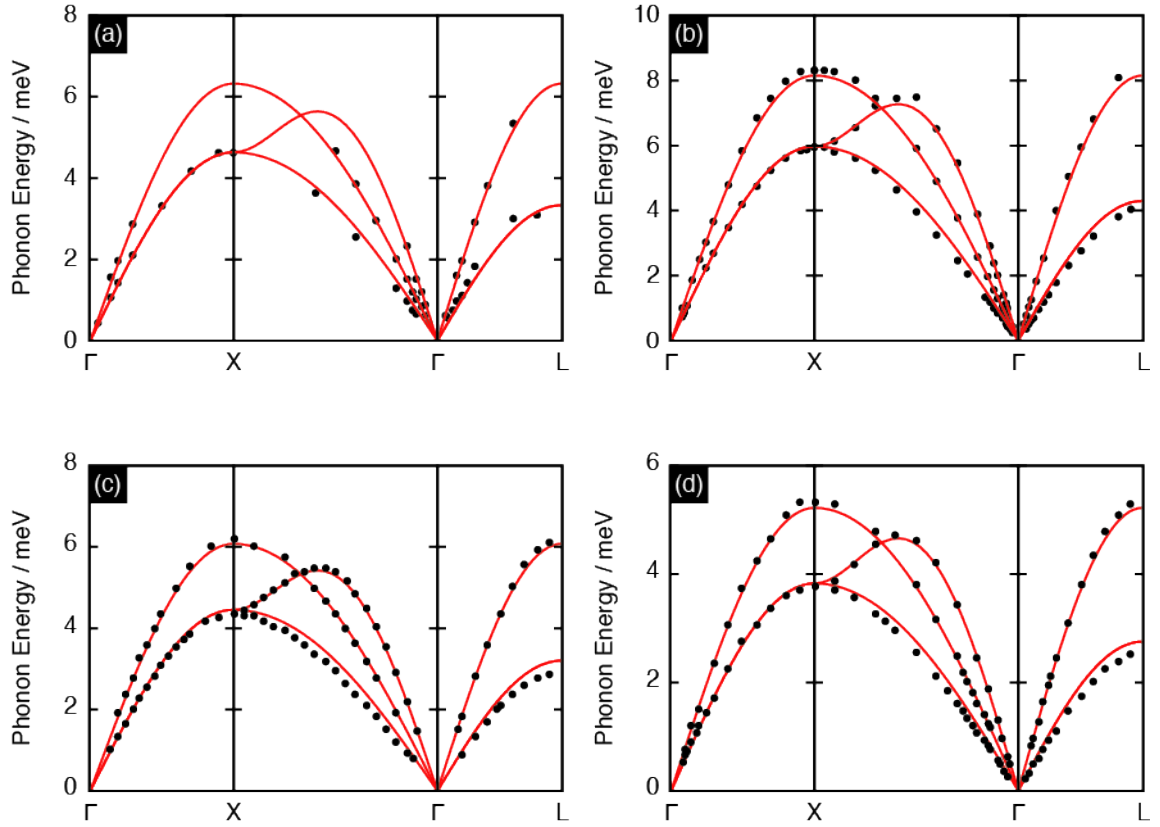


Figure 1.5: The phonon dispersion curves of the solid phases of the noble gases. The phonon spectra of the noble solids for (a) neon, (b) argon, (c) krypton and (d) xenon are presented. The form is constant, but clearly different to that of the alkali metals as these systems crystallise in an FCC array. Again the change in mass and interaction strength determines the energy scale of the vibrational states. Experimental data (black points) is adapted from Refs. [45–48] with red lines included to highlight the similarities in the vibrational behaviour.

for monatomic solids lie in a narrow range (22–30 J mol⁻¹K⁻¹) forming the basis of the Dulong-Petit law [49]. Classically, this behaviour can be explained using the equipartition principle, where solids are viewed as an array of independent harmonic oscillators vibrating in the x , y and z directions. Each axis of atomic movement contributes R to the total heat capacity resulting in $C \approx 3R = 24.942 \text{ Jmol}^{-1}\text{K}^{-1}$, where R is the universal gas constant [Fig. 1.6(a)]. According to classical mechanics the value of the heat capacity should be independent of temperature, yet this is not the case as $C \rightarrow 0$ as $T \rightarrow 0$, with a low temperature dependence of $C = \alpha T^3 + \gamma T$ where α and γ are constants [50].

The low temperature behaviour of C has been explained using two different lattice dynamical approaches—the Einstein and Debye models [Fig. 1.6(b)]. The Einstein model makes two key assumptions: (i) every atom in the lattice is an independent quantum harmonic oscillator in 3D; (ii) the atoms all vibrate with the same frequency. These assumptions result in the following expression for the heat capacity [51]:

$$C_V(T) = 3R \left(\frac{\theta_E}{T} \right)^2 \frac{\exp \left(\frac{\theta_E}{T} \right)}{\left[\exp \left(\frac{\theta_E}{T} \right) - 1 \right]^2}, \quad (1.10)$$

where θ_E is the Einstein temperature defined as

$$\theta_E = \frac{h\omega}{k_B}. \quad (1.11)$$

Here, ω is a quantity dependent on the bond stiffnesses and atomic masses, and so is unique to the solid. This approach correctly accounts for $C \rightarrow 0$ as $T \rightarrow 0$, yet the experimental values of C at low temperatures are still higher than that predicted by the Einstein model. This deviation arises from the assumptions of the model, namely that the atoms vibrate independently with the same frequency, an issue addressed by the Debye model. In this approach oscillations are viewed as collective, rather than independent, vibrational excitations. However, it is not efficient to include all phonon modes, as high frequency modes lie orders of magnitude higher than $k_B T$.

Instead, the Debye model assumes that the crystal can only support vibrations in the range $0 \leq \omega \leq \omega_D$, where ω_D is the Debye frequency for the system [52]. In the low temperature limit this is a sensible restriction as only the low energy phonon modes will be thermally accessible. The final form of the heat capacity in this model is as then follows

$$C = 3R \frac{3T^3}{\theta_D^3} \int_0^{\frac{\theta_D}{T}} \left(\frac{\theta_D}{T} \right)^4 \frac{\exp\left(\frac{\theta_D}{T}\right)}{\left[\exp\left(\frac{\theta_D}{T}\right) - 1 \right]^2} d\left(\frac{\theta_D}{T} \right), \quad (1.12)$$

which better represents the low temperature behaviour of C , while also reproducing the high temperature limit of $C = 3R$. Nevertheless, there are still oversimplifications within this model. The approach assumes all vibrations are harmonic and any curvature within the acoustic phonon branches is neglected. Moreover, the Debye temperature itself is assumed to be a parameter to be refined, such that the model well represents the experimental data over the suitable range of temperatures. In reality; however, interatomic potentials are not harmonic, which is a key factor

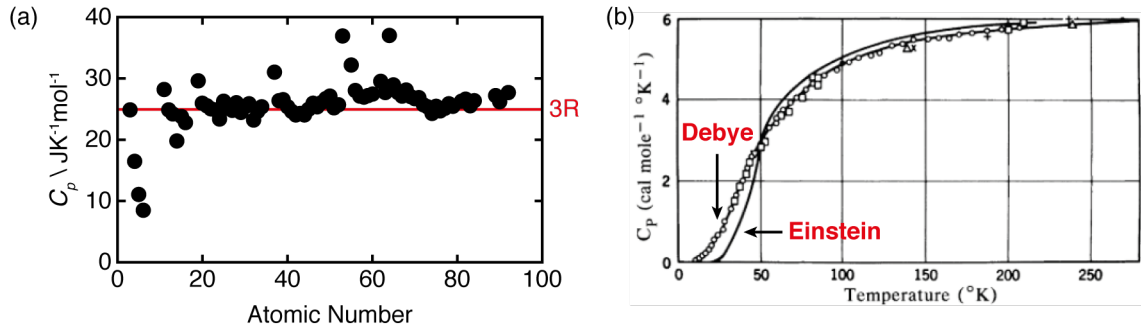


Figure 1.6: Heat capacities of monatomic solids. (a) The heat capacities measured for the elemental solids at room temperature fall in a narrow range around $3R$ —a result explained by the equipartition principle. Thermodynamic data for this figure were obtained from Ref. [53]. (b) Upon cooling the heat capacity of the solids decreases toward zero with a characteristic decay function as shown for Ag. Accounting for the lattice dynamics via two separate methods, the Einstein and Debye models, give good fits to the experimental data—where low temperature behaviour of the heat capacity is best represented by the Debye model. Reprinted from Solid State Physics, G. Burns, Some Thermal Effects in Solids, 365, copyright 1985, with permission from Elsevier [54].

in understanding the thermal expansion behaviour of materials. Anharmonic interactions are often fitted by more complex mathematical expressions, such as through the Morse or Lennard-Jones potentials [55, 56]. Here, vibrational excitation increases the internuclear distance due to the asymmetry of the potential well along the internuclear axis. In crystalline systems the excitation of phonons produces an analogous effect which contributes toward the thermal expansion of the solid, where the thermal expansion coefficient is defined as:

$$\beta = \frac{K_T \gamma C_V}{V}, \quad (1.13)$$

with K_T representing the isothermal compressibility, C_V the heat capacity at constant volume and γ the mean Grüneisen parameter where

$$\gamma = \frac{\sum_{\mathbf{k},\nu} \gamma_{\mathbf{k},\nu} \tilde{C}_{\mathbf{k},\nu}}{C_V}. \quad (1.14)$$

The individual Grüneisen parameter values, defined as

$$\gamma_{\mathbf{k},\nu} = -\frac{\partial(\ln \omega(\mathbf{k}, \nu))}{\partial(\ln V)}; \quad (1.15)$$

provide the effect of a given phonon mode on the volume of the crystal, whereby $\gamma > 0$ indicates positive thermal expansion [57]. As such, the mean Grüneisen parameter is weighted by the contribution of each individual phonon mode to the heat capacity at constant volume, $\tilde{C}_{\mathbf{k},\nu}$. Indeed, it is possible for phonon modes to exhibit $\gamma_{\mathbf{k},\nu} < 0$ which drive negative thermal expansion (NTE). In the event that the thermodynamically relevant phonon modes collectively exhibit $\gamma < 0$, then NTE is observed. This is the case for both ZrW_2O_8 [58] and $\text{Zn}(\text{CN})_2$ [59].

In network materials, so-called rigid unit modes (RUMs) are a subset of phonon modes wherein polyhedral structural features such as SiO_4 tetrahedra in quartz or BO_6 octahedra in ABO_3 perovskites move as undeformable objects which tilt,

twist and hinge about their shared vertices [60, 61]. Oftentimes, these modes are low in energy, and hence thermally accessible, as the vibrations do not stretch or compress bonds within a polyhedron. Moreover, these modes often exhibit $\gamma < 0$ —two connected polyhedra with a bond angle of 180° will necessarily be brought closer together on average, hence reducing volume, as the bond angle deviates from linearity [Fig. 1.7]. Indeed, it has been shown that RUMs contribute to the negative thermal expansion behaviour in materials such as ZrW_2O_8 [62, 63] and $\text{Zn}(\text{CN})_2$ [64].

An important corollary is that the network connectivity itself will play a key role in the thermal expansion behaviour of a given material—*i.e.* the connectivity determines the phonon modes, which in turn are responsible for the thermal expansion. Indeed, mechanical properties, in general, are well accounted for through phononic behaviour—*e.g.* the elastic modulus of a material is obtainable from the slope of the acoustic branches close to the zone-centre [2]. As such, the ordered structure of a material is a crucial factor in the design of functional mechanical responses of materials.

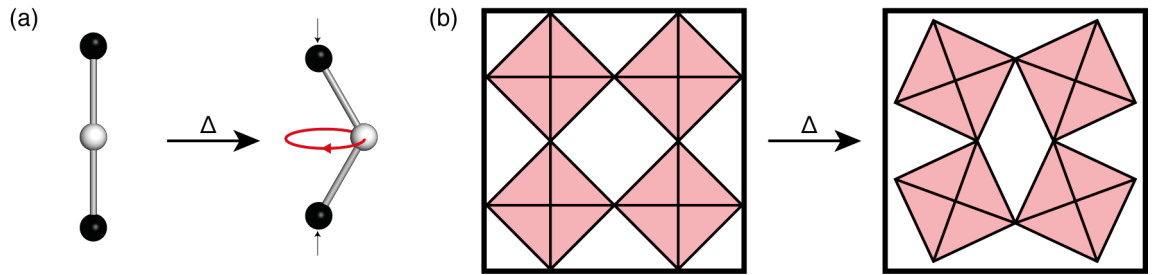


Figure 1.7: The relationship between rigid unit modes (RUMs) and negative thermal expansion. (a) An increase in temperature is necessarily accompanied by an increase in atomic motion. In the case that an atom is linearly coordinated, displacement of the central atom perpendicular to the bond axis while retaining the equilibrium bond lengths brings the terminal atoms closer together. (b) An extended network made up of rigid polyhedra can support collective vibrations consisting of the displacements described in (a). The polyhedra remain rigid as the bond lengths do not change and so is termed a rigid unit mode. Indeed, the vibrational mode decreases the overall volume of the network, as such, an increase in temperature will correspond to a more accentuated rigid unit mode vibration, and hence negative thermal expansion.

Anharmonicity also plays a key role in the thermal conductivity of a material [30]. In the harmonic limit, heat supplied at one end of a material will excite vibrational states which then transport the energy to the other end of the crystal unhindered—*i.e.* heat conduction is instantaneous. However, anharmonicity allows for phonon–phonon scattering events which can affect the heat conduction of a material, in what is known as an Umklapp process [65, 66]. These events reduce the lifetime of the phonons, which is reflected in the width of a phonon branches in the dispersion curves [67]. Again, this effect is dominated by the low-frequency phonon modes, especially those near the zone-centre, as these are the thermally accessible states.

Manipulation of the thermal conductivity is especially important in the development of thermoelectrics [68–71]. Thermoelectric materials convert a temperature gradient into an electric voltage, which is optimised through minimising thermal conductivity while maximising electrical conductivity [72]. Unfortunately, this is a somewhat conflicting design strategy as both properties are in general correlated, due to periodicity—a good electrical conductor such as copper is also a good thermal conductor. Correspondingly, considerable efforts are being made to understand materials in which the thermal conductivity is anomalously low, such as in PbTe where the low frequency phonon branches near the zone-centre broaden significantly in the so-called “waterfall” effect [73].

Phonons in crystalline materials also play a role in understanding other phenomena including superconductivity and ferroelectricity [30]. While the origin of high T_c superconductivity remains unresolved, Bardeen-Cooper-Schrieffer (BCS) theory has been developed to understand conventional superconductivity. Here, pairs of electrons at the Fermi level bind together at low temperatures to form a boson known as a Cooper pair [74, 75]. The attraction of electrons together to form a pair is unusual given the electrostatic repulsion between them. In simple terms, these states are believed to form via electron-phonon coupling, wherein the movement of a single electron couples to a lattice vibration, forming a weak positive charge in its

wake which attracts a second electron, to create the boson pair. Superconductivity is therefore proposed to be a result of the fact that bosons, unlike fermions, are allowed to occupy the same quantum state, resulting in a condensation of the pairs into the ground state with zero resistance to mobility [74, 75].

Conventional ferroelectric phase transitions are characterised by a loss of centre of symmetry in the unit cell to generate a microscopic dipole moment, which must collectively sum together to produce a macroscopic dielectric polarisation across the whole crystal [2]. These phase transitions are often driven by a phonon mode becoming frozen-in—*i.e.* the dynamical atomic displacement associated with a given mode becomes static [30]. Ferroelectric phase transitions are characterised by the phonon mode in question ‘softening’ or dropping in energy as the transition temperature is approached. Moreover, the frozen-in phonon must be associated with the Γ point to ensure that the microscopic dipole moments in each unit cell are aligned. By way of example, in PbTiO_3 the ferroelectric phase transition from a cubic to tetragonal distortion occurs at 760 K [76]. Each Ti^{4+} cation displaces in the [001] direction, away from the centre of its octahedral coordination environment, to break the centre of symmetry in the unit cell [77, 78]. However, it is important to note that a frozen-in zone-centre phonon is not necessarily associated with a ferroelectric phase transition as not all phonons at the zone-centre will break the centre of symmetry of the unit cell—*e.g.* the phase transition between the hexagonal and trigonal phases of quartz [79].

Correspondingly, a static vibration associated with the R point, $\mathbf{k} = [\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$, for a structure with a primitive cubic cell is described as an antiferroelectric phase transition as the displacements in neighbouring cells cancel out. Such phase transitions are not of strong interest to the ferroelectric community as no macroscopic dielectric polarisation can result. Nevertheless, many important phase transitions can be understood exactly in these terms. For example, if frozen-in, the rigid unit mode shown in Figure 1.7(b) describes the cubic to tetragonal transition in SrTiO_3 at 110

K in which the neighbouring TiO_6 octahdra in the (001) plane rotate in opposite directions [80, 81].

1.1.3 Electrical conductivity

Periodicity is also crucial in understanding the electronic behaviour of crystal structures. Here, the crystal orbitals—rather than atomic displacements—are viewed as waves. Crystal orbitals are infinite molecular orbitals which can be derived from a combination of the periodic atomic orbitals under the tight-binding model. The fundamental basis of chemistry lies in the interaction of these atomic orbitals, which can take place in a constructive or destructive manner depending on the relative signs of the wavefunctions of the orbitals. In an infinite crystal, these orbitals combine to form continuous bands between the limits of maximal constructive (lowest energy) and maximal destructive (highest energy) interference.

As with atomic vibrations, each of the crystal orbitals can be described by a wave-vector within the first Brillouin zone. By way of example, a one-dimensional array of atoms extending along the x -axis, the s -orbitals will overlap to produce a band where the lowest energy state (all orbitals in phase) is described by a wave-vector at the zone-centre whereas the highest energy crystal orbital lies at the zone boundary. Conversely, the p_x -orbitals switch the order of the energies. The angular node flips the sign of the p -orbital such that the lowest energy crystal orbital is now at the zone boundary and the highest at Γ . Unsurprisingly, the band constructed from s -orbitals will be lower in energy than that for p_x since the equivalent atomic s -orbital is lower in energy than p_x . Furthermore, the s -based band will also be wider—*i.e.* stretch over a larger range of energies—since the overlap of s -orbitals is superior to that of p_x , resulting in a stronger maximally bonding and anti-bonding interaction [Fig. 1.8].

Clearly, the crystal structure of a solid has an enormous effect on the electronic properties of a solid. Canonical examples such as the contrasting electrical conductance

behaviour of the two common allotropes of carbon (graphite and diamond) highlight the importance of this relationship. On the one hand, the stacked hexagonal layers of graphite are the archetypal semi-metal—there is no electronic band gap, but also no density of states at the Fermi level. On the other hand, an arrangement of carbon atoms in the diamond structure is a band-gap insulator, where the valance band is completely filled and the conduction band is empty, with a band gap of around 6 eV—*i.e.* orders of magnitude above $k_B T$ such that the conduction band is not thermally populated with electrons [Fig. 1.9] [82].

Indeed, different ordered arrangements of ions within the same structure type can also play a critical role in the conductive properties of a material. For instance in the case of the two spinels Fe_3O_4 and Co_3O_4 —with the general formula $[M^{2+}][M^{3+}]_2\text{O}_4$ —the arrangement of the two transition metal cations result in electrical conductivity in the former, while the latter is insulating [83, 84]. The two metal cations are commonly distributed in one of two arrangements in spinels, partially occupying the octahedral and tetrahedral holes of the CCP arrangement of O^{2-} anions. The

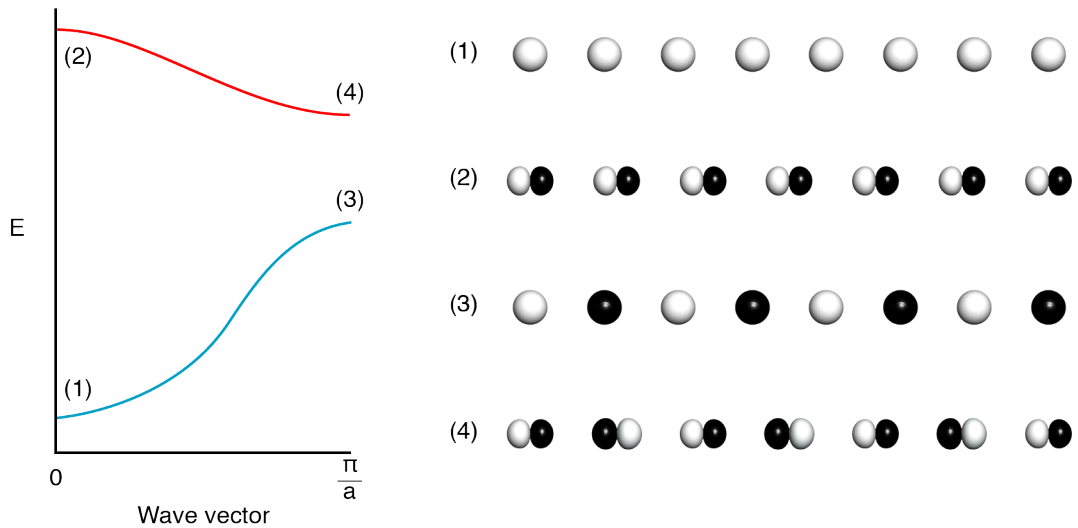


Figure 1.8: Electronic states described as waves. The interactions of atomic orbitals in a crystal under the tight-binding model determine the energy of the infinite crystal orbitals. The energy of the crystal orbitals is dependent upon the energy of the atomic orbitals, their extent of overlap, and the wavelength of the crystal orbital wavefunction (left). Representative crystal orbitals labelled on the dispersion plot of electronic states are also shown (right).

coordination environments of the cations in both the normal spinel and the inverse spinel are summarised in Table 1.1. In all cases, half of the octahedral and one-eighth of the tetrahedral sites are occupied by metal cations. The choice of either the normal or inverse spinel structure is influenced by ligand-field stabilisation energy considerations, wherein the ion with the largest ligand-field stabilisation in an octahedral coordination preferentially occupies the octahedral site.*

The two spinels Co_3O_4 and Fe_3O_4 adopt the normal and inverse spinel structure types respectively, as Co^{3+} and Fe^{2+} have an affinity for the octahedral site, due to the highly favourable low spin $t_{2g}^6 e_g^0$ configuration in the former and $t_{2g}^4 e_g^2$ in the latter. As such, Fe_3O_4 has mixed valency on the octahedral site whereas in the cobalt analogue the two coordination environments are occupied by ions of different oxidation states. In terms of conductivity, the iron spinel can facilitate electron migration from Fe^{2+} to a neighbouring Fe^{3+} across the octahedral edge with minimal energetic penalty. However, any charge transfer in Co_3O_4 is between species in different coordination environments, and as such, involves a large penalty

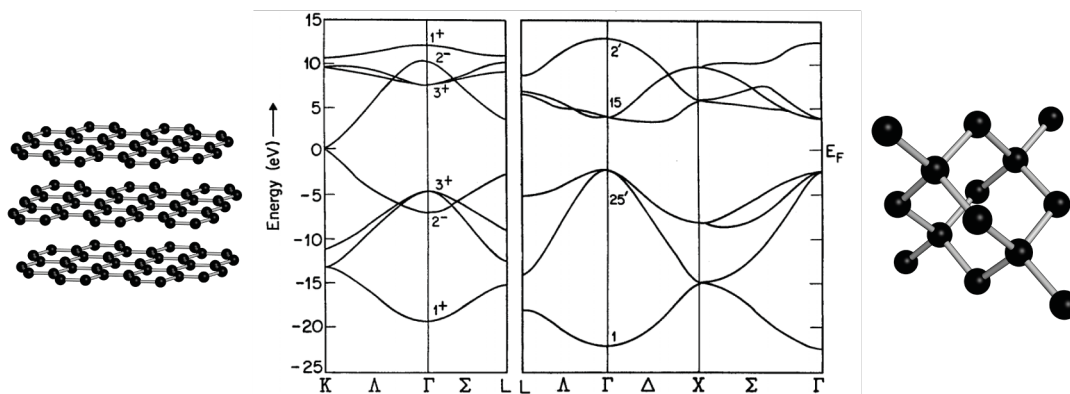


Figure 1.9: Electronic properties and crystal structure. The electronic band structures for graphite (left) and diamond (right) are shown. In neither structure is there a density of states at the Fermi level. In the case of graphite there is no electronic band gap, and as such this material is a semi-metal, whereas diamond is a band gap insulator. Reprinted from *Prog. Solid State Chem.*, **21**, J. Robertson, Hard amorphous (diamond-like) carbons, 199–333, copyright 1991, with permission from Elsevier [82].

*Octahedral coordination invariably gives higher ligand-field stabilisation splitting than tetrahedral.

to the ligand-field stabilisation, introducing crystal strain. So, while the movement of electrons throughout the Fe_3O_4 crystal is facile, the arrangement of ions in Co_3O_4 results in an insulating material [85].

The Peierls distortion

The Peierls distortion illustrates an important example in which a subtle change in periodicity alters the bulk material properties. In particular, this phenomenon is introduced here as there is a strong conceptual relevance between the Peierls distortion and the electronic behaviour of disordered states presented in Section 5.4. In simple terms, the Peierls theorem states that a one-dimensional equally-spaced chain of atoms is unstable with respect to a phase transition, if the valence band is half filled [86]. Over the transition the spacing between the atoms is altered, such that each atom moves closer to one of its two neighbours. These displacements occur in a periodic fashion, associated with the wave-vector $\mathbf{k} = [\frac{1}{2}]$. The size of the unit cell is doubled along the chain direction, effectively creating a periodic chain of dimers. The occurrence of this dimer state is accompanied by a change in the electronic properties, either because the system transitions into a Mott-Hubbard insulator—*i.e.* the electrons are localised within the dimers—or due to the formation of a band-gap insulator with delocalised electrons but with $n(E_F) = 0$ [Fig. 1.10]. In the latter case, the Peierls transition stabilises the system by creating an electronic band gap in which the occupied crystal orbitals decrease in energy, not unlike that observed in the Jahn Teller distortion commonly observed with Cu^{2+} and Cr^{2+} complexes [87]. Experimentally, these periodicity-induced metal to insulator transitions are

Table 1.1: Occupancy of sites within the normal and inverse spinels

	Coordination— Normal Spinel	Coordination— Inverse Spinel
M^{2+}	T_d	O_h
M^{3+}	O_h	O_h, T_d

observed in a wide array of chemical systems. In VO_2 and NbO_2 the Peierls transition results in metal-metal bonding [88, 89], whereas in single chains of polyacetylene [90] and in the charge transfer salt tetrathiafulvalene-tetracyanoquinodimethane (or more commonly TTF-TCNQ) the distortion is exhibited by alternating single and double bonds between carbon atoms and dimerisation of each of the components of the charge transfer salt, respectively [91].

1.1.4 Magnetic properties

Similar links between order and physical properties are also observed in the field of magnetism. At sufficiently low temperature, periodic arrays of atoms or ions with magnetic moments can form magnetic structures that exhibit long-range or-

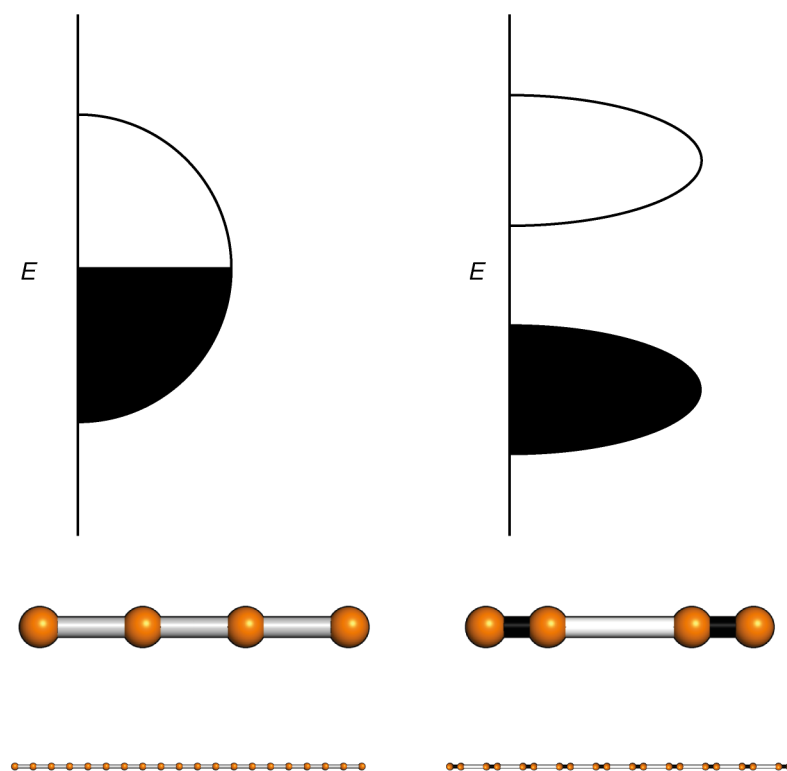


Figure 1.10: The electronic effects of the Peierls distortion. An equally spaced array of atoms in a one-dimensional chain with a half-filled electronic band (left) can distort in such a way as to dimerise and electronically stabilise the system (right).

der. Here, the magnetic structure is encompassed within a magnetic unit cell, which may deviate from the structural unit cell. Indeed, the nature of the ordering of the magnetic moments may vary from very simple, such as ferromagnetic [92] or antiferromagnetic order [93], to much more complex and requiring a large magnetic unit cell—*e.g.* helical [94]. A summary of these magnetic states is provided here as a contrast to the frustrated magnetic states discussed in Section 1.2.2 and Section 3.3.4. Obviously, magnetic ordering will clearly effect the macroscopic properties of a material. Interacting Ising spins decorating the square lattice typify this behaviour via simple ordering processes such as ferromagnetic or antiferromagnetic interactions, which cause neighbouring spins to align or anti-align respectively [Fig. 1.11]. In the case of the former, all the spins collectively sum together to produce a macroscopic magnetic moment; however, in the latter the magnetic ordering results in a state with no net magnetisation. Here, the magnetic unit cell for the ferromagnetic interaction is equivalent to that of the structural unit cell, while the lattice parameters for the equivalent magnetic unit cell of the antiferromagnetic structure are doubled in both directions. Yet, the local interactions are taking place between single atoms in neighbouring unit cells, so in this case the ordered magnetic structures may also be described via a combination of the structural unit cell and an appropriate wave-vector applied to the spin vectors, where $\mathbf{k} = [0, 0]$ and $\mathbf{k} = [\frac{1}{2}, \frac{1}{2}]$ represent the ferromagnetic and antiferromagnetic structures respectively.

1.1.5 Photonic properties

The collection of properties discussed thus far are derived from the ordered arrangements of atoms or molecules. However, the concept of periodicity-property relationships stretch beyond the atomic scale. On the mesoscale, periodic arrays are often obtained in one of two ways. Colloids and nanoparticles can form ordered arrangements often through self-assembly. Commonly, these are driven solely through entropic considerations. Here, an ordered arrangement actually increases overall

degrees of freedom for the system by allowing each individual component a cavity in which it can translate [95, 96]. Enthalpic effects can also direct the assembly through for instance the presence of binding of groups grafted to a particle surface *e.g.* DNA-functionalised colloids [97]. Alternatively, mesoscale periodic arrays may be created by etching [98] or “printing” onto a smooth surface through, for instance, lithographic methods [99]—where a highly focussed laser may be used to initiate a photochemical reaction to coat only specific portions of the surface.

So how does periodic order on the mesoscale relate to the physical properties of the material? Clearly, periodicity on the mesoscale will not affect the phononic or electronic characteristics of the material, as these properties rely on atomic arrangements. Moreover, the interaction with X-rays or neutrons will not be substantially altered either because the mesoscale periodicity is not a compatible length scale with the wavelength of the incident radiation. However, by way of analogy, the effective increase in lattice parameter in these systems will in fact cause these materials to interact with electromagnetic waves with larger wavelengths—*e.g.* visible light—and are therefore termed photonic crystals.

While a chemically crystalline material is made up of a periodic array of atoms, a

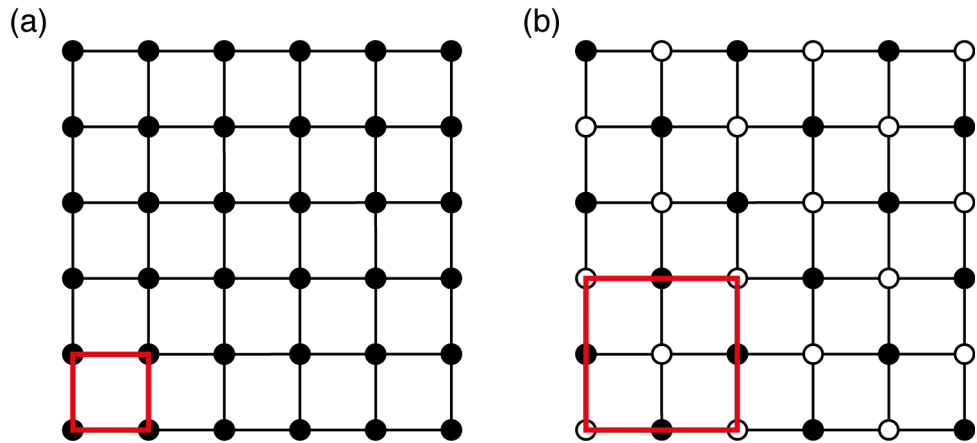


Figure 1.11: Order and magnetic structure. A decoration of Ising spins on the square lattice can exhibit two simple ordered forms through (a) ferromagnetic and (b) antiferromagnetic interactions. Here, white and black circles denote the spin state of the vector as ‘up’ or ‘down’ respectively and the magnetic unit cell in both cases is show in red.

photonic crystal is constructed from a periodic array of macroscopic dielectric media. In the case where the absorption of light by the photonic crystal is minimal, it is possible to characterise the electromagnetic modes of the system in the same manner as for the electronic or phononic states described earlier. Given the periodicity in a photonic crystal, Bloch waves and the Brillouin zone are again important, albeit on an inverse length scale orders of magnitude smaller than crystals on the atomic scale. While much of the analysis is similar to that of phonons and electrons, there are aspects that are specific to photonic band structure. In photonic crystals, modes can be categorised into one of two polarisation sets: (i) transverse electric (TE), where the magnetic component of the mode is normal to the incident plane while the electric field is in the plane of the photonic crystal and (ii) transverse magnetic (TM), in which the opposite is true—*i.e.* the electric component is perpendicular to the plane of the crystal [32]. The band structures for each of the two polarisations may exhibit large differences and often a different decoration of the photonic crystal will result in both sets of bands being altered [Fig. 1.12]. Furthermore, it is important to note that the location of the photonic band gap in frequency space is inversely proportional to the lattice parameter of the photonic crystal. As such, photonic properties are easily scalable and the frequency scale of the photonic band structure is often given in units dependent on the lattice parameter. Correspondingly, while a photonic crystal with a macroscopic unit cell ($a \simeq 1$ cm) may interact with microwaves, an analogous photonic crystal with a microscopic unit cell ($a \simeq 1$ μm) will exhibit the same behaviour for visible light.

Desired optical properties are often achieved through the manipulation of photonic band gaps. In much the same way that an electronic band gap defines a set of energies for which no electronic states exist, a photonic band gap describes the frequencies of light which cannot propagate through a material. This property is particularly desirable as it is the cornerstone of waveguide design—materials in which the propagating light, of speed c , is confined to a narrow frequency range—

and dielectric mirrors, which reflect only specific wavelengths of light [100]. It is possible to have individual band gaps within the TM and TE spectra—for example in the case of a photonic crystal made up of a square array of dielectric rods or veins respectively [Fig. 1.12]—yet a complete band gap is only achieved in the case where these individual band gaps overlap [32]. In such cases, the range of the complete band gap describes the frequencies in which no light can propagate through the material, independent of polarisation *or* incident angle. Complete photonic band gaps have been observed in both two- and three-dimensional periodic photonic crystals including a triangular arrangement of air columns in a dielectric block [32], and dielectric spheres arranged in either an fcc or diamond arrangement [101]. Yet, factors beyond the decoration within the unit cell are also important to the generation of gapped states. The dielectric contrast and the size of the holes/sphere relative to the lattice parameter also alter the photonic spectrum, to the extent that a change in sphere radius or dielectric media can cause the band gap to vanish.

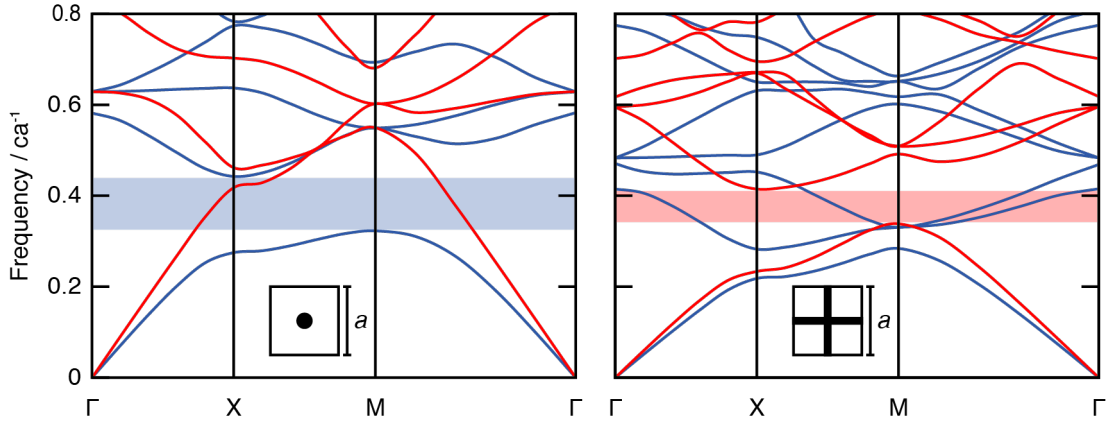


Figure 1.12: Photonic states in periodic media. The photonic dispersion curves are shown for a periodic square array of rods (left) and veins (right) with $\epsilon_r = 8.9$, embedded in air where $\epsilon_r = 1$. The columns and veins have an associated radius/width equivalent to 20% of that of the unit cell parameter, a . Gaps (shaded areas) are observed in the transverse magnetic modes (blue) but not in the transverse electric modes (red) for the periodic array of rods, while the opposite is true in the case of veins.

1.2 Aperiodicity

Since the existence of a well-defined unit cell with translational periodicity is a fundamental cornerstone of conventional crystallography, it is natural to ask how materials lacking in these respects are currently understood. The absence of translational periodicity invariably means that there is no conventional space group symmetry. However, that is not to say that conventional crystallographic methods provide no information. The exact nature of the broken periodicity is often obtained through analysis of: (i) Bragg scattering, which gives a representative average structure of the material, often with non-integer occupancies; (ii) diffuse scattering, the broad diffraction features which are directly related to the disorder correlations in reciprocal space [102]; (iii) pair distribution function (PDF) data, which provide information of the atomic pair-wise correlations in real space [103, 104].

There are numerous classes of aperiodic materials as the structural features responsible for aperiodicity can have many different origins, correlations and signatures both in real and reciprocal space. Nevertheless, while each individual class of aperiodicity is often considered independently, that does not necessarily mean that conceptual parallels or relationships cannot be drawn between them. By way of example, quasicrystalline and incommensurate modulated phases are two distinctly separate classifications of aperiodicity; yet, in both cases, the diffraction behaviour shows only a combination of single point (Bragg) and thermal diffuse scattering [105, 106]. Correspondingly, despite both classifications being aperiodic, there is no contribution to the diffuse intensity arising from disorder. This instantly separates them from, for instance, amorphous states and glassy materials which, in contrast, exhibit diffuse scattering. As such, in this particular case it is convenient to make the distinction between the families (*i.e.* sets of aperiodic classifications) of *ordered* aperiodicity and *disordered* aperiodicity. A summary of these classifications and the relationships between them is presented in Figure 1.13. This graphic is intended

to provide a point of discussion rather than an exhaustive enumeration of aperiodic states and their connections. Indeed, the main goal of this illustration, and moreover this thesis, is to develop a framework to discuss aperiodicity in a more concerted manner than perhaps the initially isolated classifications might allow.

The aim of this section is to provide an overview of aperiodicity—especially the influence of aperiodicity on physical properties—to be viewed in contrast to the periodicity–property relationships detailed previously. It should be mentioned that, given the limitations of a single section in this thesis, a comprehensive discussion of each of these fields is impossible. Instead, this section is made up of discussions of specific classifications of aperiodicity with a focus given to areas which are either of great scientific importance or those particularly relevant to the results presented later in this thesis.

The language of aperiodicity

The terminology used to describe aspects of aperiodicity is especially under-developed and where it does exist, is often ill-defined [6]. In preparation for an in-depth discussion of non-crystalline structures it is important to give specific definitions to often imprecise and vaguely used language. In the context of this thesis, randomness is taken to describe a complete lack of correlation. Under such a definition, the only system to encompass true randomness in all aspects is that of the perfect gas, in which the particles have no excluded volume and do not interact in any way. Yet, this is not to say that particular aspects of a structure cannot be described as random, but rather that it is important to define exactly which aspects are truly random and which are not—*e.g.* a simulated model of a binary alloy (AB) can be generated wherein the A and B atoms are randomly distributed over the crystallographically ordered sites. The term disorder is fairly unspecific, for instance plastic crystals and ices are both states in which molecules are orientationally disordered, the difference lies in their correlations. Within this thesis, the

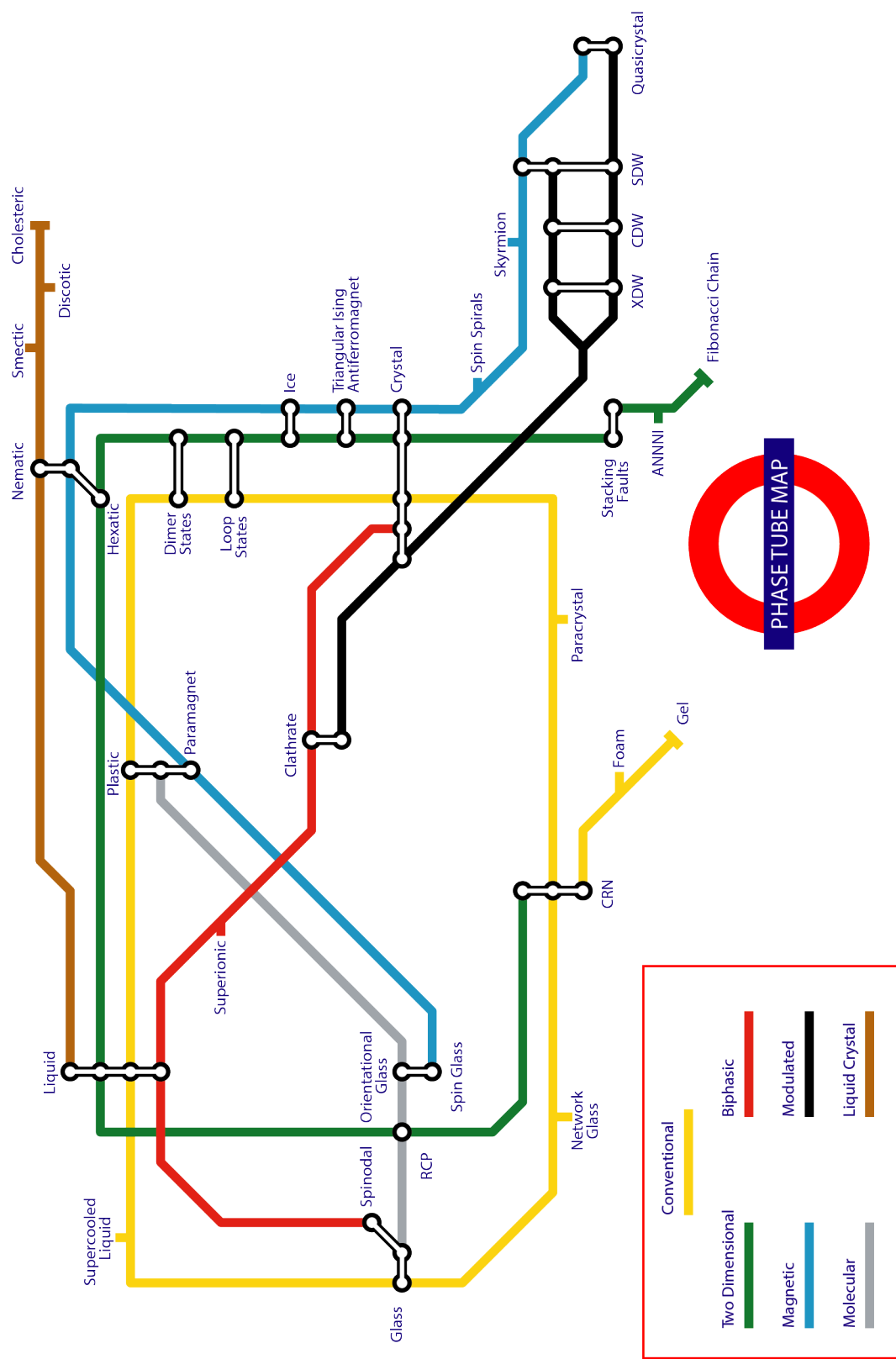


Figure 1.13: The phase tube map. A conceptual illustration highlighting the loose relationships between different categories of ordered and disordered condensed phases. Abbreviations: RCP—Random Close Packing, CRN—Continuous Random Network, ANNI—Axial Next Nearest Neighbour Ising Model, XDW—Chiral Density Wave, CDW—Charge Density Wave, SDW—Spin Density Wave.

terms weakly-correlated and strongly-correlated are used to help distinguish such states. Here, strongly-correlated disorder refers to a system in which the disorder is subject to strict constraints—*e.g.* local bonding rules in ice. Correspondingly, the term weakly-correlated disorder describes higher entropy states in which the disordered states are less restricted. For example, in a plastic crystal (weakly-correlated) the orientation of one molecule affects the orientation of its neighbours but does not constrain it; moreover, the allowed orientations are continuous as opposed to the discrete orientational states observed in ice (strongly-correlated). Indeed, a random state can be thought of as a particular subset of a disordered decoration: one in which there are no correlations. Correspondingly, in reciprocal space, disorder is characterised by the existence of diffuse scattering, both in its featureless and highly-structured forms, whereas a random state encompasses the boundary condition in which the least structured diffuse scattering is observed. As such, two structures described as disordered can be wildly different both in real and reciprocal space [6]. Consequently, throughout this thesis care is taken to give a full description of the features that give rise to the disorder and their associated correlations.

1.2.1 Ordered aperiodicity

As eluded to earlier, aperiodicity can be introduced in many different ways, the signature of which is expressed in the diffraction behaviour. The diffraction patterns of periodic materials exhibit periodic Bragg peaks with 1-, 2-, 3-, 4- or 6-fold rotational symmetry—*i.e.* only that which is commensurate with a repeating lattice. Ordered aperiodicity again only generates Bragg diffraction, where the scattering function is discrete rather than continuous; this restricts the breaking of translational symmetry to one of two principle classifications: (i) quasicrystallinity or (ii) modulated structures.

Quasicrystals

The discovery of quasicrystals was initially controversial as the diffraction behaviour seemingly broke the rules of conventional crystallography. The translational symmetry crucial to the crystalline state is broken by the existence of rotational symmetry which is incompatible with a crystalline lattice—such as 5-, 8- and 10-fold axes [Fig 1.14]. This phenomenon was first observed in Al-Mn alloys, which exhibit scattering behaviour inconsistent with that of conventional crystal structures [105]. However, all the reflections are sharp Bragg-like features, indicating that while there is not translational symmetry, the structure harbours no disorder. This juxtaposition was subsequently resolved by showing that the rotational order in quasicrystals emerges in the projection from a higher-dimensional representation [105].

The arrangement of atoms in certain quasicrystalline phases was found to provide an identical mapping onto the Penrose tilings established by Roger Penrose in the 1970s [109, 110]. These aperiodic tilings densely tile space, and can be divided into three

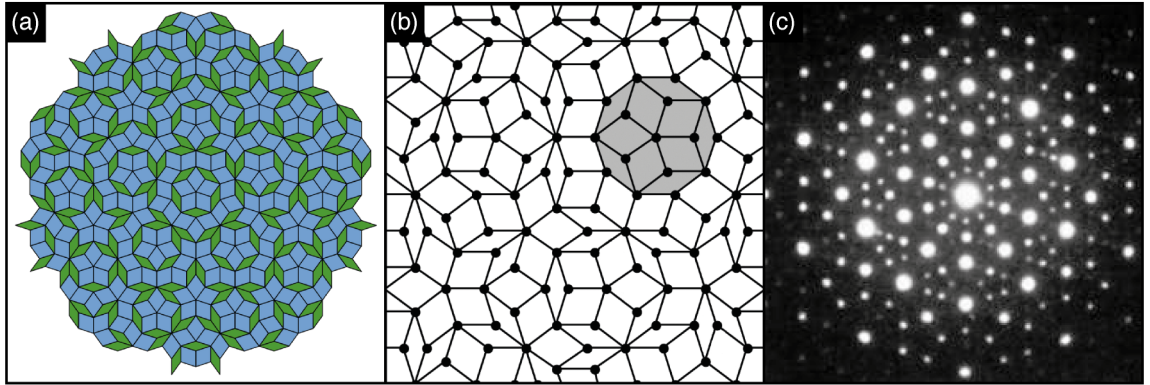


Figure 1.14: Quasicrystals and the Penrose tiling. (a) A representation of the P3 Penrose tiling containing thick (blue) and thin (green) rhombuses [107]. (b) A mapping between the Penrose tiling and the quasicrystalline state is realised when atoms occupy the vertex sites of the polyhedra. Reprinted by permission from Springer Nature: Springer Nature, *Nat. Photon.*, Optics of photonic quasicrystals, Z. V. Vardeny, A. Nahata and A. Agrawal, **7**, 177, copyright 2013 [108]. (c) The corresponding diffraction patterns of the quasicrystalline state exhibit rotational symmetry which is not commensurate with the crystalline state, in this case 10-fold symmetry. Reprinted figure with permission from D. Shechtman, I. Blech, D. Gratias and J. W. Cahn, *Phys. Rev. Lett.*, **53**, 1951–1953, 1984 [105]. Copyright 1984 by the American Physical Society.

distinct types by the shapes used in their construction. The first Penrose tiling (P1) is made up of four distinct units: pentagons, five-pointed stars, thin rhombi and boats (a star with two appendages removed). Contrastingly, the final two Penrose tilings are assembled from only two units: kites and darts (P2), or thin and thick rhombi (P3) [Fig. 1.14]. In each case, specific matching rules are used to ensure that certain local arrangements are disallowed. The overall tilings possess local five-fold rotational symmetry as each individual tile is related to the regular pentagon.

The relationship between the Penrose tilings and the golden ratio, $\phi = (1 + \sqrt{5})/2 \simeq 1.618$, is well-established [109]. The regular pentagon, from which the individual tiles are derived, is linked to ϕ via the ratio of the side and chord lengths. Correspondingly, it can be shown that in an infinitely large P2 or P3 tiling, the limiting ratio of kite to dart tiles, or thick to thin rhombi is ϕ .

The golden ratio is also closely associated with the Fibonacci sequence. Here, the ratio of successive Fibonacci numbers again yields values close to ϕ , and as such, the theoretical models of Fibonacci chains, lattices and crystals—extending in one-, two- and three-dimensions respectively—make up a subset of quasicrystalline phases—specifically those with pentagonal symmetry [111, 112].

The quasicrystalline phases initially observed in rapidly-cooled alloys have since been discovered in a wide range of materials including dendrimers [113, 114], nanoparticles [115], block copolymers [116, 117], colloids [118] and natural minerals [119]. Moreover, recent simulations have revealed that hard tetrahedra self-assemble into a dodecagonal quasicrystalline phase [120]. Here, the assembly is driven by a combination of entropic considerations and the shape of the individual units, wherein the alignment of polyhedral faces is preferred to maximise the translational and rotational degrees of freedom over the entire configuration. The discovery that such aperiodic complexity can be realised through these relatively simple factors provides a convincing explanation as to why quasicrystalline phases have been observed across such a wide variety of scientific fields.

The existence of rotational symmetry in the absence of a defined crystallographic unit cell has important implications for the properties of a material. Firstly, as translational symmetry is lost, there is no defined Brillouin zone and Bloch theory does not apply. As such, properties dependent on periodicity are severely dampened—the collective atomic translations associated with lattice dynamics are not applicable to the quasicrystalline state. Correspondingly, the transport properties of quasicrystals are similar to that of highly disordered glassy states, characterised by low thermal and electrical conductivity [121].

Moreover, there exist properties in the quasicrystalline state that are inaccessible in crystal structures. In particular the quasiparticle known as a phason describes the allowed local atomic rearrangements in a quasicrystal. These rearrangements are responsible for the difficulty in creating dislocations within these materials but also, when dislocations do exist, their ease of propagation [121]. As such, the study of phasons has helped to explain the mechanical properties of quasicrystalline alloys which have been found to be extremely hard, but also very brittle. Additionally, these materials are found to have low friction coefficients, as substances are not able to grip to a quasicrystalline surface efficiently, as there is no periodicity on the surface. Consequently, the applications of quasicrystalline materials have been focussed toward creating non-stick coatings and highly-resistive heat shields [122].

Modulated structures

In simple terms, modulation in crystal structures can be thought of as two or more independent periodicities coexisting within the same structure. This structural complexity can be further decomposed into two distinct types: (i) commensurate modulation, wherein the ratio of the two independent periodicities is rational, so the structure can be described by a finite supercell; (ii) incommensurate modulation, wherein the ratio of the two periodicities is irrational and so there is no unit cell which can be used to represent the structure. By way of example, a parent unit cell

is commensurate with a frozen-in phonon mode of $\mathbf{k} = [\frac{1}{4}, \frac{1}{4}, \frac{1}{4}]$ if the structure can be represented by a $4 \times 4 \times 4$ supercell; however, cooperative translations described by $\mathbf{k} = [\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}]$ would result in incommensurate modulation. Experimentally, modulation is expressed in the diffraction patterns as ‘satellite’ Bragg peaks at non-integer values of hkl ; for instance at $\frac{h}{4}, \frac{k}{4}, \frac{l}{4}$ for the commensurate example given previously [Fig. 1.15].

Of the two modulation types, only incommensurate modulation can be described as an aperiodic structure, as the complexity of commensurate modulation can be fully encapsulated within a supercell of finite size. These additional Bragg peaks cannot be indexed using three reciprocal lattice vectors, but the use of additional basis vectors is able to account for the extra periodicity and so allows for “conventional” indexing procedures.

Incommensurate modulation is commonly caused by competing structural driving forces that cannot be satisfied simultaneously. These structural driving forces can take many forms. As such, incommensurate modulation has been observed in a wide variety of crystal structures including oxides, host-guest structures and molecular

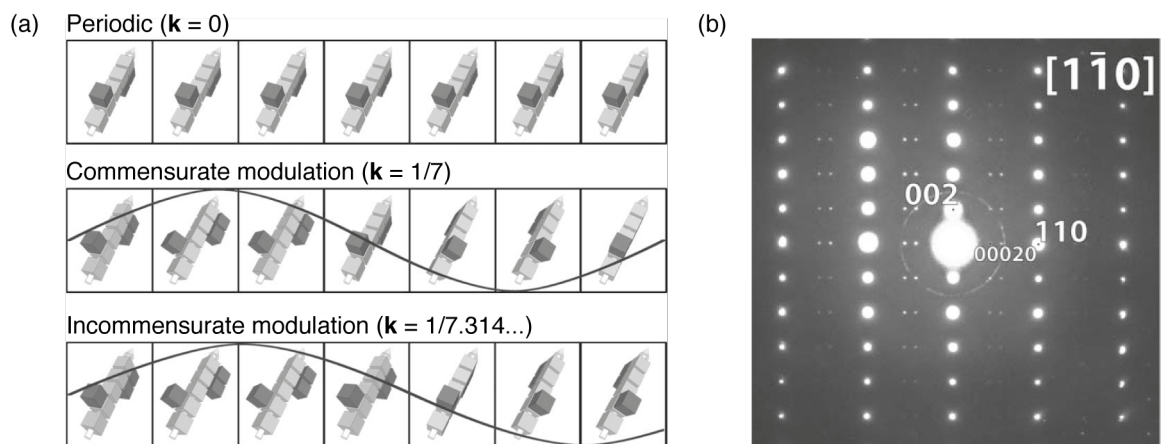


Figure 1.15: Modulation in real and reciprocal space. (a) A periodic toy molecule with static rotations of three different wave-vectors (0 , $1/7$ and $1/7.314\dots$) give crystalline, commensurately modulated and incommensurately modulated structures. Adapted from Ref. [123]. Reproduced with permission of the International Union of Crystallography. (b) In reciprocal space, the existence of modulation is characterised by the existence of satellite peaks—low intensity Bragg-like features—within the diffraction pattern. Adapted from Ref. [124].

crystals. In NaNO_2 , an incommensurate phase forms as a result of competition between dipolar ordering of the NO_2^- units and shear instabilities of the lattice [125]. Furthermore, ABO_3 perovskites (*e.g.* $\text{Li}_{3x}\text{Nd}_{2/3-x}\text{TiO}_3$ and $\text{Bi}_{0.75}\text{La}_{0.25}\text{FeO}_3$) adopt aperiodic phases, often due to conflict between tilting of the BO_6 octahedra and the off-centre displacements of the cations due to 2nd order Jahn Teller effects or stereochemically-active lone pairs [126–128]. Contrastingly, in comparatively simple molecular crystals such as biphenyl, incommensurate modulation is exhibited due to a competition between the intermolecular and intramolecular interactions [129–132]. In the gas phase, biphenyl molecules avoid steric clash between the ortho-hydrogen atoms by twisting the rings through a torsion angle of 42° ; yet, the crystal packing preferentially favours the flat confirmation. Correspondingly, aperiodicity arises through the frustration of ring rotations against the intermolecular interactions favoured by the crystalline lattice.

Incommensurate modulation is prevalent in a wide variety of host guest compounds, including perovskite-related halides containing organic cations [133, 134], urea-inclusion compounds [135–137] and occupied metal-organic frameworks [138]. These materials are particularly prone to incommensurate modulation as there is an obvious potential for guest-framework and guest-guest interactions to oppose the periodicity of the framework itself. Moreover, while guests are often identified as molecular species, modulation can also be caused by guests of low-dimensional infinite inorganic species with periodicity incommensurate with the host structure—such as the inclusion of one-dimensional AgCN chains within a $\text{Zn}[\text{Ag}(\text{CN})_2]_2$ framework [139].

Indeed, modulation can also be coupled with disorder such as in Krogmann’s salt— $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3}$ [140]. Here, the $\text{Pt}(\text{CN})_4$ units form one-dimensional stacks along the c axis due to overlap of the Pt d_{z^2} orbitals. Subsequent reduction of the Pt ion by the introduction of bromide leaves the stacks susceptible to a static, sinusoidal Peierls distortion. Correspondingly, the $\text{Pt}(\text{CN})_4$ units displace away from their average crystallographic site equivalent to a frozen-in longitudinal vibration with

$\mathbf{k} \simeq [0, 0, \frac{1}{6}]$. Yet, while the displacements within a single stack are ordered, the neighbouring stacks are thought to be uncorrelated, leading to a combination of both ordered and disordered aperiodicity [141].

Often the existence of multiple periodicities within a single material is a scientific curiosity, which greatly complicates structural solution due to the presence of satellite Bragg peaks. Nevertheless, modulation has been linked to changes in the physical properties of materials including optical and electronic responses. For instance, incommensurate modulation is observed in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ when $x < 0.4$ [142]. These phases are not superconducting due to partial charge separation on the Bi site; however, on further doping with K, the periodicity of the correlated bismuth displacements changes, and a metallic superconductor with commensurate modulation results. This is not a perfect example as the change in modulation results from a chemical *and* structural change in the material. The chemical effect is not easily decoupled from the physical property change in this case, but this does serve to demonstrate the importance of aperiodicity to the physical properties within an otherwise crystalline structure.

1.2.2 Disordered aperiodicity

Defects

The simplest and most common occurrence of aperiodicity in materials comes in the form of defects—imperfections in otherwise unaltered crystal structures. A structure is generally considered defective when the imperfections are in low concentration. Indeed, some of the examples of disordered aperiodicity described later in this section can be simply thought of as an extremely high concentration of a particular type of defect such as Ag^+ interstitials in the fast ion conductor, $\alpha\text{-AgI}$ [143].

A defective state is somewhat a catch-all term that includes atomic vacancies, interstitial atoms, dislocations, shear planes and changes in topology. The simplest

type of defects is stoichiometric, wherein the imperfection does not change the overall empirical formula of the solid. These tend to be entropically driven, as even a small number of defects greatly increases the number of microstates. Stoichiometric defects often take one of two common forms: (i) Schottky defects, where vacancies of anions and cations are generated in equal proportions such as in TiO [15]; (ii) Frenkel defects in which usually cations, due to their smaller size, move off their crystallographic position to occupy interstitial sites—*e.g.* α -AgI. While the implications for property changes in these defective materials are mainly restricted to alterations in the lattice parameter and density, other stoichiometric defects can produce more profound changes. In the hexagonal nets of graphene and carbon nanotubes, topological defects (*e.g.* Stone-Wales [144]) create reactive sites in the materials and can introduce curvature into the surface or rod—either as puckering or saddle points—as demonstrated in macroscopic weavings [Fig. 1.16].

By comparison, non-stoichiometric defects have a greater potential to impact the physical properties of a material, particularly as the oxidation states of ionic species can be altered. For instance, NiO is a Mott Hubbard insulator due to inefficient t_{2g} –

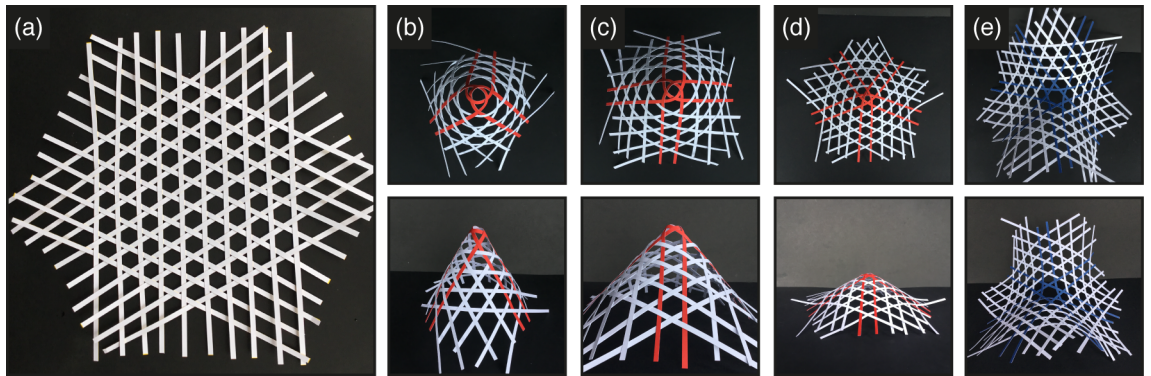


Figure 1.16: Topological defects in woven nets. (a) The triaxial (kagome) lattice is a woven version of a tri-hexagonal tiling, where the mesh—consisting of equilateral triangles and regular hexagons—covers an infinite flat plane. The presence of singularities in the mesh produces curvature in the net depending on the number of sides in the singularity. Defects with fewer than six sides produce positive curvature, with (b) three-, (c) four-, and (d) five-sided shapes resulting in progressively less-extreme effects. (e) The introduction of defects with seven sides or higher creates a woven surface with negative Gaussian curvature in the form of a saddle [145]. Included with the permission of Alison Martin.

t_{2g} overlap and high electron–electron repulsion on charge transfer. Conversely, upon heating with O_2 , the mixed valency oxide $Ni_{1-x}O$ is formed. This material contains both Ni^{2+} and Ni^{3+} ions; correspondingly, charge transfer between these species has a minimal enthalpy penalty and consequently the conductivity of the material is orders of magnitude larger than the stoichiometric starting material [146].

Amorphous solids, glasses and liquids

At the opposite end of the disordered aperiodicity spectrum lies the field of amorphous solids and liquids. The term amorphous has a different meaning depending on the field in which it is used. In general, amorphous is ubiquitously used to describe a highly disordered degree of freedom—*e.g.* topology, composition or the arrangement of crystal components in space. As such, this term covers a wide range of materials and disorder types including gels [147], high entropy alloys [148], polymeric structures [149], thin-films [150], jammed packings [151], solid dispersions (*i.e.* molecular species trapped within a polymer matrix) [152, 153], and the continuous random networks (CRNs) observed in phases of Si, SiO_2 and metal organic frameworks (MOFs) [154, 155]. These degrees of freedom often possess short range order, but show no long range correlations. As a result, the correlations do not generate Bragg scattering and instead only broad diffuse features are observed.* Accordingly, the associated pair distribution function data reveal sharp peaks at low r , but often becomes featureless at larger distances.

Glassy materials represent a subset of amorphous solids with the important distinction being that they must display a glass transition [157]. This phase transition in the field of polymers describes the change from a malleable to a brittle mate-

*That is not to say that in some fields amorphous solids cannot exhibit any Bragg scattering, only that the correlations of the degree of freedom described as amorphous does not itself exhibit Bragg scattering. For instance, Mobil Composition of Matter 41 and 48 (MCM-41 and MCM-48) are comprised of amorphous silica, yet these materials also contain long-range order due to a periodic arrangement of mesopores [156]. Also, the amorphous compositional disorder in high entropy alloys produces diffuse scattering features, but the atoms themselves occupy fixed lattice positions, so Bragg scattering is still observed.

rial as the dynamics of the polymer become restricted on decreasing temperature [158]. In the field of low-temperature magnetism, spin equivalents of amorphous states are achievable in the form of spin-glasses [159]. Here, the atoms and ions remain crystallographically ordered, but the disorder is realised through the lack of long range order in spin orientations. The spin-glass state therefore describes an arrangement of spins equivalent to a frozen paramagnetic state—*i.e.* static disordered spin orientations [160].

Given the large range of materials associated with the amorphous state, the corresponding material properties of interest are equally diverse. While it is not practical to include a fully detailed summary here, three examples from disparate scientific fields are included. Firstly, amorphisation of MOFs alters the distribution and sizes of the cavities and as such, the porosity and the gas storage applications for which they are well-studied [161]. Moreover, amorphous MOFs can be synthesised through a variety of different methods—*e.g.* ball-milling, heating and the application of pressure [162]. The resulting frameworks formed from each of the experimental methods may contain different disordered structures which can alter absorption properties to different extents. This effect is exemplified in the case of ZIF-8 where amorphisation via heating or pressure results in non-porous and highly porous structures respectively [161]. The second example concerns pharmaceuticals, where drug molecules are embedded within polymer matrices to form solid amorphous dispersions which aid the uptake of the active component into the body [152].* Finally, the disorder in high entropy alloys (HEAs) has been found to result in extreme material strength and toughness [163]. Here, the inclusion of multiple atomic components, often in excess of five, arranged in a highly disordered manner prevents fracture in a similar way to the quasicrystalline state described in Section 1.2.1 [121]. The atomic arrangements in HEAs are often considered to be random; however, a recent study using pair distribution function analysis has revealed that their lower

*Often crystalline drug formulations are only sparingly soluble, and so require much higher dosage to achieve the same level of absorption into the bloodstream [153].

entropy counterparts—*i.e.* with fewer atomic components—have a large preference for specific local coordinations, reducing their entropy yet further [164, 165].

The extent of disorder in many amorphous materials is comparable to that found in the liquid state. As one of the primary states of matter, the liquid hardly needs an introduction; however, the term encompasses more chemically diverse states than simply the condensed phases of single species such as H_2O or elemental Hg . Ionic melts and molecular ionic liquids such as molten NaCl or 1-ethyl-3-methylimidazolium tetrafluoroborate, $[\text{emim}][\text{BF}_4]$, show significantly more ordered arrangements in both the bulk and at the surface than their neutral molecular liquid counterparts due to strong electrostatic interactions [166]. Indeed, in thin films, the ordering of molecular ionic liquids has immediate implications for their charge screening properties. Large deviations from Debye-Hückel theory have recently been observed in such systems [167]. This has subsequently raised an important avenue of research paralleled with that of this thesis—to what extent can the disordered structures of a *liquid* impact the bulk materials properties?

Superionics

Fluid-like states are also found within the collection of solid-state materials known as fast ion conductors or superionic conductors. These represent an important midpoint between the crystalline solid and the ionic liquid/melt, where one of the material components is crystalline and essentially static, while the other exhibits mobility high enough to be considered as a molten sublattice [143]. The highly mobile portion of fast ion conductors has been attributed to cationic—*e.g.* as the Ag^+ sublattice in $\alpha\text{-AgI}$ [168, 169] or sodium ions intercalated into $\beta\text{-alumina}$ [170, 171]—and anionic species—*e.g.* F^- ions in PbF_2 [172] or O^{2-} anions in $\delta\text{-Bi}_2\text{O}_3$ [173, 174] and yttria-stabilised zirconia ($\text{Y}_2\text{O}_3/\text{ZrO}_2$) [175]. The existence of a ‘liquid-like’ set of ions within a solid material results in high ionic conductivities, making them perfect candidates for applications involving charge transfer in the solid state, including

electrolytes [175], and sensing applications [176].

Fast cation conduction behaviour is typified by α -AgI (the thermodynamic phase above 420 K). In this material, the iodide anions are arranged in an ordered BCC array, whereas the two silver cations per unit cell are distributed among 48 possible sites—6 octahedral, 12 tetrahedral and 24 trigonal environments [Fig. 1.17]. The large, polarisable iodide anions efficiently shield the cation charges. As such, the Ag^+ ions are able to hop from site to site and therefore move freely throughout the crystal, resulting in a high ionic conductivity [168, 169]. Further evidence of freely mobile ‘fluid-like’ silver ions is also reflected in the thermodynamic data. At low temperature, AgI adopts the β -phase, equivalent to the wurtzite structure. Upon heating, a phase transition to the α -phase occurs with an associated positive entropy change, $\Delta S_r = 14.5 \text{ JK}^{-1}\text{mol}^{-1}$; further application of heat melts the α -phase where $\Delta S_f = 11.3 \text{ JK}^{-1}\text{mol}^{-1}$ [177]. The two values are unsurprisingly extremely similar as the transitions correspond to a sequential ‘melting’ of the silver and iodide sublattices, respectively.

Conversely, oxide ion conductors frequently restrict the anions to a single crystallographic site, on which there are multiple vacancies which facilitate the oxide mobility. By way of example, $\delta\text{-Bi}_2\text{O}_3$ adopts the anion-deficient fluorite structure,

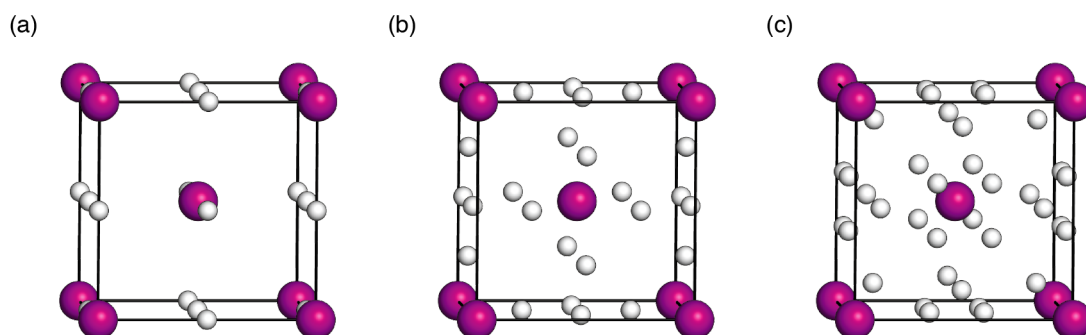


Figure 1.17: The structure of the superionic α -AgI. A static BCC arrangement of I^- ions (purple) is surrounded by a “fluid-like” array of Ag^+ ions. The two silver ions per unit cell are distributed amongst the (a) octahedral (b) tetrahedral and (c) trigonal sites, shown in white.

where Bi^{3+} ions are arranged in an FCC array with the oxide anions occupying only 75% of the tetrahedral sites [173, 174]. The same structure is observed in stabilised solid solutions of yttria-stabilised zirconia [175]. Contrastingly, the proportion of oxide vacancies, and hence ionic conductivity, is enhanced by increasing the relative fraction of Y^{3+} to Zr^{4+} within the material. However, at high levels of Y^{3+} , the proportion of anion vacancies becomes sufficiently large that ordering occurs and the ionic conductivity drastically decreases [178].

Liquid crystals

While superionics are well-renowned for their electrical conductance, in the field of liquid crystals, the impact of the disordered aperiodicity on the corresponding optical properties is of interest. Conventionally, liquid crystals are comprised of large organic molecules, usually rod-like—*e.g.* cholesteryl benzoate derivatives [179] (but can also be disc [180] or bowl shaped [181])—whose intermolecular interactions drive the formation of multiple phases in the intermediate regime between crystalline order and the liquid state. The liquid crystalline phases that are accessible and the transition behaviour of a system are dictated by the individual molecular unit; correspondingly, the physical properties can be tuned via alterations to the molecular structure, easily achievable through standard organic synthetic methods [182].

Within the field of liquid crystals, systems are commonly grouped via two considerations [183]. The first is concerned with the physical factors that effect the liquid crystal phase transitions such as temperature, concentration and composition—thermotropic, lyotropic and metallotropic liquid crystals respectively. The second set of terminology describes the specific types of molecular arrangements adopted by liquid crystal phases and so is much more relevant in the context of this thesis.

At low temperatures, thermotropic liquid crystals form conventional crystalline phases. Upon heating a series of phase transitions can occur as specific degrees of freedom are introduced into the structure, where each phase represents a distinct

change in entropy, intermediate between that of a solid and liquid. The intermediate phases exhibited by liquid crystals are primarily due to the preferential orientations between molecules. Rod shaped molecules favour parallel arrangements driving partial ordering. Perhaps surprisingly, the ordering is driven by an increase in entropy, as the total excluded volume is reduced when hard rods come together in parallel as opposed to an angular arrangements [184]. This effect increases the total entropy and a larger proportion of the configurational volume is available for small deviations in translations and rotations of the molecular rods. Further heating of the intermediate liquid crystal phases overcomes this entropically driven order and causes a transition to the more traditional liquid phase.

The two most common liquid crystal arrangements for rod-like molecules are the nematic and smectic phases [183] [Fig 1.18]. In both these phases, the molecular rods are approximately aligned—*i.e.* small deviations from perfectly parallel arrangements are observed—however, these phases differ in their translational ordering. The nematic phase exhibits no long-range positional ordering along any of the cartesian axes, or in other words the only degree of order is in the preferred orientation of the molecules. Conversely, the smectic phase consists of molecules arranged into well defined layers which are able to slide over one another, and as such represents a more ordered structure than the nematic phase. Indeed, the smectic phase is further split into two types, A and C, in which the molecules are either aligned along the axis of the layer stacking direction or tilted away from it.

Chirality is an important factor within the field of liquid crystals. The most common phase in which this occurs is within the chiral nematic (or cholesteric) phase which consists of layers of preferentially aligned molecules, but perpendicular to the stacking direction [183]. Here, the preferential alignment axis of sequential layers is rotated in the same direction, but with a finite twist angle [Fig 1.18(f)]. Typical liquid crystal displays (LCDs) make use of the chiral phases—or the more commonly termed cholesteric arrangements—to manipulate the passage of light. The

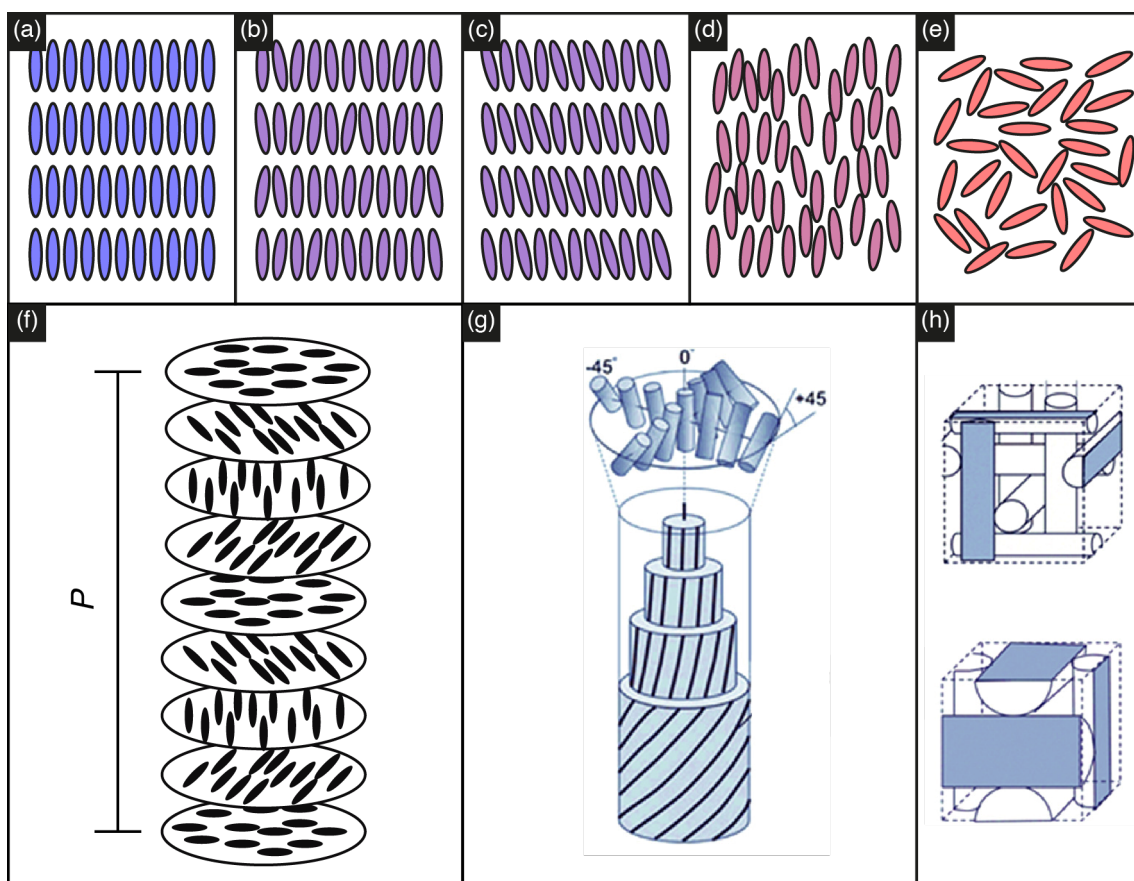


Figure 1.18: Common phases liquid crystals. When heated a crystalline array of rod shaped molecules shown in panel (a) can traverse a series of phase transitions to progressively more disordered phases as further degrees of freedom are introduced, including the (b) smectic C, (c) smectic A, (d) nematic and finally (e) liquid-like arrangements. (f) The cholesteric phase is made up of rod-like molecules, preferentially aligned in planes. The alignment axis between successive layers rotates in the same direction by a characteristic angle, forming a chiral phase with a well-defined pitch length P . (g) In the blue phases, the rod-shaped molecules aggregate to form cylindrical secondary structures. (h) These large units in turn arrange into ordered the rod packings Π^+ (top) and Π^* (bottom) as blue phases I and II respectively. Adapted from Ref. [185].

chiral pitch, or more simply the distance required to perform a full 360° rotation, of the cholesteric phase is often of the order of the wavelength of visible light and the exact pitch length can be fine tuned by temperature, electric fields or additives. In LCD applications, a thin layer of liquid crystal is sandwiched between two polarisation filters which are at 90° to one another. The layer of cholesteric phase liquid crystal rotates the polarisation of incident light, causing the display to appear transparent [186]. Application of a voltage across the layer causes the primary axes of the molecules all align to the electric field. Correspondingly, the pitch length of the cholesteric phase approaches infinity, the polarisation of light remains unrotated and transparency is lost with increasing voltage [182].

Long-range chirality is also observed within the blue phases, where the molecules align preferentially parallel to the stacking axis, aggregating to form secondary cylindrical structures in which the molecules are helically rotated. These large cylinders go on to arrange into well-established rod-packings, with blue phases I and II corresponding to the Π^+ and Π^* assemblies, respectively [Fig 1.18(g),(h)] [185, 187].

Plastic crystals

Plastic crystals are phases with three-dimensional positional order and orientational disorder [188, 192]. As such, they are closely related to liquid crystalline states. Often, plastic phases are comprised of charge-neutral molecules such as adamantane or cyclohexane [? ?]. The propensity for a given molecular solid to adopt plastic or liquid crystalline phases is a function of the shape of the molecule [95, 188]. While liquid crystal molecules are often highly anisotropic—rods, discs and bowls—plastic crystal phases tend to occur for molecules which are fairly isotropic in shape and charge density [188]. This alters the accessible degrees of freedom: the molecules remain positionally ordered in plastic crystals but with disordered orientations, whereas liquid crystals have small variations in the orientations due to preferential alignment of the anisotropic molecules (all phases) and also translational disorder in the nematic

phase [183, 188]. The effect of shape is particularly well illustrated in the entropy-driven self-assembly of hard polyhedra, which clearly show the divide between liquid crystal and plastic crystal phases lies in the extent of anisotropy [Fig. 1.19] [95]. As such, local symmetry is an important consideration for plastic crystal phases. Highly symmetrical molecules necessarily signify a pseudo-spherical electron distribution, and hence no electric dipole. In turn this results in a lack of preferred orientation and as such, unsurprisingly, isotropic molecules such as C_{60} (I_h) [?], SF_6 (O_h) [190] and CBr_4 (T_d) [191] all exhibit plastic phases.

Within plastic crystal phases, the orientation of a single molecule influences the orientation of its neighbours—*i.e.* the disordered orientations are correlated [265?]. Nevertheless, the energy of these interactions is low enough that strict orientational constraints are not enforced. Additionally, the allowed orientations are continuous—*i.e.* the molecules are not restricted to discrete rotational states. As such, the plastic crystal represents a phase with intermediate entropy between that of the crystalline and liquid state [192]. Correspondingly, the melting of plastic crystal phases is, unsurprisingly, accompanied by a lower entropy change than the melting

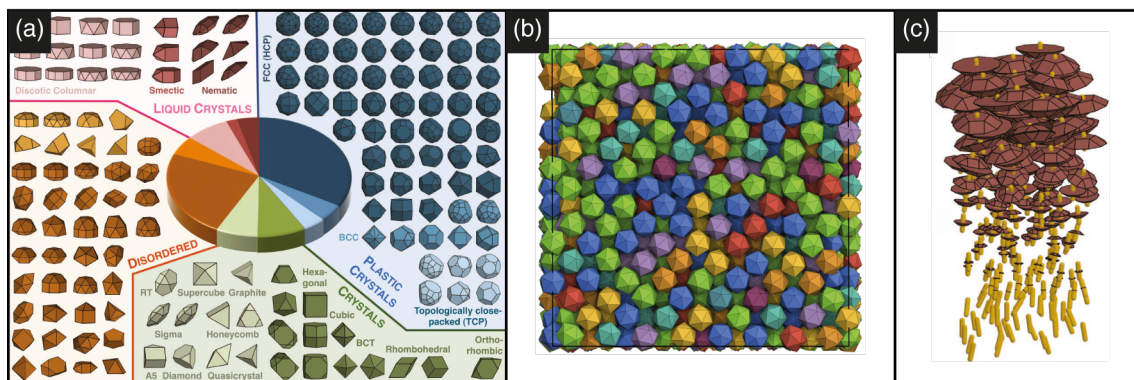


Figure 1.19: Polyhedral self-assembly and the plastic crystal phase. (a) Monte Carlo simulations of broad-spectrum of hard polyhedra demonstrate the propensity for plastic crystal formation in the case of isotropic shape and the contrasting role of an axis of anisotropy in the liquid crystal phases. Indeed the packings formed by (b) relatively isotropic isocahedra and (c) anisotropic doicosahedra highlight this effect. Adapted from Refs. [95, 193]. (a) and (c) from P. F. Damasceno, M. Engel and S. C. Glotzer, *Science*, **337**, 453–457, 2012. Reprinted with permission from AAAS.

of equivalent crystalline phases. By way of example, in the melting of the plastic phase of cyclohexane $\Delta_{\text{fus}}S = 2.27 \text{ cal K}^{-1}\text{mol}^{-1}$, whereas in the melting of methylcyclohexane, which is crystalline as the methyl group prevents orientational disorder via steric clashing, $\Delta_{\text{fus}}S = 11.00 \text{ cal K}^{-1}\text{mol}^{-1}$ [188].

Plastic crystal phases have found use as solid state ion conductors particularly in the field of organic ionic plastic crystals (OIPCs) [194]. OIPCs are comprised of two molecular ionic components—*e.g.* a binary assembly of ethyl-methylpyrrolidinium cations and bis(trifluoro-methanesulfonyl)amide anions. The arrangement of ionic molecules is translationally ordered but rotationally disordered. Here, the dynamic orientational disorder (rotational motion) of the plastic phase is key to the conduction properties. The introduction of small monoatomic cations such as Li^+ converts the crystal into an excellent ion conductor, wherein the disordered plastic crystal framework acts as a ‘solid solvent’ which supports the movement of the small ions and as such represents a clearly different mechanism of charge mobility than in superionics [194–196].

Dimer and loop states

In contrast to the continuous and liquid-like orientational disorder of plastic crystals, the dimer states also show orientational disorder but in a discrete and highly correlated manner. Indeed, the decoration of dimers and loops on a lattice are well-studied phenomena of statistical mechanics [197–199]. At their heart, these disordered configurations are a problem of combinatorial mathematics—a particular lattice is chosen, and every lattice point is then connected to one or two of their nearest neighbours to give dimer or loop decorations, respectively. These configurations are dense as no lattice points are left unconnected and in this sense the models are defect free. Therefore, within a finite dimer configuration, the number of dimers must equal half the number of lattice points; but no such restraint exists for the loop models (although there will exist a maximal number of loops). Correspond-

ingly, simple mathematical processes, such as dense, self-avoiding, random walks on a lattice represent a subset of the possible loop configurations for a given lattice type as, in this case, there is a secondary restraint in that only a single loop is allowed across the entire configuration.* On a one-dimensional lattice the resulting configurations are trivially ordered—conveniently they are related to the phase behaviour of VO₂ both above (‘loop’) and below (‘dimer’) the Peierls transition temperature (Section 1.10). However, higher-dimensional lattices such as square or primitive cubic, allow multiple configurations which satisfy the local constraints resulting in a manifold of degenerate ground states [200, 201] [Fig. 1.20]. This includes both aperiodic and periodic decorations, but the disordered arrangements are significantly more numerous and so statistically likely. Of course, the loop/dimer decorations of each lattice assemble their own individual set of ground states, so different lattices can be expected to have their own diffraction behaviour, physical properties and excitations—*e.g.* loop moves [202, 203].

So what types of scientific problems can be represented using these deceptively simple models? Perhaps the most obvious equivalence is found between the dimer configurations and aperiodic packings of polyhedra. By way of example, the dense two-dimensional packing of 2×1 dominos [204] and a tiling of rhombuses [205]—with 60° and 120° internal angles—gives the same set of solutions as dimers on a square and hexagonal lattice respectively [Fig.1.20(b)].

Dimer configurations have also found application in the field of high-temperature superconductivity of cuprate compounds, in the form of resonating valence bond (RVB) theory [12]. Here, copper oxide forms a sublattice in which electrons on neighbouring copper sites interact with their neighbours, generating a dimer decoration. The introduction of mixed valency on the copper site through doping introduces defects into the dimer state, which is believed to promote the free movement

*Perhaps the most commonly encountered example of a dense, self-avoiding, random walk on the square lattice is equivalent to the victory condition of the arcade game snake.

of electron pairs throughout the material, therefore leading to superconductivity.

At its inception RVB theory—and hence dimer configurations—were intrinsically linked to spin liquids. Geometrical frustration is crucial to the spin liquid state, where the system is unable to simultaneously minimise the energy of its interactions. This effect is exemplified by the canonical example of the triangular Ising antiferromagnet [206], where each lattice site on the triangular net is decorated with Ising spins and the neighbouring interactions favour an antiparallel alignment. While antiferromagnetic interactions can be fully satisfied on the square lattice [Fig. 1.11], the local triangular unit does not allow this to occur. In this geometry, two spins may align antiparallel, but the third has no choice but to be in a parallel arrangement to one of the first two. Connections drawn between the centre of triangular units, bisecting only the frustrated ferromagnetic pairs then relates these configurations to the dimer state on the hexagonal lattice and hence the rhombus tiling [Fig. 1.21].

Further realisations of the two-dimensional dimer models are found in the absorption of rod-like molecules onto surfaces. The arrangement of N_2 on graphite has been modelled as an ordered dimer decoration [207]; however, *p*-terphenyl-3,5,3',5'-tetracarboxylic acid (TPTC) molecules on pyrolytic graphite form an aperiodic network [208]. Disorder within the TPTC molecular network was observed through

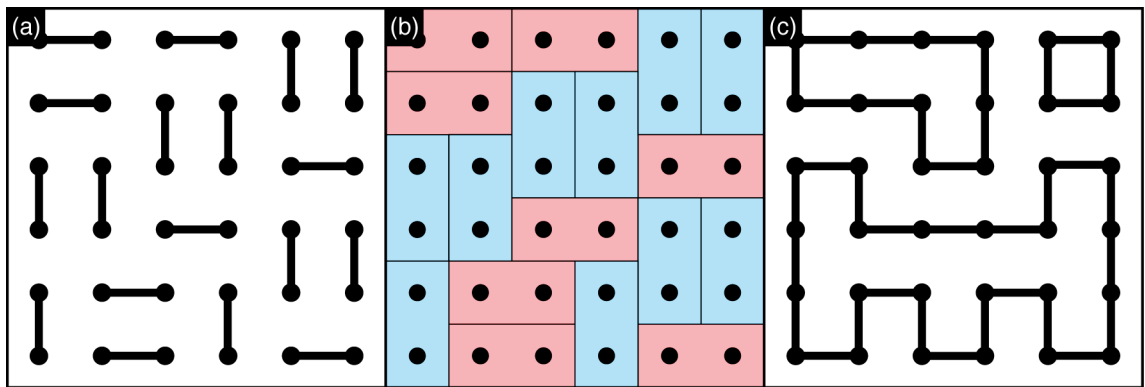


Figure 1.20: Dimer and loop models. (a) A dense decoration of dimers on the square lattice is able to exhibit aperiodic arrangements which are equivalent to (b) the tiling of dominos in a square box. (c) Loop models, wherein each lattice point is connected to two others, are not known to have a simple tiling equivalent.

scanning tunneling microscopy (STM) images and was found to be driven by strong directional intermolecular interactions in the form hydrogen-bonds. Each TPTC molecule is comprised of a linear arrangement of three phenyl rings with two carboxylate groups on each terminal ring at the meta positions. Upon deposition onto pyrolytic graphite, the TPTC molecules hydrogen-bond together via the carboxylate groups and decorate a hexagonal lattice, with a terminal phenyl ring occupying each lattice point.

But what of the origin of aperiodicity? For a pair of TPTC molecules there are two potential hydrogen-bonding modes: (i) where the primary axes of the molecules are parallel; (ii) where they are angled at 60° [Fig. 1.22]. The energetic difference between these two local bonding modes is minimal, and certainly many orders of magnitude below $k_B T$, so there is little preference in the network for either local arrangement. As such, while the terminal phenyl rings of the TPTC molecules occupy all hexagonal lattice points, the orientation of the molecules and hence hydrogen bonding network is disordered, but crucially not random. Indeed, the arrangement of the triphenyl units provides an exact mapping onto the dimer state on the hexag-

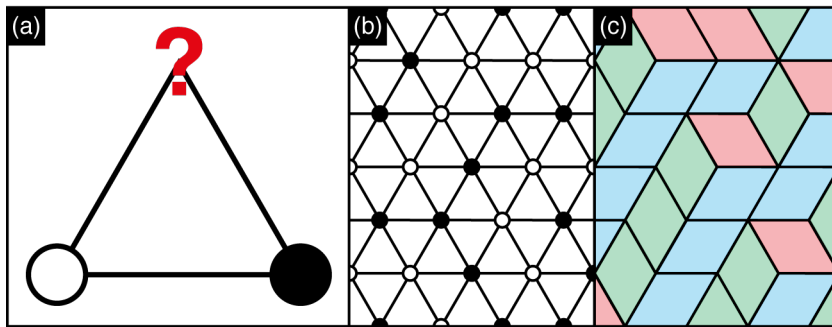


Figure 1.21: The triangular Ising antiferromagnet and the dimer state. (a) A decoration of Ising spins—where ‘up’ and ‘down’ states are represented by black and white circles respectively—on the triangular net with antiferromagnetic interactions must necessarily produce a frustrated state. On a given triangle, while two spins may anti-align, the third is forced to align parallel to one of the original two. (b) A representative network of the triangular Ising antiferromagnet is equivalent to the dimer state on the hexagonal lattice and hence (c) the rhombus tiling as each rhombus is constructed with parallel spins on opposite vertices.

onal lattice. The mapping, albeit containing a small proportion of defects, was originally realised through the equivalence of the TPTC network to the rhombus (or lozenge) tiling mentioned above.

Ices

Ice disorder is conceptually very similar to that found in plastic crystals and the loop/dimer states. The likeness of these classifications lies in their shared degrees of freedom: the local units are positionally ordered but orientationally disordered. The difference arises in their *degree* of orientational disorder; plastic crystals contain continuous orientational disorder that is weakly-correlated—*i.e.* while the orientation of a molecule will affect the orientation of its neighbours, within the crystal all rotations of the molecule are allowed. Conversely, in the ice state there are two key restrictions which are also found in dimer states (i) only a finite number of discrete orientations are allowed and (ii) the particular orientational state of a unit at a given point is constrained by the states of its neighbours. As such, these configurations are aperiodic and disordered but also contain strict local order.

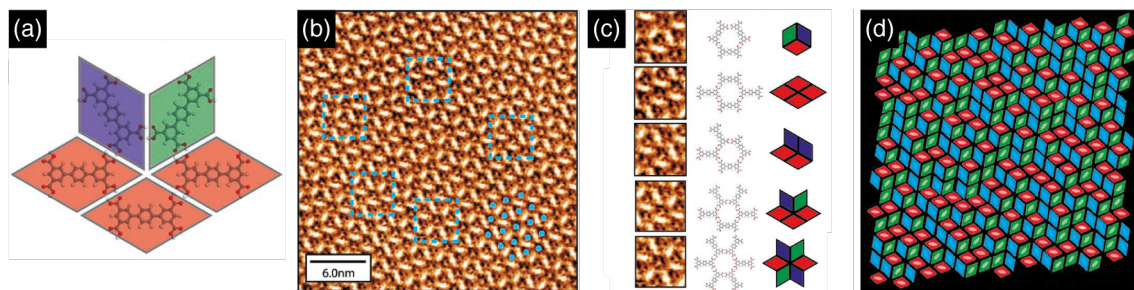


Figure 1.22: The aperiodic network of TPTC molecules. (a) TPTC molecules, which can be visualised by the simple rhombus, form intermolecular hydrogen bonds in one of two local arrangements—parallel or angled. (b) An STM image of the subsequent network formed by deposition on pyrolytic graphite reveals the retention of a hexagonal lattice while also exhibiting aperiodicity. (c) In total there are five different possible arrangements of TPTC molecules around each lattice point which are all observed in the STM image. (d) A subsequent conversion of the STM image into a tiling of rhombuses highlights the aperiodic nature of the network. From M. O. Blunt, J. C. Russell, M. d. C. Giménez-López, J. P. Garrahan, X. Lin, M. Schröder, N. R. Champness and P. H. Beton, *Science*, **322**, 1077–1081, 2008 [208]. Reprinted with permission from AAAS.

This classification of disorder has long been associated with that of water ice—particularly its square and cubic variants. In the former system, water molecules with an internal bond angle of 90° occupy the lattice points of the square lattice and interact with their neighbours to satisfy sensible hydrogen bonding rules—*i.e.* every molecule accepts and donates two hydrogen bonds. The three-dimensional analogue of this model, cubic ice (I_c), contains water molecules with a more realistic bond angle, 109.5° , which occupy the tetrahedral sites of the diamond net [Fig. 1.23(a)]. In order to hydrogen bond with their neighbours, the water molecules orient their two covalently bonded hydrogen atoms toward two of the four vertices of the local tetrahedral environment, in doing so distinguishing one of the six polyhedron sides [203]. There is no unique way of satisfying these constraints and the resulting configurations are not random but are predominantly disordered.* Correspondingly, in the absence of other effects, the degenerate set of ground states results in a non-zero ground state entropy—*i.e.* at very low temperatures—equal to $R \ln \left(\frac{3}{2}\right) = 3.37 \text{ JK}^{-1}\text{mol}^{-1}$ which is close to the experimental value of $3.64 \text{ JK}^{-1}\text{mol}^{-1}$ [203].

The disorder imprinted by chemically sensible bonding rules is well-characterised in their real-space structures. In terms of long-range structure, ices contain both periodic (the positions of water molecules) and aperiodic components (their orientations); however, locally every water molecule lies within the same environment. Furthermore, the local bonding rules in square ice further manifest longer range features. Along any row or column within the configuration all hydrogen atoms are oriented in the same direction, but there are no correlations between the rows and columns.

At its heart, ice disorder in I_c originates from the decoration of a low symmetry C_{2v} molecule on the T_d site which have local bonding rules. As such, disordered configurations equivalent to that found in ice can be realised through decorations of

*Ordered configurations are possible, but they make up only a small minority of the degenerate set of ground states.

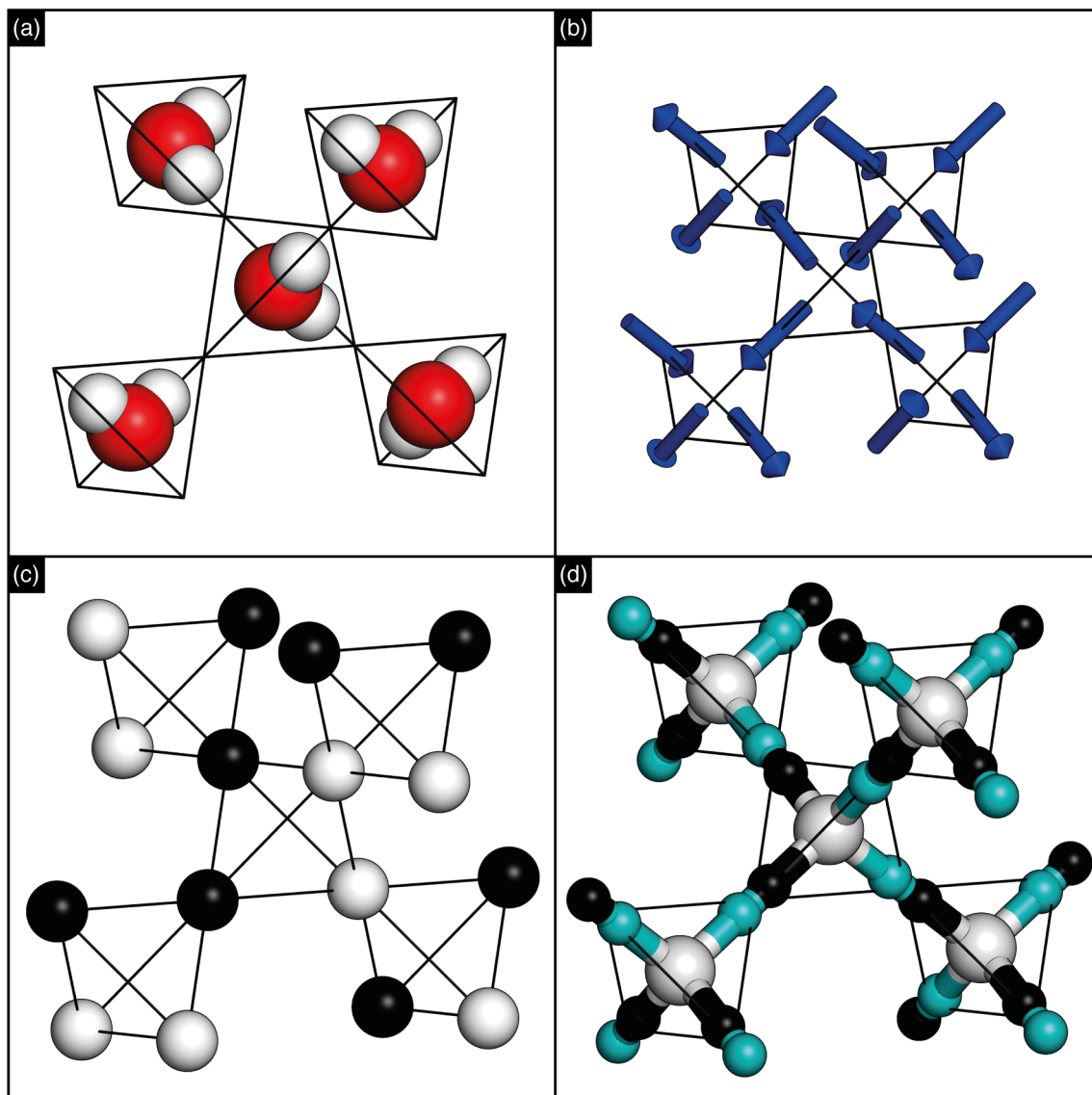


Figure 1.23: Ice disorder in I_c and its analogues. (a) Water molecules occupy the centre of each tetrahedron in the diamond structure. In order to satisfy chemically sensible intermolecular interactions, the hydrogen atoms (white) are directed toward the neighbouring oxygen atoms (red) in such a way as that each water molecule accepts and donates two hydrogen bonds. Analogous disorder configurations can be realised by (b) spin orientations, (c) charge disorder and (d) linker orientation disorder. The spin and linker orientations reproduce the directionality of the hydrogen bonds in the water ice. Conversely, the charge disorder representation in panel (c) highlights the tetrahedral edges distinguished by the water molecules, with a checkerboard mapping—*i.e.* the white ions highlight the chosen edge for the central tetrahedron, whereas the black ions perform the same role for the neighbouring tetrahedra.

any C_{2v} unit on the diamond net with the same bonding rules.

Correspondingly, analogous states have been observed in apparently unrelated systems, including decorations of charges, linker decorations, ion displacements and spin-orientations. In the magnetic analogues, known as the spin ices—*e.g.* $\text{Dy}_2\text{Ti}_2\text{O}_7$ and $\text{Ho}_2\text{Ti}_2\text{O}_7$ [209]—rather than a water molecule situated at the centre of the tetrahedral environment, magnetically active ions (or more simply spins) decorate the corners of the vertex sharing tetrahedra. Here, the spin orientations lie on a fixed axis—along the vector connecting the centres of the two vertex sharing tetrahedra—and so each spin points directly toward the centre of one of the two connected tetrahedra and directly away from the centre of the other [Fig. 1.23(b)]. The local bonding rules and C_{2v} symmetry are therefore established as each individual tetrahedron consists of two spins pointing in and two pointing out. This 2-in-2-out local rule of spins maps directly onto the “accept-two-donate-two” hydrogen bonding rules of water ice where in essence, each spin orientation describes the direction of the $\text{O}\cdots\text{H}-\text{O}$ bond [Fig. 1.23(a),(b)].

Equivalent local arrangements of mixed charges are believed to make up the structure of the mixed valency compound LiV_2O_4 , where two V^{3+} and two V^{4+} ions occupy the vertices of each tetrahedron on the diamond net [Fig. 1.23(c)] [210]. Conveniently, the corresponding ice-like disorder of linker orientation and displacements are both found in $\text{Cd}(\text{CN})_2$. Here, the cyanide linkers follow a 2-in-2-out rule with each tetrahedrally coordinated Cd^{2+} being bound to two carbon and two nitrogen atoms. The Cd^{2+} ions then displace with the same imprinted disorder as the off-centring is driven by the CN decoration. The electrostatic attraction between Cd and C is larger than Cd and N, so the Cd^{2+} ions displace toward the tetrahedral edge occupied by the two carbon atoms, essentially providing a double occurrence of the same ice disorder configuration [Fig. 1.23(d)] [211].

Hyperuniformity

In contrast to the ices, the classification of hyperuniform arrangements is solely concerned with the distribution of points in space. As such, the aperiodicity in these configurations stems entirely from positional disorder rather than, for instance, molecular orientation. At its most simple level, the hyperuniform state can be thought of as an array of points which are uniformly distributed in the long range, *i.e.* with an absence of long-range fluctuations; however, this criterion does not necessitate any local order or translational periodicity [212].

So what is the exact definition of the hyperuniform state? Here, an arbitrary array of points in d -dimensional space is considered. A regular domain window (such as a sphere), ω , is then constructed around a central point a , and the number of points encapsulated within the window, N_ω , is counted. The existence of hyperuniformity is then concerned with two key factors: (i) how does N_ω vary as the size of the domain window is uniformly expanded/contracted and (ii) what impact does the position of a within the configuration have on N_ω ?

In the case of a Poisson point pattern—*i.e.* a random array—the variance of N_ω is equivalent to the average number density:

$$\langle N_\omega^2 \rangle - \langle N_\omega \rangle^2 = N_\omega. \quad (1.16)$$

Furthermore, in the event that ω is a d -dimensional sphere with radius, r , the variance is directly proportional to the sphere volume:

$$\langle N_\omega^2 \rangle - \langle N_\omega \rangle^2 \propto r^d. \quad (1.17)$$

Although these results are consistent for Poisson point patterns, these relations are not exclusive to this state as correlated irregular patterns may also exhibit these properties. Nevertheless, it is possible for the variance to grow more slowly with

increasing size of ω . Indeed, it has been mathematically proven that the variance growth cannot be smaller than the equivalent growth of the surface area of ω , and it is this state that defines hyperuniformity—where variance grows minimally with ω size [212], or

$$\langle N_\omega^2 \rangle - \langle N_\omega \rangle^2 \sim r^{d-1}. \quad (1.18)$$

All periodic point arrays follow this relation, but periodicity is not a prerequisite of the hyperuniform state. In essence, Equation 1.18 effectively separates for configurations for which there are no infinite wavelength fluctuations in the variance, of which periodic arrays are a subset. Furthermore, aperiodic systems which lie on a periodic lattice such as plastic crystals and ices, also trivially fall under the hyperuniform definition.

Yet, aside from systems that occupy a fixed lattice, further assemblies of hyperuniform structure are largely limited to those on larger length scales than those of atomic arrangements. Potentially the best known example of disordered hyperuniformity is found in the eyes of chickens [213]. Chickens have tetrachromatic colour vision supported by five types of photoreceptive cells which form a dense two-dimensional packing across the retina. Because of the difference in size of the cone cell types, there is no optimal ordered arrangement for uniform cone cell coverage. Instead, the individual types of cone cells arrange in a disordered, yet well-spaced manner to provide adequate photon sensitivity across the entire retina. Other proposed hyperuniform arrangements are found in the jammed random packings of spheres [212], quasicrystals [214] and potentially the distribution of fairy circles—disordered, circular, barren patches of earth found on the grassy plains of Namibia and Western Australia [215].

There is great difficulty in creating hyperuniform arrangements on the atomic scale that are distinct from structures that fall under other classifications. As such the development of hyperuniformity–property relationships has focussed on properties

impacted by arrangements on larger length scales, where the structure can be manually constructed—*i.e.* photonic properties. Recent reports have shown that structures developed from hyperuniform arrangements are able to generate photonic band gaps, simultaneously in the both the transverse electric and transverse magnetic spectra [216, 217]. Here, the two-dimensional photonic structure is generated from the Voronoi-Dirichlet network of the hyperuniform point patterns, with pillars and walls decorating the vertices and edges of the Voronoi-Dirichlet cells respectively [Fig. 1.24]. The observance of large ($> 10\%$) complete band gaps in these disordered aperiodic materials is an important development in the field of photonics. In creating functional photonic devices, the absence of order causes the band gaps to be considerably more isotropic than those found in quasicrystalline or crystalline photonic structures, which is a desirable feature in the manufacture of efficient isotropic thermal radiation sources [218, 219].

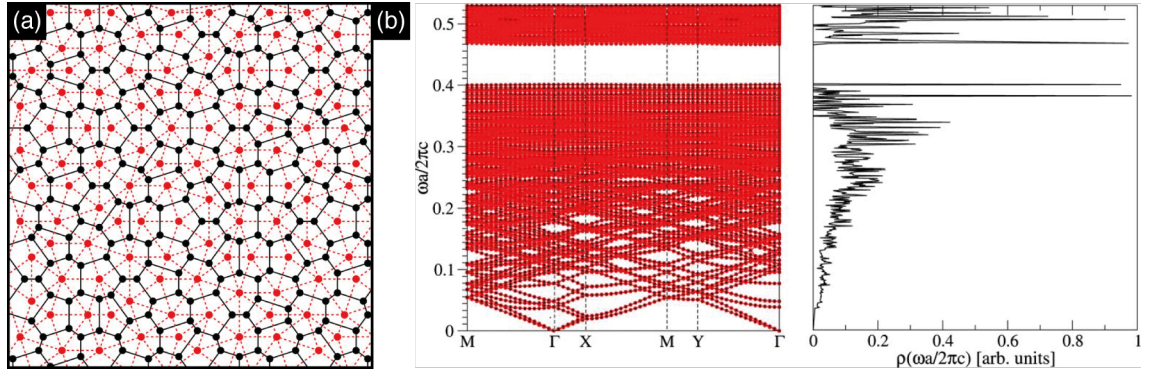


Figure 1.24: Hyperuniformity and photonic properties. (a) A quasicrystalline hyperuniform array of points (red) can be readily converted into the quasicrystalline hyperuniform photonic structure (black) by decorating the corresponding Voronoi-Dirichlet network with dielectric pillars and veins (black). (b) These arrangements of dielectric media have been shown to exhibit large complete photonic band gaps, clearly shown in both the photonic dispersion (left) and density of states (right) both in the quasicrystalline case shown, and in disordered hyperuniform media [216, 217]. Reprinted figure with permission from M. Florescu, S. Torquato and P. J. Steinhardt, *Phys. Rev. B*, **80**, 155112, 2009 [220]. Copyright 2009 by the American Physical Society.

1.3 Motivation and aims of this thesis

The main theme running throughout this thesis is an emphasis on developing a more comprehensive approach to understanding correlated disorder—the middle ground between crystalline order and random disorder—and its impact on material properties. Throughout this chapter many different types of aperiodic materials have been discussed; however, as yet, very few relationships have been drawn between them. Indeed, each classification is often considered in isolation, and as such, scientific insight and desirable disorder-induced properties are often considered to be largely system specific.

Correspondingly, there are three key questions which make up the motivation of this thesis: (i) to what extent can correlated disorder be understood in a broader context such that comparisons might be able to be drawn between seemingly unrelated systems in disparate areas of science? (ii) Are there signatures in the scattering behaviour for particular types of disorder correlations such that disordered aperiodicity might be more simply characterised? (iii) By way of analogy to crystalline order, can robust disorder-property relationships also be established?

This thesis is structured as follows: Chapter 2 contains the methodological details of the approaches employed throughout this thesis, including scattering, lattice dynamical and photonic theory along with a description of the computational approaches and software utilised in this research. The following four chapters make up the results section of this thesis, followed by a final section providing a critical discussion of the research as a complete body of work.

The first set of results presented in this thesis (Chapter 3) establishes the concept of the procrystalline state—a generalisation of ice rules. These configurations are constructed using geometrical approaches, and are found to contain both local order and long range disorder. The classification of procrystallinity is given a strict

definition and distinctly different models containing procrystalline disorder are enumerated. For each of these models, their characteristic diffraction behaviour and an estimate of their ground state entropy given. Finally, through the use of several characterisation methods including single crystal diffuse scattering and pair distribution function methods, realisations from a wide variety of scientific fields are identified as belonging to the procrystalline state.

Having established the definition and common occurrences of procrystalline disorder, the research in this thesis moves on to establish relationships between specific types of geometrical disorder and physical properties. In the field of lattice dynamics, much of the existing theory relies upon translational order, and so is not equipped to tackle systems containing correlated disorder. Chapter 4 addresses this methodological lacuna by detailing the supercell lattice dynamical (SCLD) method. This work demonstrates that the phonon dispersion curves for a large supercell, perhaps containing disorder, can be determined through a combination of conventional lattice dynamical calculations—to obtain the phonon eigenvectors and eigenvalues at Γ for the supercell—and a band unfolding process onto the Brillouin zone of the parent unit cell of the average structure. The SCLD method is then applied to a variety of test cases, revealing the presence of disorder-induced phonon broadening which is impacted by both the origin of disorder and simple disorder correlations.

The research presented in Chapter 5 applies the SCLD method, detailed in Chapter 4, to a selection of procrystalline configurations enumerated in Chapter 3. The resulting analysis finds that phononic band gaps can appear selectively in the presence of particular procrystalline disorder—an effect not observed in the corresponding vibrational spectra of the ordered or randomly disordered analogues. This result is believed to be particularly significant as it demonstrates that systems containing correlated disorder may exhibit physical properties which are not found in their ordered or randomly disordered counterparts. Indeed, equivalent studies are presented to show the effect of correlated disorder on the electronic and photonic band struc-

ture. In both spectra, the opening of a band gap is demonstrated in the case of the procrystalline decoration, revealing the ubiquitous impact of geometrically driven disorder on the collective properties of materials.

Having established robust disorder-property relationships via the procrystalline state, the research in Chapter 6 is focussed on understanding how the extent of disorder might alter the magnitude of physical responses. Here, the methods used to generate procrystalline states were employed to construct one-dimensional fibre entanglements with varying degrees of disorder. The property of interest in these systems is that of the swelling response—how much can a dense packing of one-dimensional fibres unravel to increase pore volume? This mechanical response was specifically chosen, as even in the limit of ordered fibre packings, swelling responses vary hugely—the reasoning for which is yet to be fully understood. As ordered fibre packings produce a large range of swelling responses, the work in Chapter 6 is concerned with revealing the effect of disorder on this mechanical property. The results of this study find that small quantities of disorder tend to diminish any swelling response of ordered packings as the collective mechanism associated with swelling response is interrupted. Nevertheless, in highly disordered entanglements, with little relation to any ordered fibre packing, extreme swelling responses, in excess of those found in the ordered limit, can be observed. Correspondingly, this supports the conclusion of the previous chapter by showing that correlated disorder can result in physical properties inaccessible to ordered analogues.

The thesis then concludes with a critical discussion of this research as a whole, with an emphasis on the future direction of research that may have emerged from this work.

Chapter 2

Methodology

This thesis is concerned with the correlated disordered arrangements of objects in space—*e.g.* atoms, spin orientations and one-dimensional fibres—and their impact on the physical properties of the material. In this chapter, the methods and theory relevant to this thesis are detailed.

This chapter begins with a discussion of the techniques used to analyse disordered crystal structures, specifically diffraction theory. This section is focussed on detailing the origins of Bragg scattering (order) and diffuse scattering (static disorder and lattice vibrations). In Section 2.2 the generalised Monte Carlo approach used in the generation of the disordered models at the centre of this thesis is described. The theory of lattice dynamics is then presented, followed by a brief overview of the relevant software used in dynamical simulations—the General Utility Lattice Program (GULP). Finally, a summary of photonic theory is given alongside the simulation details of the MIT Photonic Bands software (MPB) used to calculate photonic band structures.

2.1 Scattering theory

The determination of atomic and molecular structure is a fundamental cornerstone of solid-state chemistry, and as such the X-ray and neutron diffraction techniques, from which crystallographic information is obtained, are crucial to the field. In this section an overview of scattering theory is provided, with a focus on understanding the origin of Bragg and diffuse scattering which arise from the ordered and disordered correlations in the crystal structure respectively.

2.1.1 Bragg scattering

The diffraction of X-rays by crystals was first observed by Max von Laue, Paul Knipping and Walter Friedrich in 1912 [221, 222]. An incident X-ray beam was found to split as the result of interference with atomic structure of a crystal to produce a regular pattern of spots on photographic film. Subsequent experiments showed that the pattern of diffraction spots was dependent on the crystal in the beam [223]. W. L. Bragg and W. H. Bragg discovered that this phenomenon was due to a direct link between the diffraction pattern and the atomic arrangements within the crystal structure through what is now known as Bragg's law [38, 224]

$$n\lambda = 2d \sin \theta, \quad (2.1)$$

where X-rays of wavelength λ are diffracted by planes of atoms with spacing d . Here, n is a positive integer and θ represents the angle between the lattice planes and the incident X-ray beam. A simple analogy can be drawn between Bragg's law for the diffraction of X-rays by parallel planes of atoms and the equivalent diffraction of light by equally-spaced parallel semi-transparent mirrors. Here, light reflected by the mirror planes is only in phase if the additional path length is equal to an integer number of wavelengths of the incident beam—*i.e.* $\Delta L = n\lambda$. The difference in path lengths is dependent on the spacing of the planes given by a simple trigonometric relation: $\Delta L = 2d \sin \theta$. A combination of these two equations produces the Bragg condition. As such, by measuring the diffraction pattern of a single crystal in many orientations, or using a polycrystalline sample, the spacing between many different planes of atoms in the crystal, and hence a three-dimensional model of the material, can be determined.

Bragg diffraction therefore originates from the constructive interference of waves scattered from a perfectly periodic lattice. Here, three-dimensional periodicity in real space (lattice vectors—**a**, **b** and **c**) results in a periodic reciprocal lattice (lattice

vectors— $\mathbf{a}^*$, $\mathbf{b}^*$ and $\mathbf{c}^*$). Due to the well-established relationship between the two sets of lattice vectors (detailed in Section 1.1.1), these sharp features in the diffraction data are key in determining the ordered atomic structure. The positions of the Bragg peaks are related to the size and shape of the unit cell, while their phases and amplitudes give positional information of atoms within the unit cell. The amplitude and phases of the scattered waves associated with each (hkl) plane are described by the structure factor:

$$F_{hkl} = \sum_j^N f_j \exp[2\pi i(hx_j + ky_j + lz_j)], \quad (2.2)$$

where each atom, j , is situated at x_j , y_j , z_j within the unit cell, and N represents the number of atoms in the unit cell. The scattering power, f_j , is dependent on the atom/ion and the nature of the incident beam of radiation. X-rays are scattered by electrons, and as such, f_j varies linearly with the number of electrons associated with the atom/ion, so atoms with higher atomic number scatter more strongly. Conversely, neutrons scatter from the atomic nuclei and the scattering power has seemingly random variations between neighbouring atoms on the periodic table and even between atomic isotopes [225]. The measured quantity within a diffraction experiment is the intensity of the scattered beam, which is related to the structure factors by

$$I_{hkl} \propto |F_{hkl}|^2. \quad (2.3)$$

Therefore, the intensity does not relate to the complex component of F_{hkl} and as such an information of the phase of the diffracted waves is lost—a paradigm more commonly known as the “phase problem”.

2.1.2 Diffuse scattering

Diffuse scattering was observed even in the initial X-ray scattering experiments where longer exposures revealed a low intensity background made up of streaks and

spots [223]. However, given the underdeveloped nature of the theory and experimental techniques—especially in the production of monochromatic X-rays—the origin of this phenomena remained poorly understood. In 1940 Lonsdale and Smith presented an overview of the previous work involving diffuse scattering and its causes, concluding that while Bragg diffraction arises from the periodic arrangements of atoms, diffuse scattering occurs due to Bremsstrahlung (radial streaks and Laue spots), or deviations from the ordered crystal lattice (non-radial spots and streaks) [226, 227]; this thesis is concerned with the latter case. These deviations from the average structure often occur in one of two forms: (i) thermal diffuse scattering, where the motion of atoms away from their crystallographic sites is due to the excitation of low energy phonons; (ii) diffuse scattering emerging from static disorder [Fig. 2.1]. The work presented in this thesis is primarily concerned with static diffuse scattering; nevertheless, a brief description of thermal diffuse scattering is provided for comparison.

The position and pattern of diffuse scattering occurring from the thermal motion of atoms is directly related to the wave-vector of the excited lattice vibration. As

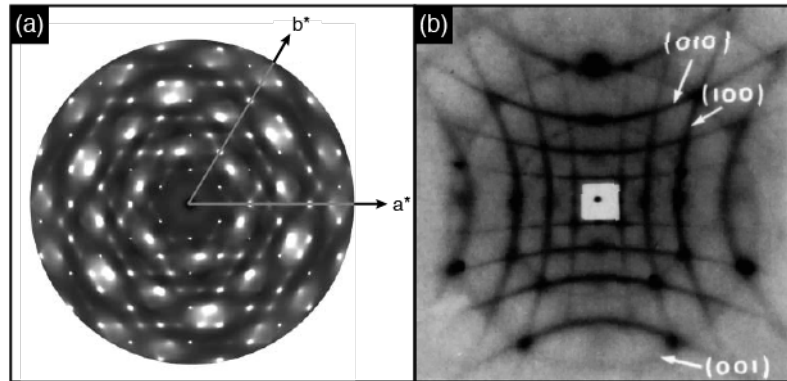


Figure 2.1: The origins of diffuse scattering. (a) A single crystal image of pentachloronitrobenzene in the $(hk0)$ plane reveals thermal diffuse scattering due to the thermal population of low-energy phonon modes. Adapted from Refs. [102, 228]. Reproduced with permission of the International Union of Crystallography. (b) Contrastingly, in the case of BaTiO_3 the streaks of diffuse scattering are caused by static correlated off-centre displacements of the Ti^{4+} ions. Adapted from Ref. [9]. Reproduced with permission of the International Union of Crystallography.

such, thermal diffuse scattering appears in the regions of reciprocal space that are associated with low frequency phonon modes [102, 229–231]. This form of diffuse scattering is often observed as a broadening of scattered intensity around the Bragg peaks—*i.e.* phonons centred around Γ —or less commonly, streaks of intensity along high symmetry directions of the Brillouin zone [226]. The intensity of thermal diffuse scattering and, moreover, the phonon frequencies themselves may be temperature dependent. Here, a decrease in $k_B T$ results in a decreased population of excited vibrational states according to Boltzmann statistics and hence a decrease in thermal diffuse scattering intensity.

By comparison, the form of diffuse scattering arising from static disorder is commonly less restricted in $\mathbf{k}$ -space as it is not related to the excitation of low frequency phonon modes. Moreover, the intensity of the diffuse scattering is largely temperature independent if the occurrence of any order-disorder phase transitions are discounted. The scattering behaviour of statically disordered crystals often still contains Bragg peaks. Here, the Bragg scattering reflects the average structure of the crystal—with conventional crystallographic analysis, yielding all the structural information superimposed upon a single unit cell. Conversely, diffuse scattering gives information of the divergence from the average structure.

The pattern of the diffuse scattering is impacted by the pairwise disorder correlations and as such is independent of the origin of the diffuse scattering [102]. A general expression for the intensity of diffuse scattering can be obtained from a Taylor expansion of the kinematic scattering equation, whereby

$$\begin{aligned}
I(\mathbf{k}) &= \sum_{n=1}^N \sum_{m=1}^N f_m f_n \exp[i(\mathbf{k} \cdot \mathbf{R}_m + \mathbf{u}_m - \mathbf{R}_n + \mathbf{u}_n)] \\
&\simeq \sum_{n=1}^N \sum_{m=1}^N f_m f_n \exp[i(\mathbf{k} \cdot \mathbf{R}_m - \mathbf{R}_n)] \\
&\quad \times \left(1 + i\mathbf{k} \cdot (\mathbf{u}_n - \mathbf{u}_m) - \frac{1}{2}[\mathbf{k} \cdot (\mathbf{u}_n - \mathbf{u}_m)]^2 + \dots \right).
\end{aligned} \tag{2.4}$$

Here, the pair-wise correlations of atoms n and m with scattering power, f , contribute to the total scattered intensity, $I(\mathbf{k})$. The atoms are then situated at average position $\mathbf{R}$ with a small displacement $\mathbf{u}$. Correspondingly, structures with hydrogen-bonding disorder, compositional or displacive disorder will produce the same underlying diffuse scattering pattern if they share the equivalent underlying pairwise disorder correlations. However, the form factor will be heavily dependent on the nature of the disordered object. Unfortunately, due to the nature of the scattering experiment, there can be no distinguishing within diffraction data between two configurations with equivalent pairwise correlations but different correlations at higher orders *e.g.* three-body correlations [Fig 2.2] [232]. Qualitatively, the form of the diffuse features reflect the strength of correlation of the static disorder, with highly featured diffuse scattering reflecting strong correlations. Accordingly, an absence of disorder correlations (*i.e.* random disorder) is associated with an absence of structured diffuse features and so in this regime the diffuse scattering is equally distributed across reciprocal space, with the intensity simply decaying with increasing wave-vector.

The intensity of the diffuse scattering is derived from the degree of deviation of the crystal from the average structure. By way of explanation, two examples are drawn upon. Firstly, a structure containing displacive disorder will have an increased diffuse scattering intensity with larger displacement magnitudes from the average crystallographic site. Similarly, a generalised disordered binary AB alloy will exhibit stronger diffuse scattering when the difference in scattering factors, Δf_j , of the two components A and B is maximised [102].

Unfortunately, both the measurement and analysis of diffuse scattering is far from routine. Experimentally, the intensity of diffuse scattering is often orders of magnitude smaller than that of the Bragg scattering [102]. As such, extremely high flux is needed to ensure that all of the diffuse scattering is observed. Moreover, diffuse scattering from static disorder occurs across a wide range of reciprocal space, so

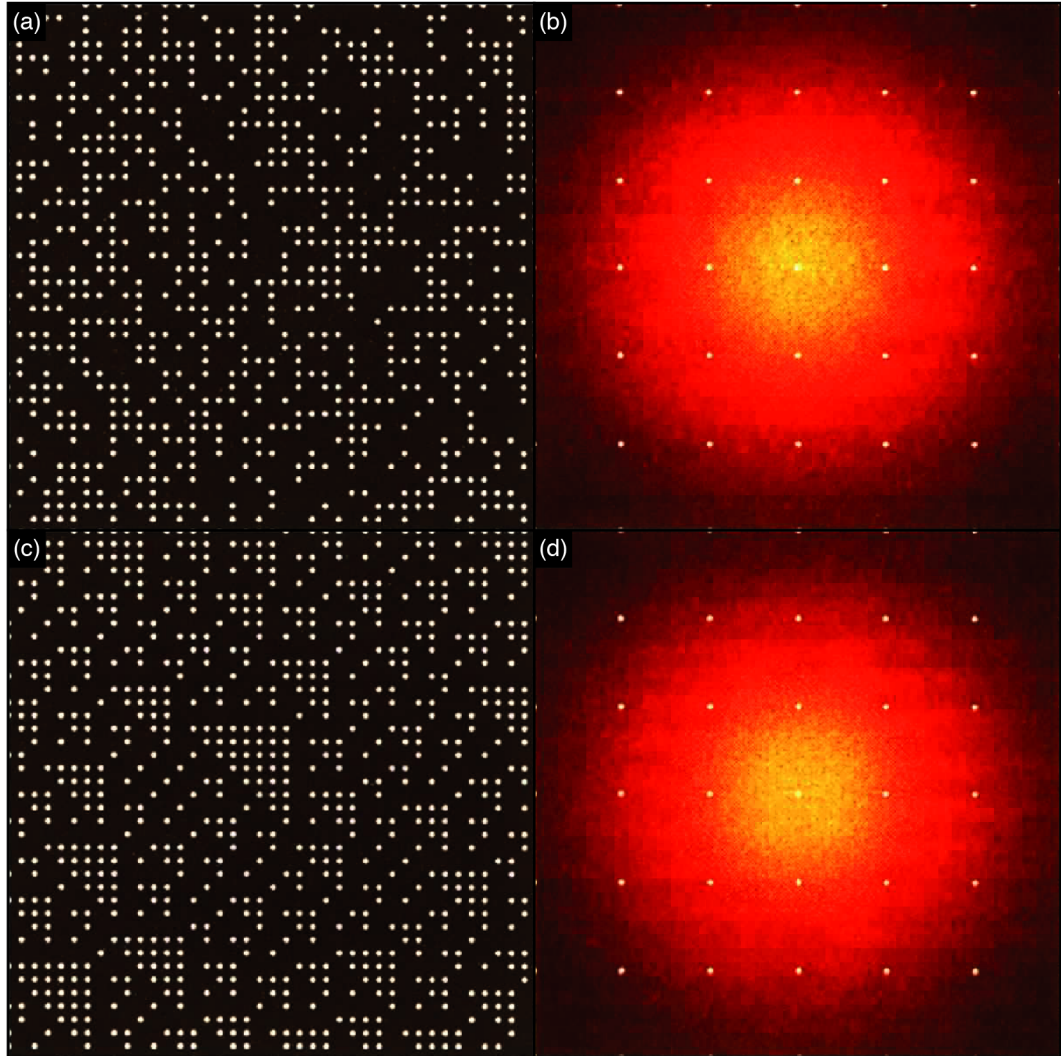


Figure 2.2: The effect of high-order disorder correlations on the diffuse scattering signature. Panels (a) and (c) show two independent disorder models with the same two-body correlations, in this case zero. While (a) shows no other correlations, (c) has a large three site correlations resulting in large triangular regions. The two configurations are clearly different; however, their diffraction patterns, shown in (b) and (d) respectively, are equivalent as the scattering behaviour is only sensitive to two body correlations. Adapted from Ref. [232]. Reproduced with permission of the International Union of Crystallography.

for a single crystal diffraction experiment, many crystal orientations are required to determine the form of the diffuse scattering in reciprocal space [233]. Furthermore, given the low intensity of the diffuse contribution, great care must be made in determining the contribution from the background scattering and other non-elastic scattering events—*e.g.* Compton scattering and fluorescence—such that accurate data normalisation can be conducted [102].

Having successfully collected the data, there are two main approaches used in its analysis: (i) matching (rather than refining) the reciprocal space diffraction data to those generated from large supercells of model systems containing chemically sensible correlated disorder [234, 235]; (ii) the use of 3D- Δ PDF maps—the Fourier transform of the diffuse scattering—to reveal the difference in atomic correlations from the average structure in real space [236, 237]. While both approaches are powerful, neither has proved to be completely generalisable. Making chemically sensible and rationalisable alterations to the supercell of the average structure to contain the correct disorder correlations for pattern matching is far from simple and can only be performed on a case by case basis, whereas the generation and analysis of 3D- Δ PDF maps is an involved process requiring high levels of expertise. Given the high barriers to static diffuse scattering analysis, disordered crystal structures are often reported as their average structure, where only the Bragg scattering has been analysed in a conventional manner and diffuse scattering, where it is mentioned, is only discussed in passing.

2.2 The Monte Carlo algorithm

Monte Carlo (MC) simulations have been employed to tackle problems in many, seemingly unrelated, areas such as artificial intelligence for playing the board game Go [238], financial valuation [239], and in search and rescue operations [240]. Within solid state research the MC approach is key to the study of disordered materials including fitting experimental data [241, 242], investigating specific heat anomalies

[243], and modelling order-disorder phase transitions [244]. In this thesis I have made extensive use of Monte Carlo (MC) simulations to generate correlated disordered configurations. The central aim of the MC approaches used in this thesis is the achievement of structural optimisation through random sampling. Here, I will present the general MC procedure, with the details of specific simulations being included in later chapters.

In this thesis, the Monte Carlo simulations make use of the Metropolis-Hastings algorithm [245] to generate configurations which achieve a minimal energy defined by a given Hamiltonian. The procedure begins with the generation of a starting configuration, where the initial states of the features of interest are usually randomly assigned. An individual feature is then randomly selected and a trial move is proposed *e.g.* a spin flip or bond reorientation. This trial move is then accepted with a given probability established from the Boltzmann statistics:

$$Q = \exp \left[- \frac{\Delta E}{k_B T} \right], \quad (2.5)$$

where k_B is the Boltzmann constant, T represents the temperature of the simulation and ΔE is the change in energy upon the trial move. A random number r is then generated where $0 \leq r < 1$ —the trial move is accepted if $Q > r$ but is otherwise rejected. This criterion stipulates that any move which reduces the energy of the configuration is accepted while a move where $\Delta E > 0$ results in a probability of acceptance dependent on the magnitude of ΔE . The acceptance of ‘bad’ moves increases the configurational energy and prevents the simulation from remaining in a local energy minimum. This process of selecting a random feature, testing a trial move before acceptance/rejection is then repeated until the configurational energy reaches a stable equilibrium. However, when generating structural models, it can be useful to exit the simulation at a predetermined configurational energy, rather than at equilibrium.

2.2.1 Optimisation processes

When generating structural models with low configurational energies, simulations using Monte Carlo-like methods often have difficulty in reaching the exit conditions despite the acceptance of some bad moves. In this event, the temperature of the simulation is commonly varied to achieve a global minimum. The most well-established approach is simulated annealing, whereby the MC simulation begins at a high temperature and gradually cools as the simulation progresses [246, 247]. In this way, local energy minima can be overcome early in the process, allowing the configuration to settle into the global energy minimum.

The MC simulations employed in this thesis were concerned with generating a structural model at a particular energy—a ground state configuration in which all the local bonding rules were satisfied. In many cases, a simulated annealing approach was not sufficient to reach a true ground state. In these situations, a thermoadaptive method was instead used. This approach is similar to that of simulated annealing—as T generally decreases during the simulation. However, as these simulations were only concerned with generating ground state configurations (rather than those at equilibrium), more complex variations in T were used to avoid local configurational energy minima. Here, the MC simulations began at high temperature. Subsequently, over a predetermined number of trial MC moves ($> 10^7$), the number of accepted moves, m , was counted. In cases where $m > 0$, the temperature of the simulation was decreased; however, if $m = 0$ and the predetermined exit condition had not been met, the temperature was raised. This procedure was then repeated until the exit condition was reached. Crucially, this approach allows the temperature to both increase and decrease which prevents the simulation from becoming trapped in a high energy local minimum and therefore allows the configuration to settle into a lower energy state.

2.3 Lattice dynamical theory

In this section, the theoretical framework necessary to generate phonon dispersion curves for a generalised system is detailed. Here, the derivation of the dynamical matrix is adapted from that presented in Ref. [30].

2.3.1 Derivation of the dynamical matrix

In deriving the dynamical matrix, an infinite one dimensional diatomic chain is considered, where atomic motion is restricted to lie along the chain axis—*i.e.* only longitudinal vibrational modes are allowed. In this model, there are two atoms with masses m and M in the unit cell interacting via harmonic bonds with two separate strengths, G and g [Fig. 2.3]. The lattice parameter is a .

Classically, the energy of the harmonic bond is only dependent on the bond strength between the atoms and the displacement of the atoms with regard to their equilibrium positions. As such, the harmonic energy of the entire crystal can be simply written as:

$$E = \frac{1}{2} \sum_n \left[G(U_n - u_n)^2 + g(u_{n-1} - U_n)^2 \right], \quad (2.6)$$

where U and u represent the displacements along the lattice vector of atoms of mass M and m from their equilibrium positions, and n indexes the unit cell in positive increments along the lattice vector. From classical mechanics, the equations of

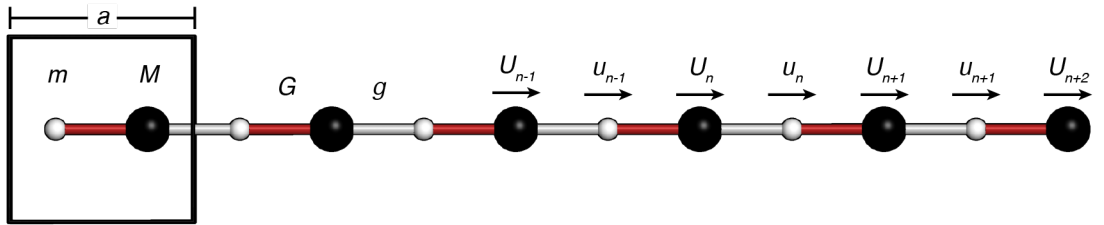


Figure 2.3: The one-dimensional diatomic chain model. A representation of the model considered in the derivation of the dynamical matrix. Atoms of mass M and m , with displacement vectors U and u , are shown in black and white respectively. The bond strengths G and g are represented in red and grey and the unit cell is shown with a black outline.

motion for each of the generalised atoms M and m can be simply stated:

$$M \frac{\partial^2 U_n}{\partial t^2} = - \frac{\partial E}{\partial U_n}, \quad (2.7)$$

$$m \frac{\partial^2 u_n}{\partial t^2} = - \frac{\partial E}{\partial u_n}. \quad (2.8)$$

Substituting into Equation 2.6 gives

$$M \frac{\partial^2 U_n}{\partial t^2} = -G(U_n - u_n) - g(U_n - u_{n-1}) = -(G + g)U_n + gu_{n-1} + Gu_n, \quad (2.9)$$

$$m \frac{\partial^2 u_n}{\partial t^2} = -G(u_n - U_n) - g(u_n - U_{n+1}) = -(G + g)u_n + GU_n + gU_{n+1}. \quad (2.10)$$

From this stage, the generalised one-dimensional analogue of the wave equation shown in Equation 1.6 is required. Here, the time dependent motion of each atom is assumed to be a superposition of all travelling waves defined by

$$U_n = \sum_{\mathbf{k}} \tilde{U}_{\mathbf{k}} \exp(i[\mathbf{k}na - \omega_{\mathbf{k}}t]), \quad (2.11)$$

$$u_n = \sum_{\mathbf{k}} \tilde{u}_{\mathbf{k}} \exp(i[\mathbf{k}na - \omega_{\mathbf{k}}t]). \quad (2.12)$$

In these equations, $\mathbf{k}$ is the one-dimensional wave-vector (as the crystal is one-dimensional) and $\omega_{\mathbf{k}}$ is the angular frequency of the particular vibrational mode, while $\tilde{U}_{\mathbf{k}}$ and $\tilde{u}_{\mathbf{k}}$ represent the complex amplitudes of each travelling wave. Together, $\tilde{U}_{\mathbf{k}}$ and $\tilde{u}_{\mathbf{k}}$ encompass the relative phases of the atoms in each vibration and also the difference in the comparative magnitude of atomic motion of the two atom types due to their difference in mass. When considering each individual wave-vector separately,

simple substitution of Equation 2.11 into Equation 2.9 yields

$$\begin{aligned} -M\tilde{U}_{\mathbf{k}}\omega_{\mathbf{k}}^2 \exp(i[\mathbf{k}na - \omega_{\mathbf{k}}t]) &= -(G + g)\tilde{U}_{\mathbf{k}} \exp(i[\mathbf{k}na - \omega_{\mathbf{k}}t]) \\ &+ g\tilde{u}_{\mathbf{k}} \exp(i[\mathbf{k}(n-1)a - \omega_{\mathbf{k}}t]) + G\tilde{u}_{\mathbf{k}} \exp(i[\mathbf{k}na - \omega_{\mathbf{k}}t]), \end{aligned} \quad (2.13)$$

which after cancelling the common factors, Equation 2.13 becomes

$$-M\omega_{\mathbf{k}}^2\tilde{U}_{\mathbf{k}} = -(G + g)\tilde{U}_{\mathbf{k}} + (G + g \exp[-i\mathbf{k}a])\tilde{u}_{\mathbf{k}}, \quad (2.14)$$

with the analogous treatment of Equation 2.10 giving

$$-m\omega_{\mathbf{k}}^2\tilde{u}_{\mathbf{k}} = -(G + g)\tilde{u}_{\mathbf{k}} + (G + g \exp[i\mathbf{k}a])\tilde{U}_{\mathbf{k}}. \quad (2.15)$$

These two relations can be treated as simultaneous equations written in terms of the complex amplitudes $\tilde{U}_{\mathbf{k}}$ and $\tilde{u}_{\mathbf{k}}$; however, for the derivation of the dynamical matrix, it is convenient to change the variables such that

$$E = M^{\frac{1}{2}}\tilde{U}_{\mathbf{k}} \quad \text{and} \quad e = m^{\frac{1}{2}}\tilde{u}_{\mathbf{k}}. \quad (2.16)$$

Correspondingly, Equations 2.14 and 2.15 become

$$-\omega_{\mathbf{k}}^2 E = -(G + g)M^{-1}E + (G + g \exp[-i\mathbf{k}a])(mM)^{-\frac{1}{2}}e, \quad (2.17)$$

$$-\omega_{\mathbf{k}}^2 e = -(G + g)m^{-1}e + (G + g \exp[i\mathbf{k}a])(mM)^{-\frac{1}{2}}E, \quad (2.18)$$

which can be written collectively as the eigenvalue problem

$$\begin{pmatrix} E \\ e \end{pmatrix} \omega_{\mathbf{k}}^2 = \mathbf{D}(\mathbf{k}) \begin{pmatrix} E \\ e \end{pmatrix} \quad (2.19)$$

where $\mathbf{D}(\mathbf{k})$ is the dynamical matrix defined as

$$\mathbf{D}(\mathbf{k}) = \begin{pmatrix} (G + g)M^{-1} & -(G + g \exp[-i\mathbf{k}a])(mM)^{-\frac{1}{2}} \\ -(G + g \exp[i\mathbf{k}a])(mM)^{-\frac{1}{2}} & (G + g)m^{-1} \end{pmatrix}. \quad (2.20)$$

2.3.2 Properties of the dynamical matrix

The dynamical matrix is a function of the wave-vector; correspondingly, for each value of $\mathbf{k}$ there is an associated dynamical matrix. Nevertheless, there are two important symmetry properties true of all dynamical matrices which simplify the subsequent determination of the phonon dispersion curves: (i) $\mathbf{D}(\mathbf{k})$ and $\mathbf{D}(-\mathbf{k})$ are complex conjugates; (ii) the matrix is Hermitian, or more simply:

$$\mathbf{D}^*(\mathbf{k}) = \mathbf{D}(-\mathbf{k}), \quad (2.21)$$

$$\mathbf{D}^*(\mathbf{k}) = \mathbf{D}^T(\mathbf{k}). \quad (2.22)$$

Furthermore, $\mathbf{D}(\mathbf{k})$ is usually a $dZ \times dZ$ diagonalisable square matrix, where d is the number of degrees of freedom of the system and Z the number of atoms in the unit cell—*i.e.* a 2×2 matrix for the one-dimensional diatomic example described above. The dynamical matrix can then be converted to recognisable eigenvalue and eigenvector form:

$$\mathbf{\Omega} = \mathbf{e}^{-1} \mathbf{D}(\mathbf{k}) \mathbf{e}, \quad (2.23)$$

where,

$$\mathbf{\Omega} = \begin{pmatrix} \omega_1^2 & 0 \\ 0 & \omega_2^2 \end{pmatrix} \quad ; \quad \mathbf{e} = \begin{pmatrix} E_1 & e_1 \\ E_2 & e_2 \end{pmatrix}. \quad (2.24)$$

From this relation, there are a number of simple, yet important, results to consider. Firstly, the diagonal matrix $\mathbf{\Omega}$, more commonly known as the frequency matrix, is

made up of the squared phonon mode frequencies, ω^2 , at the chosen wave vector. Correspondingly, the eigenvector matrix, $\mathbf{e}$, contains information of the atomic displacements and phases, for each of the phonon modes at $\mathbf{k}$. The eigenvectors and eigenvalues can be accessed through a diagonalisation routine, either analytically or computationally using software such as LAPACK [248]. Since $\mathbf{\Omega}$, $\mathbf{e}$ and $\mathbf{D}(\mathbf{k})$ must be of the same dimensionality, it follows that there must be dZ phonon modes per wave vector. Furthermore, as the dynamical matrix is Hermitian, the eigenvalues of $\mathbf{\Omega}$, must necessarily be real. The vibrational frequencies are then the square root of the eigenvalues. Negative eigenvalues therefore indicate a complex phonon frequency, which, in turn, implies that the structure is unstable with respect to the vibration. In simpler words, the energy of the system can be lowered by applying the atomic displacements contained within the associated eigenvector.

It is also important to note that, by convention, each eigenvector in $\mathbf{e}$ is normalised such that

$$E_1^2 + e_1^2 = E_2^2 + e_2^2 = 1. \quad (2.25)$$

As such, the eigenvector matrix only provides the relative magnitude of atomic motion. Furthermore every eigenvector is orthogonal:

$$E_1 E_2 + e_1 e_2 = 0. \quad (2.26)$$

Under the harmonic approximation, phonon modes can be treated as independent, non-interacting species, which can be added linearly to encapsulate all possible atomic motion, in keeping with the previous assumptions.

The corresponding phonon dispersion curves for any given structure can be obtained by determining the dynamical matrix at a suitable set of wave-vectors—usually those along high symmetry directions within the Brillouin zone—from which the associated phonon frequencies can be obtained. In this way, each individual point on the phonon dispersion curve represents an independent vibration in the crystal

structure, while phonon bands represent the continuous evolution of these vibrations with changing wave-vector.

2.4 General Utility Lattice Program

The General Utility Lattice Program (GULP) is a software package used in the simulation of solid-state structures [249]. GULP is commonly used for lattice energy minimisation and structural optimisation. But this software package includes many additional features including the calculation of surface energies and bulk properties such as Poisson’s ratios, refractive indices and piezoelectric constants. The research presented in this thesis makes extensive use of the lattice dynamical calculation aspects of GULP, which represent the focus of this section.

2.4.1 Structural optimisation

A typical GULP simulation begins with a suitable input of crystallographic information—atomic positions, space groups and lattice parameters—and interatomic potentials chosen from a suite of common forms including Buckingham, Lennard-Jones, harmonic, three-body and electrostatic interactions. In the limit of pair-wise interactions, such as harmonic bonds, the determination of the energy of the crystal is merely a trivial summation of the individual bond energies. However, the electrostatic interactions in ionic structures require the use of Ewald summation techniques [250].

One of the main roles of GULP involves the minimisation of the crystal energy, a key step in solid-state simulations. Within GULP the optimisation process makes use of Newton–Raphson methods. Here, the internal energy of the crystal with respect to the minimisation variable is initially calculated. The second order derivative of the energy—otherwise known as the Hessian matrix—is key in the optimisation process. The Hessian matrix, when inverted, in combination with the gradient

vector, allows calculation of the energy minimum for a given search direction. The optimisation process then proceeds via the conjugate gradients algorithm where each step considered is orthogonal to previous steps. The Hessian matrix is then updated via the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm when the energy of the simulation has dropped by a value over a certain threshold. When the energy of the structural relaxation meets the convergence condition, the requested structural data is generated [249].

2.4.2 Lattice dynamical simulations

After structural optimisation, GULP can then be further employed to determine the dynamical matrix at any desired wave-vector and correspondingly provide the phonon frequencies and their associated eigenvectors. Indeed, in the cases where multiple wave-vectors along high-symmetry directions or an isotropic $\mathbf{k}$ -mesh is provided, GULP is capable of calculating the phonon dispersion curves and the phonon density of states for a given structure. In order to perform its lattice dynamical function, GULP makes use of the Hessian matrix with respect to atomic displacements in Cartesian space to generate the force constant matrix

$$\Phi_{\alpha\beta} \begin{pmatrix} j & j' \\ 0 & l' \end{pmatrix} = \frac{\partial^2 W}{\partial u_{j0}^\alpha \partial u_{j'l'}^\beta}, \quad (2.27)$$

which is subsequently used to determine the dynamical matrix as

$$\mathbf{D}_{\alpha\beta j'j'}(\mathbf{k}) = \frac{1}{(m_j m_{j'})^{1/2}} \sum_{l'} \left[\Phi_{\alpha\beta} \begin{pmatrix} j & j' \\ 0 & l' \end{pmatrix} \times \exp\{i\mathbf{k} \cdot [\mathbf{r}(j'l') - \mathbf{r}(j0)]\} \right], \quad (2.28)$$

where atom j in unit cell l lies at position $\mathbf{r}(jl)$ and α, β represents the cartesian axes x, y, z . Examples of lattice dynamical simulations on unit cells of primitive cubic (α -Po) and body-centred cubic structures are presented in Figure 2.4. Here, the model systems are made elastically stable by harmonic stretching potentials and

bond angle potentials between nearest neighbours of the form

$$E_{\text{harm}} = \frac{1}{2}k_{\text{harm}}(r - r_0)^2, \quad (2.29)$$

$$E_{\text{L}} = \frac{1}{2}k_{\text{L}}(\theta - \theta_0)^2. \quad (2.30)$$

The values of the parameters used in these calculations are given in Table 2.1.

2.5 Photonic theory

In this section, the theoretical concepts that form the basis of calculating photonic band structure for dielectric materials are detailed, specifically the derivation of the photonic equivalent of the dynamical matrix [32]. The optical responses of photonic materials are governed by classical electrodynamical theory, as such the generalised derivation photonic states begins with Maxwell's equations:

$$\nabla \cdot \mathbf{D} = 4\pi\rho, \quad (2.31)$$

$$\nabla \cdot \mathbf{B} = 0, \quad (2.32)$$

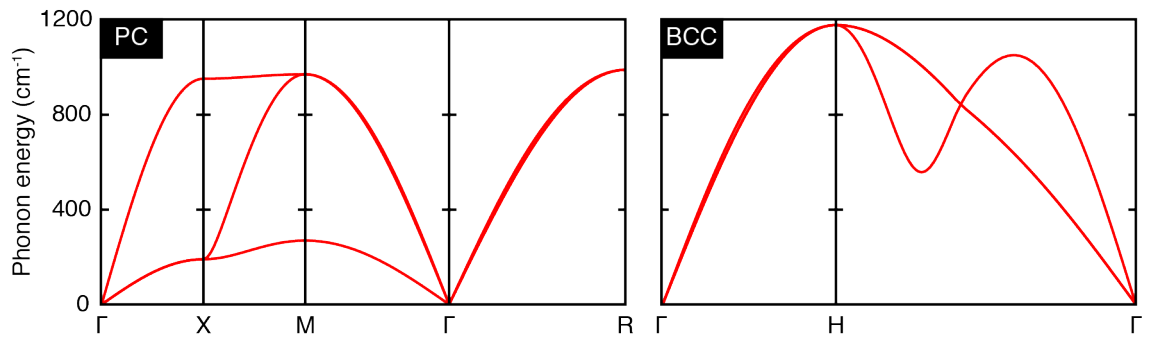


Figure 2.4: Lattice dynamical calculations of phonon band structure. The phonon dispersion curves for the (a) primitive cubic (α -Po) and (b) body-centred cubic structures calculated using GULP [249].

$$\nabla \times \mathbf{E} + \frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} = 0, \quad (2.33)$$

$$\nabla \times \mathbf{H} - \frac{1}{c} \frac{\partial \mathbf{D}}{\partial t} = \frac{4\pi}{c} \mathbf{J}. \quad (2.34)$$

Here, $\mathbf{E}$ and $\mathbf{H}$ are the macroscopic electric and magnetic fields, $\mathbf{D}$ and $\mathbf{B}$ are the electric displacement and magnetic induction fields and ρ and J represent the charge and current density. For simplicity, it is assumed that the material is isotropic, lossless, and that the response of the material is linear. Correspondingly, the auxiliary electric and magnetic fields are comparable to their macroscopic counterparts via a scalar function, $\epsilon(\mathbf{r})$ or $\mu(\mathbf{r})$, within the constitutive relations:

$$\mathbf{D}(\mathbf{r}, t) = \epsilon(\mathbf{r})\mathbf{E}(\mathbf{r}, t) + \mathbf{P}(\mathbf{r}, t), \quad (2.35)$$

$$\mathbf{B}(\mathbf{r}, t) = \mu(\mathbf{r})\mathbf{H}(\mathbf{r}, t) + \mathbf{M}(\mathbf{r}, t), \quad (2.36)$$

where $\mathbf{P}$ and $\mathbf{M}$ are the polarisation and magnetisation of the material. Yet, in dielectric media $\mathbf{P} = 0$, $\mathbf{M} = 0$, $\rho = 0$ and $J = 0$. Moreover, $\mu(\mathbf{r})$ is often close to

Table 2.1: A summary of the parameter values used in the conventional lattice dynamical calculations.

Parameter	Primitive cubic	Body-centred cubic
$a / \text{\AA}$	10	10
m / amu	60	60
$k_{\text{harm}} / \text{eV}\text{\AA}^{-2}$	50	50
$k_{\text{L}} / \text{eVrad}^{-2}$	50	50
$r_0 / \text{\AA}$	10.0	8.66
$\theta_0 / ^\circ$	90.0	70.5

unity, as such Maxwells' equations can be easily simplified:

$$\nabla \cdot \epsilon(\mathbf{r})\mathbf{E}(\mathbf{r}, t) = 0, \quad (2.37)$$

$$\nabla \cdot \mathbf{H}(\mathbf{r}, t) = 0, \quad (2.38)$$

$$\nabla \times \mathbf{E}(\mathbf{r}, t) + \frac{1}{c} \frac{\partial \mathbf{H}(\mathbf{r}, t)}{\partial t} = 0, \quad (2.39)$$

$$\nabla \times \mathbf{H}(\mathbf{r}, t) - \frac{\epsilon(\mathbf{r})}{c} \frac{\partial \mathbf{E}(\mathbf{r}, t)}{\partial t} = 0. \quad (2.40)$$

In this thesis, the photonic properties of interest are time independent, and as Maxwell's equations are linear in time, the time dependence can be separated by expanding the electric and magnetic fields into a set of harmonic modes.

$$\mathbf{H}(\mathbf{r}, t) = \mathbf{H}(\mathbf{r}) \exp(i\omega t), \quad (2.41)$$

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{E}(\mathbf{r}) \exp(i\omega t). \quad (2.42)$$

This approach is not a limitation as any solution can be constructed from a combination of the separated harmonic modes through the use of Fourier analysis. Correspondingly, the Maxwell equations for a linear, lossless, isotropic dielectric medium become

$$\nabla \cdot \epsilon(\mathbf{r})\mathbf{E}(\mathbf{r}) = 0, \quad (2.43)$$

$$\nabla \cdot \mathbf{H}(\mathbf{r}) = 0, \quad (2.44)$$

$$\nabla \times \mathbf{E}(\mathbf{r}) + \frac{i\omega}{c} \mathbf{H}(\mathbf{r}) = 0, \quad (2.45)$$

$$\nabla \times \mathbf{H}(\mathbf{r}) - \frac{i\omega\epsilon(\mathbf{r})}{c} \mathbf{E}(\mathbf{r}) = 0. \quad (2.46)$$

Combination of Equations 2.45 and 2.46 yields an expression purely in terms of $\mathbf{H}(\mathbf{r})$:

$$\nabla \times \left(\frac{1}{\epsilon(\mathbf{r})} \nabla \times \mathbf{H}(\mathbf{r}) \right) = \left(\frac{\omega}{c} \right)^2 \mathbf{H}(\mathbf{r}), \quad (2.47)$$

which is analogous to the eigenvalue problem in Equation 2.19:

$$\Theta \mathbf{H}(\mathbf{r}) = \left(\frac{\omega}{c} \right)^2 \mathbf{H}(\mathbf{r}). \quad (2.48)$$

Here, Θ acts as the photonic equivalent of $\mathbf{D}(\mathbf{k})$ in lattice dynamical approaches. Indeed, there are many further similarities: Θ is also Hermitian, the eigenvalues are proportional to the squared mode frequencies and the eigenvectors are also orthogonal. However, Equation 2.47 only provides eigenvectors and eigenvalues for the transverse magnetic modes. As such, the corresponding transverse electric modes are determined by revisiting Equation 2.46 and solving for $\mathbf{E}(\mathbf{r})$ having already solved the modes of $\mathbf{H}(\mathbf{r})$. Photonic dispersion curves are then constructed by employing Bloch's theorem to solve Equation 2.47 at a variety of $\mathbf{k}$ -vectors as

$$\mathbf{H}_{\mathbf{k}}(\mathbf{r}) = \mathbf{H} \exp[i(\mathbf{k} \cdot \mathbf{r})], \quad (2.49)$$

which subsequently facilitates the determination of the $\mathbf{k}$ -dependence of the transverse magnetic and transverse electric modes frequencies.

2.6 MIT Photonic Bands

In this thesis, the MIT Photonic Bands (MPB) software is used to calculate the photonic band structure of arrangements of dielectric media [251]. MPB requires an input containing structural information such as the distribution of dielectric material within a unit cell and relative lattice parameter values, alongside the desired output information—*i.e.* the number of bands and suitable $\mathbf{k}$ -vector values. The corresponding wave-vector dependent frequency values for the photonic modes are then determined starting with Equation 2.47 and converting to the frequency domain by

$$\mathbf{H}_{\mathbf{k}}(\mathbf{r}) \simeq \sum_{m=1}^N h_m b_m. \quad (2.50)$$

This expression transforms Equation 2.47 into a finite problem, with an infinite number of basis functions b_m with coefficients h_m (*i.e.* $N = \infty$). Correspondingly, the eigenproblem becomes

$$\Theta_b h = \left(\frac{\omega}{c}\right)^2 B h, \quad (2.51)$$

where h represents the column vector of the basis coefficients h_m , Θ_b is defined as $\langle b_\ell | \Theta | b_m \rangle$ and B is equivalent to $\langle b_\ell | b_m \rangle$. The MPB package chooses a planewave basis to represent b_m :

$$b_m = \exp(i\mathbf{G}_m \cdot \mathbf{r}), \quad (2.52)$$

such that the truncation of N can be achieved by applying a cut-off to the magnitude of $\mathbf{G}_m$. MPB then makes use of an iterative eigensolver to determine the mode frequencies at a given wave-vector in ascending order—*i.e.* the lowest frequencies first.* The result of a photonic calculation of a two-dimensional dielectric slab with $\epsilon_r = 10$ using MPB is shown in Figure 2.5.

*Here, two eigensolver methods have been employed within MPB with similar convergence results (i) conjugate-gradient minimisation of the Rayleigh coefficient and (ii) the Davidson approach.

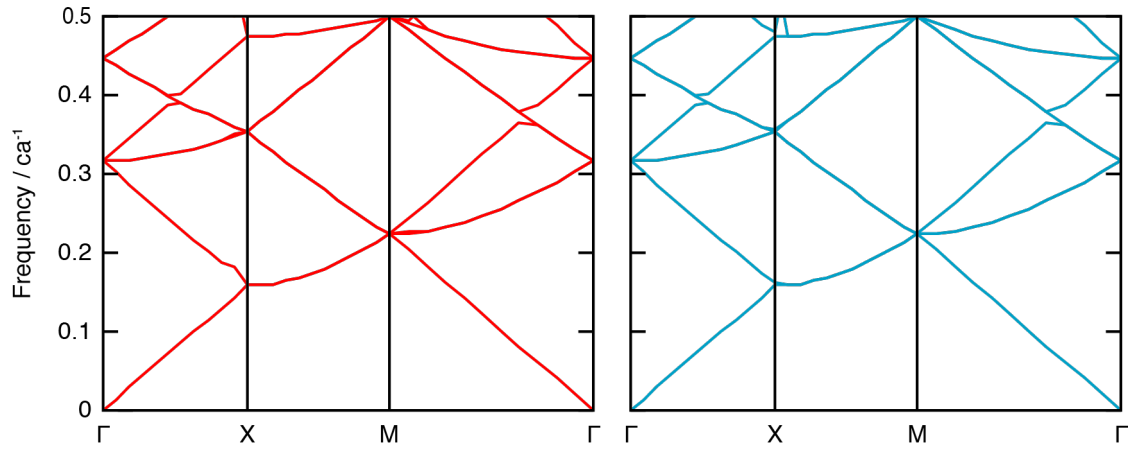


Figure 2.5: The calculation of photonic band structure using MPB. The photonic band structure of a two-dimensional dielectric slab ($\epsilon_r = 10$) is shown with transverse electric (left) and transverse magnetic (right) modes shown in red and blue respectively.

Chapter 3

The procrySTALLine state

The work presented in this chapter is largely derived from the publication “Design of crystal-like aperiodic solids with selective disorder-phonon coupling” [252] and represents the underlying basis for the majority of the research presented in this thesis. This study is focussed on understanding strongly-correlated disorder in the solid state. Within this thesis, the term strongly-correlated disorder is used to describe states which are subject to strict local bonding constraints such as in the dimer, loop and ice models. This is in contrast to the less restricted forms of disorder—*i.e.* higher entropy states—found in plastic crystals and amorphous states, which for the purposes of this thesis are described as weakly-correlated disorder.

Here, a fundamental approach is developed such that certain types of disorder correlations might be easily identified by their signature diffraction behaviour such that realisations of these states across a wide variety of scientific fields might be easily compared. The disorder studied here is conceptually similar to that found in ice, where local bonding considerations result in a locally ordered structure containing both periodic and aperiodic features. This chapter begins with a generalisation of the rules that govern the disorder in ice via a reticular approach, and goes on to enumerate the possible ice-like states on different lattices. A clear definition of this broad class of disorder is then presented followed by a consideration of the entropy in each of these configurations. Important physical realisations of these states are subsequently identified, either directly from the literature or via experimental characterisation techniques: powder and single-crystal diffraction, pair distribution function measurements and microscopy images. Within this chapter, the oxyfluoride samples were prepared by Prof. Peter Slater and refinement of BaFeO_2F and

$\text{Pd}(\text{CN})_2/\text{Pt}(\text{CN})_2$ conducted by Dr. Philip Chater and Dr. Andrew Cairns, respectively.

3.1 Generalisation of ice rules

3.1.1 Square ice

The focus of this thesis is on the concept of strongly-correlated disorder and the simple toy model of square ice proposed by Pauling serves as a suitable starting point [203].

Here, fictional “water molecules” with a bond angle of 90° decorate the lattice points of the square lattice. Each H_2O molecule lies in the plane and satisfies sensible hydrogen bonding rules—*i.e.* every water molecule donates and accepts two hydrogen bonds. There is no unique way of solving this problem, resulting in a degenerate manifold of disordered ground states, yet if the orientations of the “water molecules” were randomly assigned, the local bonding rules would not be satisfied [Fig. 3.1(a)]. Within every ground state, all the water molecules are in the same local environment and further evidence of order can be identified in each row and column where all hydrogen bonds are arranged in the same direction. In recent years, this disordered phase of ice has been observed within graphene nanocapillaries using high resolution electron microscopy imaging [253].

3.1.2 Square ice analogues

The hydrogen bond disorder present in the square ice model is fundamentally geometrical in nature, meaning that any system with the *same* building block geometry on the *same* lattice will be associated with the *same* configurational disorder. For example replacing the $\text{H}-\text{O}\cdots\text{H}$ bonding motif with the $M-\text{C}-\text{N}-M$ linkage provides a mapping onto the cyanide linker orientational disorder found in transition

metal cyanides [Fig. 3.1(b)] [211]. The equivalence of these states is highlighted by the simulated single crystal diffraction behaviour which reveals the same highly structured diffuse scattering in both instances. A further example is found in the ordering of O/N atoms in the layers of transition metal oxynitrides [254, 255]—in this case there is a requirement to perform a geometry inversion from one site to the next (*i.e.* a checkerboard transformation) to recover the identical mapping, but the underlying disorder is exactly the same [Fig. 3.1(c)]. In reciprocal space, the checkerboard flipping translates the diffuse scattering in the single crystal diffraction patterns by $\mathbf{k} = [\frac{1}{2}, \frac{1}{2}]$ —*i.e.* such that it lies between, rather than over, the Bragg peaks—but does not alter the structure of the diffuse scattering in any other way. These three examples all involve compositional or orientational disorder; however

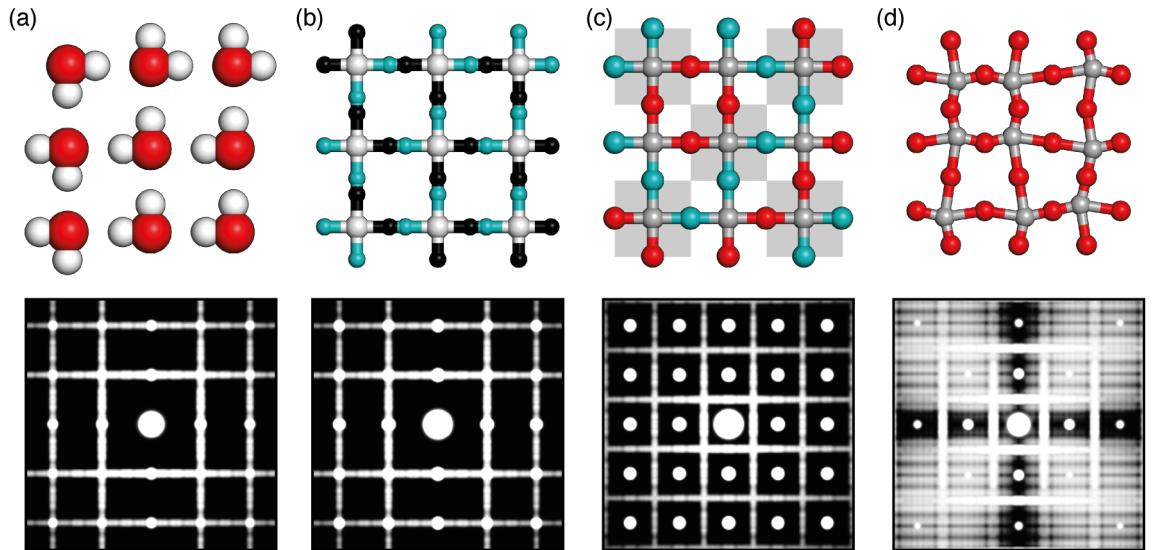


Figure 3.1: Correlated disorder in square ice analogues and their diffraction behaviour. (a) A configurational fragment of square ice (top) and associated diffraction pattern (bottom). (b) A square planar transition metal cyanide that maps onto the square ice state. Each metal atom (white) is surrounded by two carbon atoms (black) and two nitrogen atoms (teal). (c) A transition metal oxynitride presents an identical form of disorder. Each metal cation is surrounded by two oxygen atoms (red) and two nitrogen atoms (teal). Topological equivalence to the square ice state is obtained by considering the N–M–N and O–M–O linkages alternately (shaded regions) (d) Displacements of the M atoms in an MO_2 lattice in one of the $\langle 11 \rangle$ directions related to the oxynitride disorder in (c). Representative configurations are shown above their simulated single crystal diffraction behaviour, which reveals that the geometrical origin of the correlated disorder results in the same structural diffuse scattering pattern in each case. In each case the periodic component possesses four-fold symmetry.

the geometrical nature of the disorder means that it lends itself to application in a large variety of systems including the self-assembly of hard polyhedra [95], charge density [210, 256], orbitals [7], spin orientations [209] and atomic displacements [257] [Fig. 3.1(d)]. The wide range of possibilities in which this disorder can be expressed, along with its applicability across multiple length scales, means that this geometrical approach is relevant to a large diversity of material properties for which disorder is known to be important, such as the mechanical responses of crystalline solids [211, 258] and macroscopic networks [259, 260], ferroic behaviour [261], vibrational behaviour [30, 262] and photonic band structure [219, 263].

3.1.3 Generalisation of ice-like disorder

When seeking to generalise the geometrical disorder present in square ice, the reticular approach for generating network structures was considered [264]. Here, the central idea of interest involves the construction of well-known net topologies through a combination of nodes and linkers. For instance, the square net and primitive cubic net can be constructed by square or octahedral building block geometries respectively connected by linear linkers, shown in blue and pink in Figure 3.2. In the limit of linear linkers the shape of the highly symmetrical node building block trivially determines the corresponding lattice [Fig. 3.2] [15, 264]. In this way, the geometric disorder present in square ice can be considered as a perturbation of the reticular form of the square net by lowering of symmetry of the square building block—in this case distinguishing two adjacent linkers from the original four. Connecting these low-symmetry building units via linear linkers produces configurations that are geometrical representations of the disorder in square ice [Fig. 3.4(b)]. Ultimately this disorder is fundamentally governed by the lattice and the symmetry of the building unit. So the key idea here is that *different* ice-like states may be generated by considering *different* lattices and *different* suitable building unit geometries.

So what are the suitable building unit geometries? For each high symmetry unit

which, in combination with linear linkers, forms a recognisable periodic net—*e.g.* the square unit and the square net—there is a set of building unit geometries which can be considered in the generation of ice-like disorder. The key idea involves taking the high symmetry unit—*i.e.* the square building block—and enumerating the building unit geometries that are possible if different combinations of the arms of a single building block are distinguished. In simpler terms, this process can be viewed as a systematic removal of building block appendages in all the possible different arrangements.

In total there are six different local geometries to consider for perturbations of the square net which are all show within Figure 3.3. The first two are trivial: distinguishing either all, or none of the linkers, in both cases retaining the local D_4 point symmetry of the building unit, and $P4mm$ symmetry of the square lattice [Fig. 3.3(a)]. The next two cases are equivalent to one another—as distinguishing three linkers is equivalent to distinguishing one—and a T-shaped building block can be used to represent the local unit in both [Fig. 3.3(b)]. The resulting configurations have trivial $P1$ symmetry and represent a dense decoration of dimers on the square lattice, a well-established model in statistical mechanics [197, 198]. There are many different realisations of this state including the domino tiling of a square box [204] and Anderson’s resonant valence bond description of cuprate supercon-

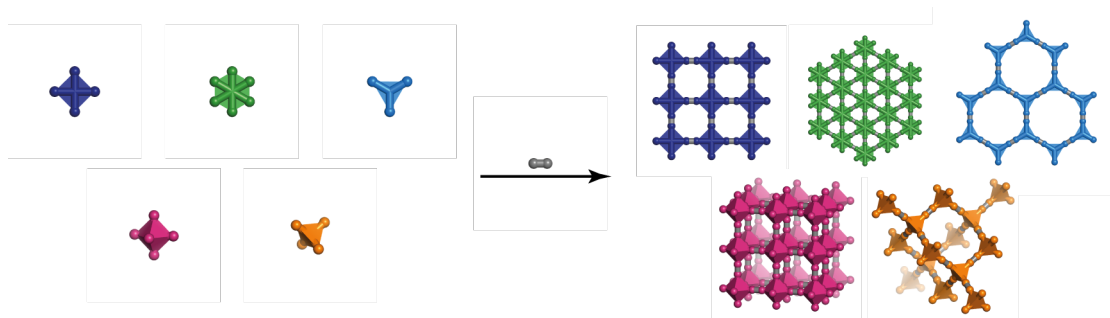


Figure 3.2: An illustration of the reticular approach to produce common topologies. Simple high-symmetry building units are connected with linear linkers to generate the recognisable square (indigo), triangular (green), hexagonal (blue), primitive (pink) and diamond (orange) nets.

ductors [Fig. 3.4(a)] [12]. The final two building units distinguish two linkers but differ by their local stereochemistry. The first distinguishes linkers adjacent to one another (cis), producing configurations with trivial $P1$ symmetry and has already been discussed in detail under the guise of square ice [Fig. 3.3(c)]. The second case, in which the linkers are distinguished opposite to one another (trans) is ordered, which results in a symmetry breaking of the square lattice to $P2mm$ [Fig. 3.3(d)].

Yet, ice-like configurations are not confined to the square lattice; analogous states for other two-dimensional (hexagonal and triangular) and three-dimensional (primitive, diamond) nets are enumerated in Figure 3.4(d)–(r). Complete summaries of each individual state including point symmetry, approximated entropy, diffraction behaviour and known realisations are presented in Appendix A. This full description also includes an enumeration of the nine possible states on the pyrochlore net.

3.1.4 Methodology for generating ice-like states

Each of these configurations were generated using a custom suite of Monte Carlo codes. For each lattice type, a suitably large supercell of the corresponding parent

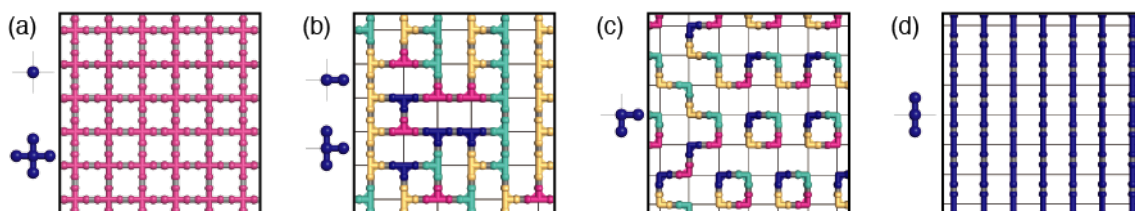


Figure 3.3: An enumeration of the building block geometries available upon the square lattice. There are six building unit geometries which can be considered on the square lattice, of which four are independent. (a) Distinguishing all or none of the arms of the building block gives an ordered net equivalent to that of the square net. (b) The T-shaped building unit formed when one appendage is distinguished from the square building block is equivalent to the case where three arms of the building block are distinguished. The configurations generated when the building blocks are joined by linear linkers are disordered. There are two possible building unit geometries available when two arms of the building unit are distinguished, either when they are adjacent (c) or arranged opposite to one another (d). The former when connected by linear linkers forms a disordered configuration equivalent to that observed in square ice and the transition metal oxynitride systems discussed in Section 3.1.2. Contrastingly, the connection of the building blocks in (d) with linear linkers produces an ordered configuration.

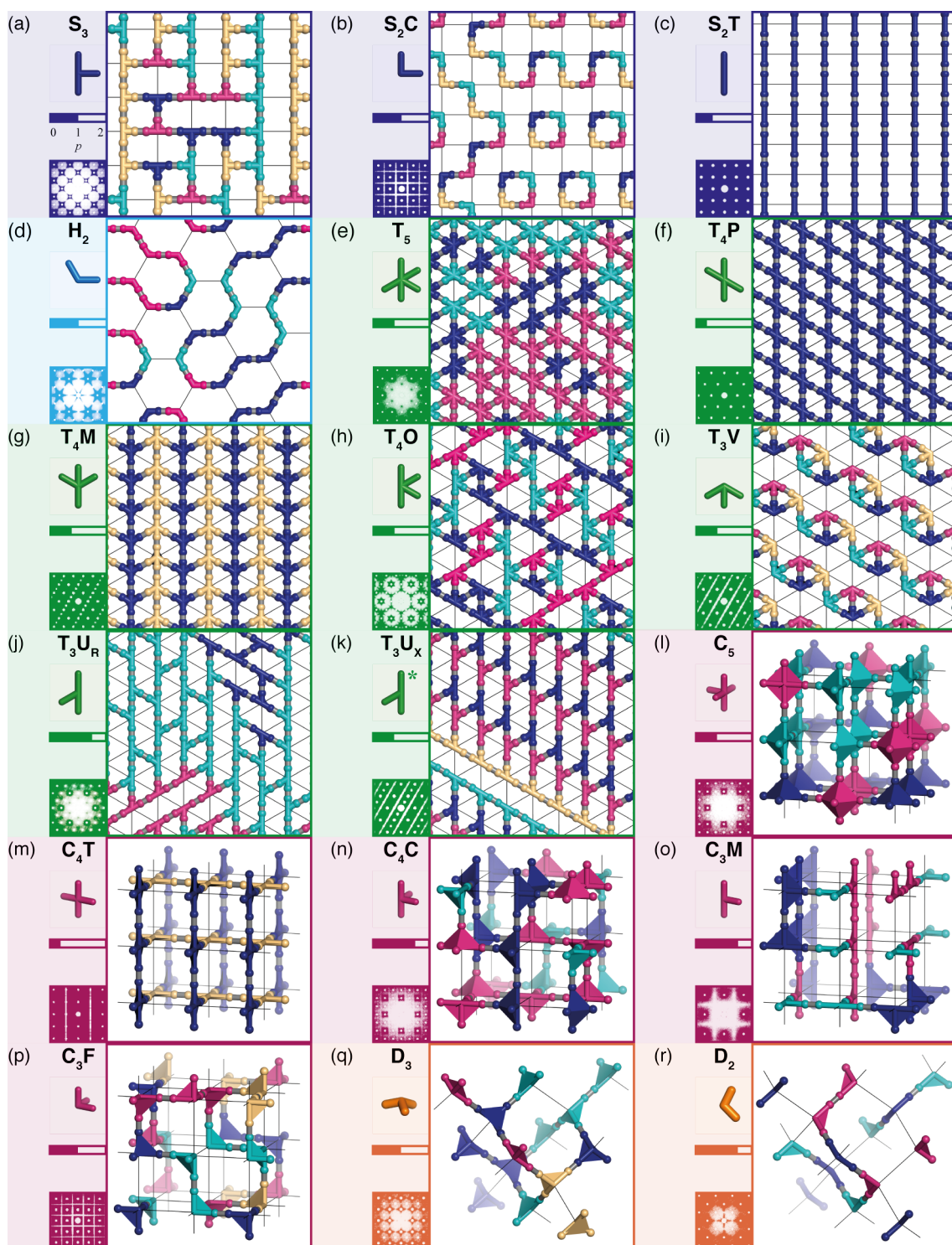


Figure 3.4: Generalised ice-like states. Ice-like states on the square (indigo), hexagonal (blue), triangular (green), diamond (orange) and primitive (pink) nets. Shown on the left of each panel—the appropriate label for the configuration (see Section 3.2.2), the building unit, the Pauling number, p , as a bar chart (see Section 3.2.3) and the single crystal diffraction behaviour, containing structured diffuse scattering in the case of correlated disorder. The main image shows a representative configuration of the building unit connected via linear linkers (node orientations are grouped by colour). The asterisk in (k) indicates that a single enantiomer of the node is considered; the node is chiral when confined to lie in two-dimensions. Illustrations for ice-like states on the pyrochlore net are shown in Appendix A.

crystallographic cell was generated and periodic boundary conditions applied.* The linkers within the supercell were then assigned one of two initial states, $e = \pm 1$, where states of +1 and -1 indicate occupied and vacant linker sites respectively. A fictitious configurational energy, E , was then calculated:

$$E = \sum_{i \in \text{nodes}} \left| \left(\sum_{j \in \text{linkers}} e_{ij} \right) - \bar{e} \right|^2, \quad (3.1)$$

where e_{ij} is the state of the j^{th} linker surrounding the i^{th} node and $\bar{e}$ represents an expectation value specific to the local building block. The expectation value essentially serves as a function to penalise local geometries with the incorrect stereochemistry but with the same number of surrounding occupied linker sites. In the simple example of ice-like states on the diamond net $\bar{e} = 0$ as each node is surrounding two linkers each of $e = +1$ and $e = -1$, and there are no competing stereochemical alternatives. However, in other cases such as in distinguishing between the states shown in Figure 3.4(b) and 3.4(c), $\bar{e} > 0$ in the case of the unwanted local stereochemistry, but $\bar{e} = 0$ for the desired node geometry. All Monte Carlo minimisations proceeded via the Metropolis algorithm [245], with moves consisting of $e_{ij} \rightarrow -e_{ij}$, *i.e* flipping the occupancy state of a linker. This particular study is focussed on ‘defect-free’ disordered configurations, where every one of the local states completely obeys the minimum energy state. Correspondingly, the Monte Carlo simulations were terminated at $E = 0$, to yield a configuration comprised the only of the chosen building block on the selected lattice.

*The supercell is needs to be large enough to obtain sufficient diffuse scattering resolution, but not so large that the Monte Carlo simulations do not converge. Moreover, in certain procrySTALLINE cases, the periodic boundary conditions caused the size of the supercell to require certain multiplicities (usually 2, 4 or 6) without which the Monte Carlo energy could not be minimised fully.

3.2 The procrySTALLine state

Many of the configurations presented in Figure 3.4 possess aperiodic components. There is no traditional unit cell and no space group, other than $P1$, which can be used to fully describe these structures. Yet, each procrySTALLine phase is distinctly different—*i.e.* the states in Figure 3.4(a) and Figure 3.4(b) are clearly not equivalent as evident from their diffuse scattering signatures. Moreover, referring to them as random or defective is not precise as each configuration contains a single local environment exhibiting discrete orientational disorder effected by its neighbours. As such these states should not be described either as ordered crystals or as random; indeed a key argument of this thesis is that these states comprise a separate class of aperiodic solid with its own characteristics and properties. The term ‘procrySTALLine’ has been chosen to describe this type of disorder [252] as it emphasises that the ordered crySTALLine state is a subset of the following definition.

3.2.1 Definition of procrySTALLinity

The procrySTALLine state is a dense, overlapping array of identical fundamental structural units, defined as neighbourhoods. In essence, neighbourhoods encompass the building unit symmetry and ensure their complete connectivity. For each high symmetry lattice, neighbourhoods are constructed as follows. First, the Voronoi-Dirichlet cell for the chosen lattice is identified [33, 34]. This cell is then augmented to include the neighbouring points which are connected in the parent net. As the tilings of the Voronoi-Dirichlet cells provide a dense covering of space, the augmented cell will provide a dense *overlapping* tiling of space.

Every neighbourhood is decorated with the local bonding information—*i.e.* the building unit and its connectivity to neighbouring nodes. Here, the overlapping regions of the neighbourhoods are essentially a means of enforcing the bond-matching rules, which ensure every node is in the same local environment, and that the pro-

crystalline structure is defect-free. Generalised neighbourhood constructions for the 2D and 3D lattices of those investigated in this study are shown in Figures 3.5 and 3.6 respectively. It is important to note that for more complex lattices the Voronoi-Dirichlet cell may not be able to identify the procrystalline neighbourhood, for instance in the case where the Voronoi-Dirichlet cells of a 3D lattice do not share faces. In this instance, it is anticipated that the correct neighbourhood may be identified through the use of different tilings of the lattice, such as the affine transformations of the Voronoi decomposition—where the connectivity and the parallel nature of lines and planes is preserved, but bond lengths and angles are free to be altered.

The neighbourhoods are periodically positioned but can vary in orientation according to the point symmetry of the neighbourhood itself. In the case of a crystalline state the orientations of the neighbourhoods are themselves ordered and periodic; however, in the more general procrystalline case the orientations vary discretely and in a correlated fashion as the neighbourhoods overlap. In simpler terms, the chemical environment within each neighbourhood is identical, but the orientations may differ. Moreover, because the neighbourhoods overlap, they give rise to the correlations. In turn, these strict constraints distinguish the procrystalline state from the weaker correlations of orientational disorder found in plastic crystals [188, 191, 265].

As the underlying neighbourhoods are positioned periodically, all procrystalline configurations exhibit Bragg scattering and have a reciprocal lattice. As such, the analysis of any corresponding diffraction pattern using conventional crystallographic methods will simply yield the average structure wherein each neighbourhood orientation is superimposed, masking the true local symmetry. By way of example, the two procrystalline configurations in Figure 3.4(o),(p) exhibit identical Bragg scattering and so will share the same average structure despite their different local structures.

In summary, it is logical to consider procrystalline configurations as a separate class

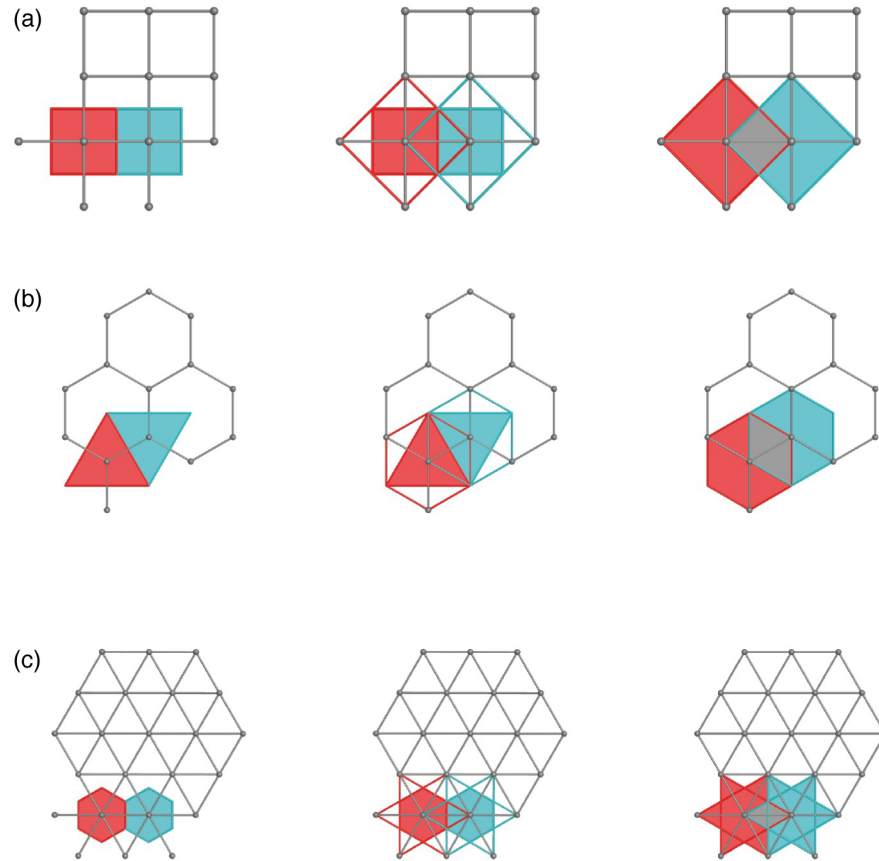


Figure 3.5: Constructions of neighbourhoods in two dimensions. Construction are shown for the (a) square, (b) hexagonal and (c) triangular nets. The Voronoi-Dirichlet cells are shown (left), augmented to include neighbouring lattice points (middle) and the complete neighbourhood constructed (right). The overlapping region is shown in grey in each case.

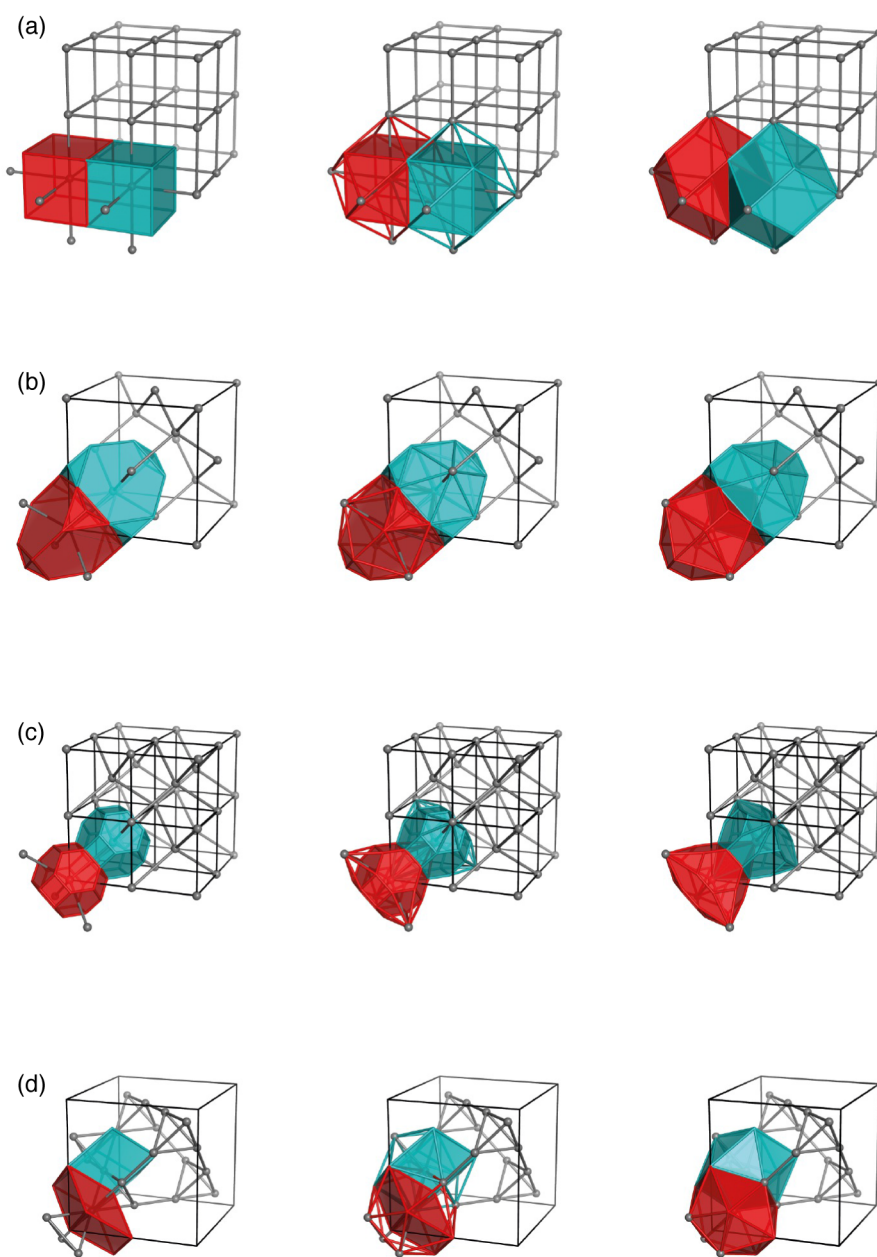


Figure 3.6: Constructions of neighbourhoods in three dimensions. Constructions are shown for the (a) primitive, (b) diamond, (c) doubly interpenetrating diamond and (d) pyrochlore nets. The Voronoi-Dirichlet cells (left) are augmented to include connected lattice points (middle) to form overlapping neighbourhoods (right).

of solid. They share some characteristics with crystals (such as local point symmetry, an underlying periodic lattice and well-defined Brillouin zones) and so are a separate class from quasicrystalline and incommensurate phases. Yet, while the sites on which the building units are situated are periodic in procystals, the orientations of the building units are aperiodic, and as such, there is no conventional unit cell which can be used to fully describe these systems.

3.2.2 Nomenclature

Each of the node geometries shown in Figure 3.4 forms an independent subset of the procristalline state. These disordered configurations are central to much of the work in this thesis, so it is prudent to discuss the notation with which each individual subset can be clearly identified and discussed. Each descriptor makes use of the relevant distinguishing features for each state and is of the form $\mathbf{A}_n(\mathbf{B}_\mathbf{C})$ where,

- $\mathbf{A}$ describes the underlying the parent lattice,
- n gives the number of linkers distinguished for each node,
- $\mathbf{B}$ denotes the stereochemistry of the distinguished linkers, where necessary, and
- $\mathbf{C}$ identifies racemic or chiral forms of node, when applicable.

The abbreviations for the lattices and local stereochemistries are given in Table 3.1, with the analogous labels for the pyrochlore lattice and associated stereochemistries given in Appendix A. Correspondingly, the disorder in square ice (square net, two distinguished linker directions, *cis*) and cubic ice (diamond net, two distinguished linker directions) is described by the labels $\mathbf{S}_2\mathbf{C}$ and $\mathbf{D}_2$, respectively.

3.2.3 Entropy

The extent of disorder in each configuration can be rudimentarily estimated from the simulated single crystal diffraction patterns, which contain increased structure in the diffuse scattering in the case of decreased configurational degeneracy [102, 266].

Here, the scattering behaviour of the configurations was determined using the Single-Crystal software—see Appendix A for details. The resulting patterns reveal a highly non-trivial link between node geometry and configurational disorder, where a significant fraction of the procrySTALLINE states support structures containing strongly-correlated disorder. By way of example, in the $\mathbf{T}_4\mathbf{P}$, $\mathbf{T}_4\mathbf{M}$ and $\mathbf{T}_4\mathbf{O}$ configurations [Fig. 3.4(f-h)], each of the node geometries decorate the same lattice and comprise the same number of distinguished linkers; only the local stereochemistry differs. Yet, $\mathbf{T}_4\mathbf{P}$ and $\mathbf{T}_4\mathbf{M}$ are ordered and so exhibit only Bragg scattering whereas the $\mathbf{T}_4\mathbf{O}$ configuration is disordered and produces structured diffuse scattering. So how might the relationship between the building block geometry and configurational entropy be better understood?

Pauling’s efforts to estimate the configurational entropy of ice provide an excellent foundation to explore this relationship [203]. In an ideal, perfect crystal of cubic ice, each water molecule accepts and donates two hydrogen bonds. Beyond this stipulation it is assumed there are no other energetic considerations which will influence the arrangement of water molecules. The ground state entropy of I_c is given by

Table 3.1: A summary of the notation developed to describe the different procrySTALLINE configurations.

Lattice	Notation	Stereochemistry	Notation	Relevant Lattice
Square	S	Cis	C	S, C
Hexagonal	H	Trans	T	S, C
Triangular	T	Ortho	O	T
Primitive Cubic	C	Meta	M	T
Diamond	D	Para	P	T
		Vicinal	V	T
		Unsymmetrical (Racemate)	U_R	T
		Unsymmetrical (Chiral)	U_X	T
		Symmetrical	S	T
		Facial	F	C
		Meridional	M	C

Boltzmann’s equation:

$$S = k_{\text{B}} \ln W, \quad (3.2)$$

where k_{B} is the Boltzmann constant and W , in this case, is the number of states accessible by the crystal. In determining W , Pauling noted that there are six possible orientations that a water molecule of C_{2v} symmetry can take on the node site of T_d symmetry. But, there is only a $\frac{1}{4}$ chance that the adjacent molecules will allow a given orientation under sensible hydrogen-bonding rules. As such,

$$W = \left(\frac{6}{4}\right)^N = \left(\frac{3}{2}\right)^N, \quad (3.3)$$

where N is the number of water molecules in the crystal. Conveniently, this approach for determining the entropy arising from degenerate ground states can be generalised for the procrySTALLINE configurations enumerated in Figure 3.4:

$$S \simeq k_{\text{B}} \ln \frac{n}{2^{d/2}}. \quad (3.4)$$

Here d represents the connectivity of the node in the parent structure, for example it takes the values 4 and 6 in the case of square and primitive cubic nets respectively. Correspondingly, n represents the number of orientations in which the low symmetry building block can be oriented on the node site. This variable is more rigorously given as the ratio of the orders of the point groups between the symmetry of the parent and perturbed node geometries—*e.g.* $n = |D_{4h}|/|C_{2v}| = 4$ for a square ice configuration. In Equation 3.4 the argument of the logarithm is the only variable. Here, this is named the Pauling number:

$$p = \frac{n}{2^{d/2}}. \quad (3.5)$$

The magnitude of p for each configuration is shown in Figure 3.4 and the absolute values presented in Appendix A. The Pauling number therefore represents an ap-

proximation of the ground state degeneracy for a given lattice and building unit geometry, wherein decorating a high-symmetry lattice with low-symmetry nodes increases the propensity for disorder and so maximises p .

There are three limiting cases which predict the extent of disorder in a given procrystalline configuration purely from the building block geometry and underlying parent lattice symmetry: (i) $p < 1$: there are no bulk degrees of freedom in the structure and so an ordered configuration results, (ii) $p = 1$: the configurational entropy is balanced and likely to be subextensive, with the configuration potentially containing low-dimensional order and (iii) $p > 1$: a highly degenerate set of ground states is predicted, and hence a disordered configuration [252]. Indeed, Equation 3.4 appears to underestimate the configurational entropy, especially in the dimer states such as $\mathbf{S}_1 \mathbf{H}_1$ and $\mathbf{T}_1$. In this way, the propensity for a given lattice/building unit combination to form a disordered structure is predicted prior to any configuration being generated via the Monte Carlo method detailed in Section 3.1.4.

3.3 Realisations of procrystalline phases

In addition to the various realisations described in Section 3.1, many systems (both well- and lesser-known) are relatively simple to identify as exhibiting procrystalline disorder. Here, the procrystalline state is used as a common framework to understand and compare correlated disorder in a range of ostensibly unrelated systems.

3.3.1 Ices

It stands to reason that any system that exhibits disorder equivalent to that of square ice or cubic ice will also fall under the procrystalline definition. Specifically, these systems are equivalent to the $\mathbf{S}_2\mathbf{C}$ and $\mathbf{D}_2$ procrystalline configurations respectively but the mappings themselves can be less than straight-forward. Realisations of square ice disorder are discussed in detail within Section 3.1.2. Here, the rela-

tionships between the $\mathbf{D}_2$ procrySTALLINE configuration and cubic ice (along with its analogues discussed in Section 1.23) are developed.

The $\mathbf{D}_2$ configuration is equivalent to distinguishing two linkers at each tetrahedral node on the diamond net. This can be represented in two basic forms which can be converted between using the checkerboard mapping (also described in Section 3.1.2) [Fig. 3.7]. These two forms differ in how a given linker state is viewed, or interpreted, by the two nodes to which it is connected—referred to as Node A and Node B. In the first form, the state of the linker is considered to switch if viewed from Node A or Node B. While this may seem odd, it is equivalent to hydrogen-bonding in cubic ice—if the oxygen atom at Node A is covalently bonded to the linking hydrogen atom, the oxygen atom at Node B does not experience the same relationship, and is instead hydrogen bonded. Contrastingly, if the state of the linker is viewed equally by both Node A *and* Node B an equivalence to compositional disorder is found. Here, a linker state of $e = \pm 1$ might refer to a linker site being occupied or vacant, but both neighbouring nodes will experience the same relationship with the linker state—*i.e.* a vacant site is vacant for both Node A and Node B. While these states may *look* different they describe the exact same decoration of disorder and as such have the same ground-state degeneracy and equivalent structural diffuse scattering (which is shifted by $\mathbf{k} = [\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$ due to the checkerboard transformation). In this way it becomes simpler to observe the disorder equivalence between cubic water-ice and its coulomb phase analogues through spin, displacement, orbital, compositional and charge disorder [210, 211, 267, 268].

3.3.2 KH_2PO_4

The family of ferroelectric phases related to KH_2PO_4 also map onto the $\mathbf{D}_2$ procrySTALLINE model [262]. Here, much like in water ice, the disorder originates from the displacement of protons. The tetrahedral $[\text{PO}_4]^{2-}$ units are situated at the node site and play an equivalent role to the oxygen atoms in ice. Each tetrahedron is bonded

to the four neighbours through a proton. Each proton is more closely bound to one of the two $[\text{PO}_4]^{2-}$ tetrahedra, displacing to one end of the $\text{O}\cdots\text{H}\cdots\text{O}$ bond. However, in this case the unit cell is tetragonal, so the six possible proton arrangements are not equivalent. The elongated c axis of the tetragonal cell breaks the energetic degeneracy of ground states, and enforces a preferential positioning of the hydrogen atoms, resulting in an ordered, ferroelectric procrySTALLINE state [269, 270].

3.3.3 Loops and dimers

Further procrySTALLINE examples are found in the statistical mechanical models for loops [271] and dimers [272, 273] presented in Section 1.2.2. These directly map onto the procrySTALLINE phases where two linkers (S_2C , S_2T , H_2 , T_2O , T_2M , T_2P , C_2C , C_2T and D_2) and one linker (S_1 , H_1 , T_1 , C_1 , D_1) are distinguished respectively. Correspondingly any realisation of these theoretical loop states—such as SrTaO_2N

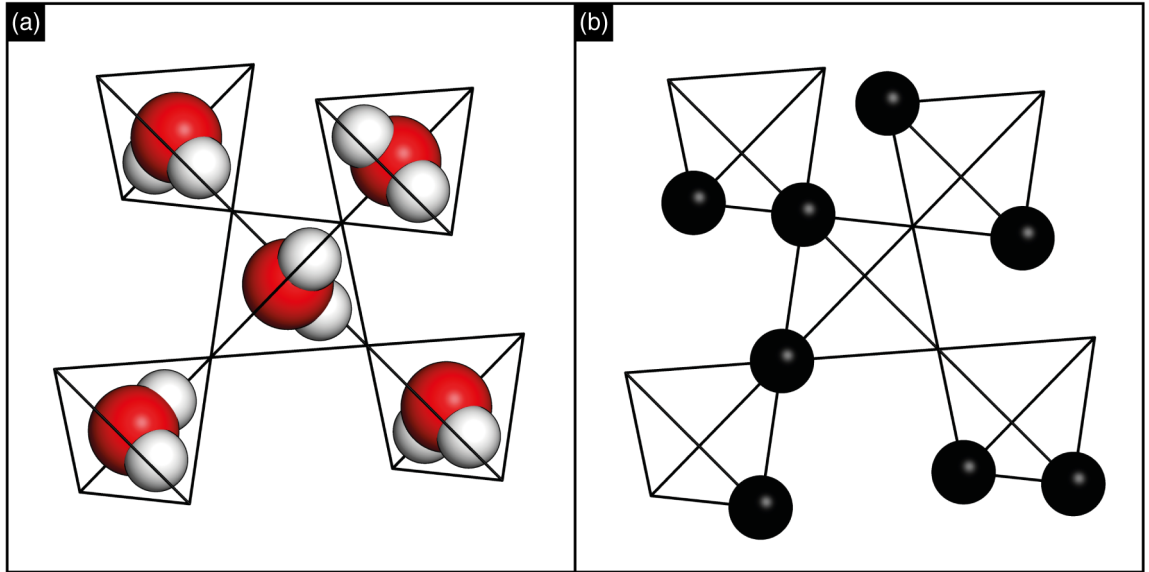


Figure 3.7: Cubic ice and the checkerboard mapping. Both the (a) cubic water ice and (b) vacancy ice map onto the D_2 procrySTALLINE phase. Here, the exact same disorder decoration is embedded in each structure, with an additional checkerboard mapping that relates one structure to the other. This transform essentially ‘flips’ the state of every other connected node. In this case the central unit can be viewed as Node A, with all the neighbours being of Node B type. Correspondingly, the water molecule orientations in the outer tetrahedra are well-represented by the black spheres in (b), yet the central water molecule is reproduced by their absence.

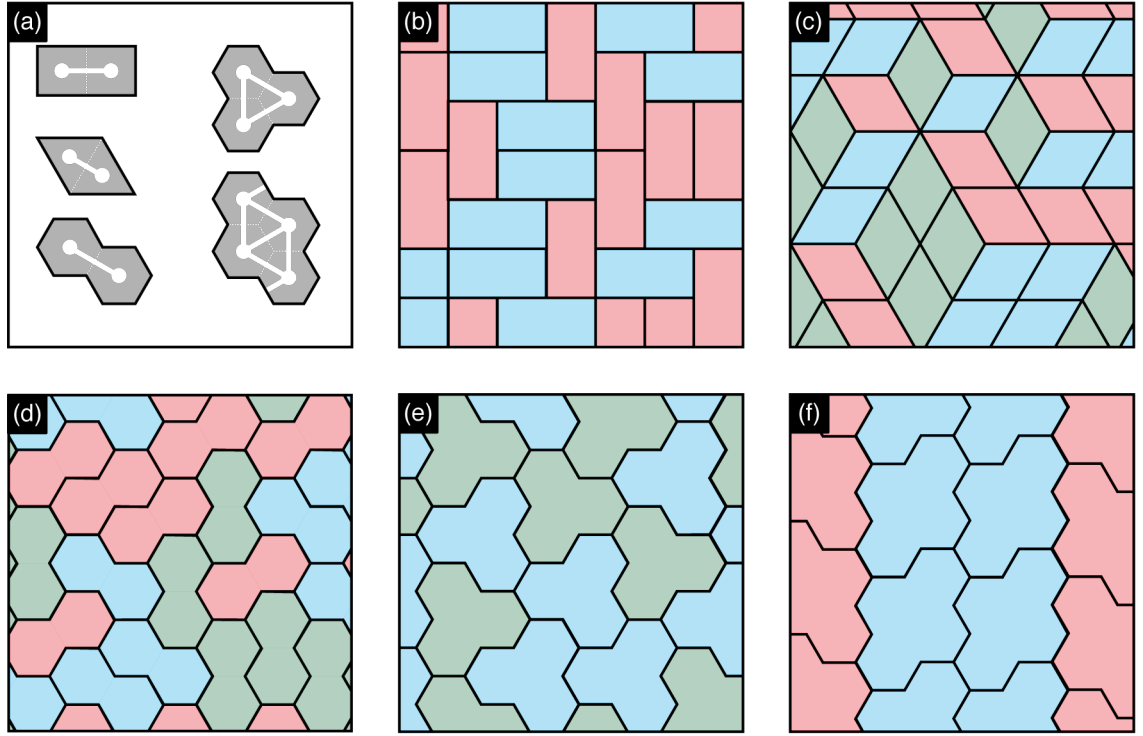


Figure 3.8: Mapping between polyhedral tilings and procristalline states. The local units in (a) highlight the relationship between the local procristalline bonding rules and the construction of the tile. Aperiodic tilings of the two-dimensional dimer states are constructed from the pairwise fusion of the Voronoi-Dirichlet cells of neighbouring lattice points. Here the tilings of $\mathbf{S}_1$ [Fig. 3.4(a)], $\mathbf{H}_1$ [Fig. 3.4(d)] and $\mathbf{T}_1$ [Fig. 3.4(e)] procristalline states are shown in panels (b), (c) and (d) respectively. However, the tiling realisations are not only applicable to dimer states but also other procristalline configurations as shown in (e) and (f) where the $\mathbf{T}_2\mathbf{O}$ loop states and $\mathbf{T}_3\mathbf{V}$ network states are representable by more complex tile units.

[254, 255, 274], TaS₂ [275]— or dimer states—including resonant valence bond (RVB) states [12], and mathematical tilings of simple shapes [204]—will also fall under the procrySTALLINE definition [Fig. 3.8].

Equivalent polyhedral realisations are also possible for the three-dimensional procrySTALLINE configurations, such as the equivalence of an assembly of $2 \times 1 \times 1$ cuboids and the **C**₁ state. The three-dimensional dense polyhedral tilings have not been included in Figure 3.8 due to the inherent difficulty in clearly showing the dense packing.

In the case of more complex examples, the interpretation of experimental data is required to identify an appropriate procrySTALLINE phase. In the remainder of this section the characterisation of procrySTALLINE phases using experimental data of four different forms will be discussed: scanning tunnelling microscopy images (Section 3.3.4), pair distribution function measurements (Section 3.3.5), powder diffraction (Section 3.3.6) and single crystal diffraction data (Section 3.3.7).

3.3.4 Self-assembly of TPTC molecules

Ideally the structural characterisation of a material would be possible through direct imaging as it provides the simplest method of identifying disorder/defects. In recent years the resolution of microscopy techniques has increased substantially, to the extent that the electron density in individual covalent and intramolecular hydrogen bonds can be observed (although the latter is still the topic of debate) [276, 277]. Unfortunately, this approach is limited to two-dimensional arrangements of atoms and molecules.

In the context of identifying procrySTALLINE phases, the self-assembly of *p*-terphenyl-3,5,3',5'-tetracarboxylic acid (TPTC) molecules provides an ideal example [208]. Despite being previously detailed in Section 1.2.2, for completeness the disordered TPTC arrangements are reintroduced here, but with a focus on the procrySTALLINE

nature of the system. TPTC molecules are each comprised of four carboxylate groups bonded to a linear arrangement of three phenyl rings—two on each terminal phenyl ring, meta to the central ring [Fig. 3.9(a)]. The carboxylate groups are available for intramolecular bonding which can occur in one of two arrangements—where the long axes of the two molecules are parallel, and where they are arranged at a 60° angle [Fig. 3.9(b-c)]. The corresponding assembly of TPTC molecules on a pyrolytic graphite surface forms an aperiodic network which is evident from the scanning tunnelling microscopy (STM) images [Fig. 3.10(d)].

The disordered network is formed for two main reasons: (i) there is little energetic preference for either of the two local arrangements and (ii) the internal distance within the molecule and the corresponding distance between two hydrogen bonded molecules—shown as d_1 and d_2 in Figure 3.9(b)—is approximately equivalent, ensuring that a regular hexagonal lattice is maintained irrespective of the local bonding arrangement. Each lattice point is located at the centre of the terminal phenyl rings of every TPTC molecule. The overall TPTC arrangement was originally mapped onto the rhombus or lozenge tiling [Fig. 3.8(c)], a state that also describes the RVB state description of π bonding in graphene [197, 198], both of which are related to the triangular Ising antiferromagnet [206] [Fig. 3.10(b-c)]. These decorations

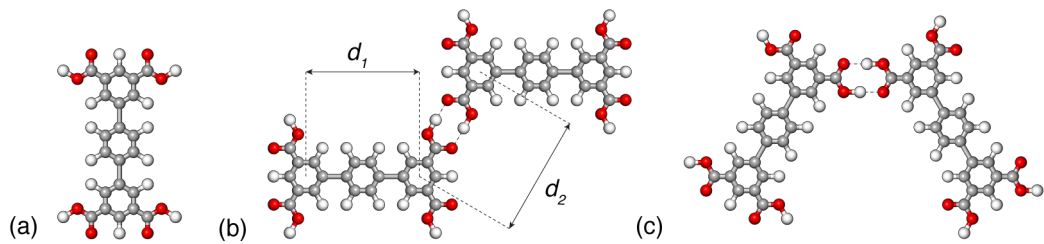


Figure 3.9: Orientational freedom of hydrogen-bonded TPTC molecules. (a) A representation of the TPTC molecule comprised of 3 linear phenyl rings and four carboxylate groups. Two TPTC molecules can hydrogen bond via the carboxylate groups in one of two orientations: (b) where the primary molecule axes are parallel and (c) where the molecules are arranged at a 60° angle. Two separations are marked in (b): d_1 , the distance between terminal phenyl rings of one TPTC molecule, and d_2 , the distance between terminal phenyl rings over an intramolecular hydrogen bond. For the TPTC molecule $d_1 \simeq d_2$. In each panel carbon, oxygen and hydrogen atoms are shown in black, red and white, respectively.

correspond to both dimers *and* loop states on the hexagonal lattice as $\mathbf{H}_1$ and $\mathbf{H}_2$ states are equivalent. Moreover, a Fourier transform of the STM image and the corresponding simulated single crystal scattering of the geometric model reveal identical distribution of the broad diffuse scattering including the pinch-point features around the Bragg peaks, cementing the equivalence both in real and reciprocal space [Fig. 3.10(e-f)].

Indeed, further studies of TPTC networks have shown that the specific procrys-
talline arrangement of TPTC molecules can itself be altered. A combination of temperature, solvent and chemical additives (*e.g.* coronene) are able to shift the energetics of the two local bonding modes shown in Figure 3.9(b-c) in both directions [278]. In turn, this establishes an intriguing approach for controlling the resulting disordered arrangements by favouring certain procrys-
talline configurations over others by breaking the ground state degeneracy through alteration of the local energetics.

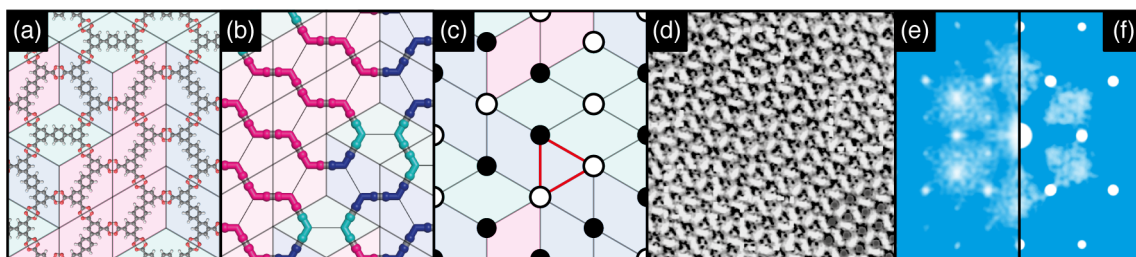


Figure 3.10: Mappings of the hydrogen bonded TPTC network. A self-assembly of TPTC molecules on pyrolytic graphite forms a network (a) with disorder equivalent to that found in the $\mathbf{H}_2$, and trivially also the $\mathbf{H}_1$, procrys-
talline configuration (b) shown in Figure 3.4(d). The TPTC molecules and their hydrogen bonds occupy the missing and occupied linker sites respectively. The rhombus tiling shown in the background highlights the equivalence to the procrys-
talline phase [Fig. 3.8(c)] and also reveals a further mapping to the triangular Ising antiferromagnet (c), wherein the opposite vertexes of each rhombus is decorated with either spin-up (white) or spin-down (black) states in such a way that local triangular motifs (red) contain at least one spin of each kind. Panel (d) shows the experimental STM image of the TPTC network. From M. O. Blunt, J. C. Russell, M. d. C. Giménez-López, J. P. Garrahan, X. Lin, M. Schröder, N. R. Champness and P. H. Beton, *Science*, **322**, 1077–1081, 2008 [208]. Reprinted with permission from AAAS. The Fourier transform of the STM image (e) reveals identical diffuse features to the simulated single crystal diffraction of the $\mathbf{H}_2$ procrys-
talline phase (f), further reinforcing the equivalence of the two states in reciprocal as well as real space.

3.3.5 Oxyfluoride phases

Interest in inorganic materials containing both oxide and fluoride anions, known as oxyfluorides, increased significantly after the identification of superconductivity in the system $\text{Sr}_2\text{CuO}_2\text{F}_{2+x}$ [279]. Furthermore, the partial substitution of fluoride into an oxide material allows the possibility of tuning the electronic structure without radically altering its structure. In this section the oxyfluoride material of interest, BaFeO_2F , adopts the perovskite structure with a nominal cubic crystallographic symmetry of $Pm\bar{3}m$ [280]. Although there were indications from neutron powder diffraction data that the Fe^{3+} ion significantly off-centres, conventional Bragg analysis delivered an average cubic symmetry with a lattice parameter of 4.060 Å. Here, an attempt is made to develop further insight into the local structure of BaFeO_2F using pair distribution function (PDF) methods. A powder sample of BaFeO_2F was prepared by Prof. Peter Slater using methods described in Ref. [280] and neutron pair distribution function data were collected on the POLARIS instrument at the ISIS Neutron Spallation Source.

For reasons of charge balancing it is reasonably assumed that the octahedral coordination environment of each Fe^{3+} ion is comprised of four O^{2-} and two F^- anions. In this study, four separate models, each corresponding to distinctly different disorder correlations, were generated for comparison to the experimental PDF data. The first two models are directly related to the C_4C and C_4T procrySTALLINE configurations, wherein the local octahedral 4–O–2–F environment is either in a cis or trans arrangement [Fig. 3.4(n),(o)]. For comparison, two further models were also considered (i) configurations wherein each Fe^{3+} ion is surrounded by four O^{2-} and two F^- anions but with no preference for either the trans or cis stereochemistry, resulting in a mixture of these states ($\text{C}_4\text{C}+\text{T}$); (ii) a random decoration of O^{2-} and F^- species on the anionic sites, with the caveat that the stoichiometry of the sample was retained (RND).

For each model, four $6 \times 6 \times 6$ supercell configurations were generated making use of the Monte Carlo method detailed in Section 3.1.4. Given the lack of contrast in the neutron scattering lengths between the ^{18}O and ^{19}F atoms ($b_c = 5.803$ and 5.654 fm, respectively [225]), an attempt to ascertain their arrangements using neutron scattering methods might initially seem futile. However, the difference in charge between the two anions will necessarily alter the electrostatic attraction experienced by the Fe^{3+} ion, with the potential to cause off-centre displacements. As such, in each model a fixed static displacement of $0.1985 \text{ \AA}$ was applied to the Fe^{3+} ion directly away from each coordinated F^- ion—*i.e.* the weaker attracting species. Correspondingly, in the $\mathbf{C}_4\mathbf{C}$ model each Fe^{3+} ion experiences an off-centre displacement along a $\langle 110 \rangle$ direction whereas a $\mathbf{C}_4\mathbf{T}$ decoration results in the ion remaining at the centre of the octahedral coordination environment as the F^- ions are arranged on opposite vertices.

Each supercell configuration was refined against the observed neutron pair distribution function data and neutron Bragg diffraction data using the TOPAS-Academic software [281]. The Bragg data were included to ensure that the local structure refinements were in accordance with the long-range average structure. As there is little scattering power difference between O and F, a bond valence sum (BVS) penalty was applied to chemically differentiate between them. For each atom in the unit cell, the BVS penalty, P_{BVS} , took the form of

$$P_{\text{BVS}} = \left[\left(\sum_{i=1}^N \exp \left(\frac{R_{0,i} - R}{0.37} \right) + \sum_{j=1}^N \exp \left(\frac{R_{0,j} - R}{0.37} \right) \right) - Z \right]^2, \quad (3.6)$$

where Z is the ideal charge of the central atom and i, j represent summations over all (O,F) or (Fe,Ba) species around each central atom up to a distance of $2.5 \text{ \AA}$. Here, R represents the observed bond distance from the central atom, where the equilibrium value, R_0 , was assigned values of $1.759 \text{ \AA}$, $1.679 \text{ \AA}$, $2.285 \text{ \AA}$ and $2.188 \text{ \AA}$ for BVS interactions between $(\text{Fe}^{3+}, \text{O}^{2-})$, $(\text{Fe}^{3+}, \text{F}^-)$, $(\text{Ba}^{2+}, \text{O}^{2-})$ and $(\text{Ba}^{2+}, \text{F}^-)$

respectively.

Refinement of the supercell configurations [Fig. 3.11] gave average weighted pattern fit statistics, R_{wp} of 13.56(5), 15.78(9), 13.63(6), and 13.86(7) for C_4C , C_4T , $\text{C}_4\text{C}+\text{T}$ and RND models respectively (see Appendix B for further details), where

$$R_{\text{wp}} = \left[\frac{\sum w_i [y_{i,\text{obs}} - y_{i,\text{calc}}]^2}{\sum w_i [y_{i,\text{obs}}]^2} \right]^{\frac{1}{2}}. \quad (3.7)$$

Here, $y_{i,\text{obs}}$ and $y_{i,\text{calc}}$ represent the observed and calculated values at each data point respectively and w_i is the weighting given to data point, i , based on the estimated error in the measured value.

It is perhaps unsurprising that the C_4C and $\text{C}_4\text{C}+\text{T}$ models give similar fits, R_{wp} , as the $\text{C}_4\text{C}+\text{T}$ configurations contain a significant proportion of cis environment. What is more clear however, is that random and trans configurations provide worse fits to the observed data. While definitive conclusions are hard to draw from these results, the refinements do show that configurations containing a high proportion of cis environments are more consistent with the observed data. Here, it is demonstrated that, even without complete three-dimensional diffuse scattering data available from single crystal methods, PDF and powder diffraction data can still give in-

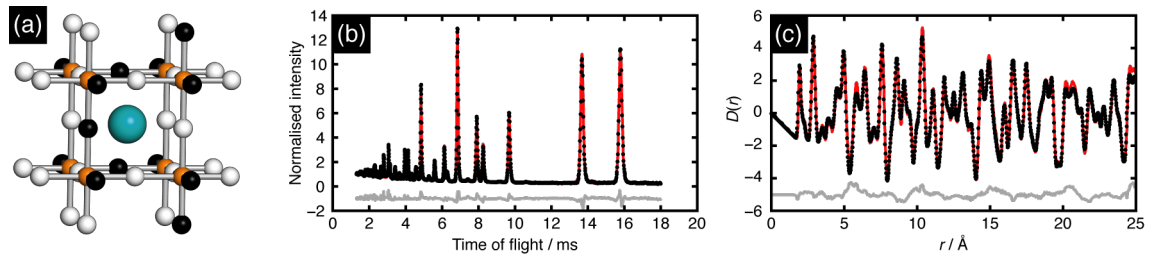


Figure 3.11: PDF refinement of a C_4C model of BaFeO_2F . (a) A representative local portion of the C_4C model of the BaFeO_2F perovskite structure, wherein each Fe^{3+} ion (orange) is octahedrally coordinated by two F^- (black) and four O^{2-} (white) anions in a cis arrangement. The Ba^{2+} ion (blue) is situated in the 12-coordinated cubeoctahedral site. For clarity, the Fe^{3+} displacements away from the F^- neighbours are omitted. Experimental neutron (b) Bragg and (c) PDF data (black circles) is compared to the calculated powder diffraction/PDF (red lines) for a representative C_4C configuration. The difference between the fit and the experimental data, offset in the vertical direction, is shown as a grey line.

dications of the local ordering. In these cases, it is important to consider additional information—*e.g.* from chemical intuition or bond valence sum restraints—alongside the experimental data to determine the existence of disorder correlations.

3.3.6 Pd(CN)₂ and Pt(CN)₂

In solid-state chemistry, the synthesis of quality single crystal samples is often extremely difficult, if not impossible. As such, it is important to demonstrate how diffraction data from a system only available as a powder sample—in this case Pd(CN)₂ and Pt(CN)₂—might be used to characterise procrySTALLINE disorder. Unsurprisingly, due to the absence of three-dimensional reciprocal space data, the determination of the disordered structures from solely powder diffraction data is particularly difficult as the diffuse scattering is only observable in the form of anisotropic peak shape broadening of the Bragg component.

The structures of Pd(CN)₂ and Pt(CN)₂ have long been thought to be equivalent to that of Ni(CN)₂ [Fig. 3.12(a)] [282]. The nickel cyanide structure is comprised of square planar [M(CN)₄]^{2−} units which connect in two dimensions to form a square grid. The layers themselves stack aperiodically in the *c* direction. There are two possible arrangements for each pair of layers, relative displacement by half a unit cell in either the *a* or *b* directions such that nickel cations of one layer sit above one of two possible cyanide anions in the adjacent layer.

These models of Pd(CN)₂ and Pt(CN)₂, based on the Ni(CN)₂ structure, contain sharp peaks at (00*l*) which are not observed in the experimental X-ray powder diffraction patterns [283]. Moreover, broad diffuse scattering is observed for both compounds, so too for the mixed metal compound Pd_{0.5} Pt_{0.5}(CN)₂. Nevertheless, previous studies have fitted the experimental data to the Ni(CN)₂ structure. Using a combination of powder diffraction, total scattering and spectroscopic data, a nanocrystalline model—in which the crystallite dimensions in the stacking axis *c* are particularly small—has been previously proposed [283]. These constraints preserve

the $\text{Ni}(\text{CN})_2$ structural model while significantly broadening the $(00l)$ reflections such that they are no longer observed in the simulated diffraction data. Indeed this analysis employed a broadening term so extreme that the corresponding structural model is essentially delaminated. The complimentary experimental PDF data confirmed the local square planar geometry of the $[\text{M}(\text{CN})_4]^{2-}$ unit, but significant broadening consistent with the axis perpendicular to the plane was revealed. So in the same study a second model, juxtaposed with the first, based on offset stacking was proposed. Here, the $P4/mmm$ symmetry within the sheets was maintained but the correlations between the sheets were key to fitting the PDFs.

Clearly the structures of $\text{Pd}(\text{CN})_2$, $\text{Pt}(\text{CN})_2$ and the mixed metal $\text{Pd}_{0.5}\text{Pt}_{0.5}(\text{CN})_2$ cannot be both laminated and delaminated, so in the study of procrySTALLINE materials a structure based on the C_4T model [Fig. 3.4(m)] was proposed as a consistent representation. In this phase the metal cations sit above one another, forming a primitive cubic lattice. Given the nature of the experimental data, the diffuse features cannot originate from disorder of the C/N atoms of the cyanide linker as the

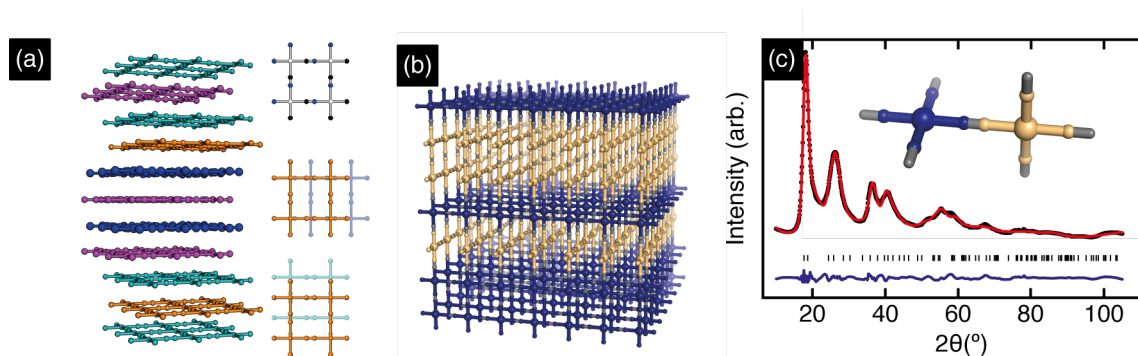


Figure 3.12: Proposed structures of $\text{Pd}(\text{CN})_2$ and $\text{Pt}(\text{CN})_2$. The originally proposed structure, based on that of $\text{Ni}(\text{CN})_2$, is shown in (a). Here, the metal cation is coordinated to four cyanide linkers to form an extended two-dimensional square planar net. These are stacked in an aperiodic manner as each layer can shift by either $\frac{1}{2}\mathbf{a}$ or $\frac{1}{2}\mathbf{b}$ compared to the previous layer. This gives four unique translations which are grouped by colour. The proposed procrySTALLINE structure based on the C_4T model [Fig. 3.4(m)] is shown in (b). Here there are two possible orientations of the $\text{M}(\text{C/N})_4$ nodes shown in indigo and gold. The Reitveld fit for the procrySTALLINE model is shown as a red line in (c). The experimental X-ray diffraction data is represented as black points ($\lambda = 1.54 \text{ \AA}$), the difference is shown in blue and tick marks indicate the location of Bragg peaks.

scattering factors of the two atoms in X-rays is minimal. Instead, a topological disorder is proposed wherein the cyanide linkers are positioned such that the local symmetry remains square planar; however, the connections are such that a three-dimensional network structure with stacking disorder is formed. Each individual layer is ordered, but subsequent connected layers take one of two states: (i) an exact repeat of the previous layer or (ii) a state in which every $M(C/N)_4$ unit in the layer has been rotated 90° in the stacking axis [Fig. 3.12(b)]. The stacking arrangement is random in the C_4T model, or more simply stacking neither favours a repetition of a layer or a rotation. This disordered, extended network structure better describes the experimental powder diffraction data without the requirement for extreme broadening terms, and so represents a more logical structural model [Fig. 3.12(c)]. The peak broadening is accounted for by a combination of strain, crystallite size—which is significantly larger than the previously reported model [283]. Moreover, the procristalline disorder within the model gives a significant contribution to the scattered intensity in the form of diffuse scattering. Importantly the proposed model remains consistent with the local structure determined from the PDF data. Crystallographic details for the $Pd(CN)_2$ and $Pt(CN)_2$ structures determined from the refinement X-ray powder diffraction can be found in Appendix B.

3.3.7 $BaTiO_3$ and $KNbO_3$

The final and likely most powerful characterisation method discussed in this chapter is that of single crystal diffraction. The characteristic simulated diffraction behaviour of each of the procristalline networks is presented in Figure 3.4, with further suitable projections available in Appendix A. It is anticipated that in the case of disordered procristalline networks, the highly structured diffuse scattering will act as a signature of the specific disorder correlations found in these materials.

The single crystal scattering behaviour of the high-temperature, cubic phases of

BaTiO₃ and the related compound, KNbO₃, provide important examples in which the diffuse scattering of a procrySTALLine network is able to act as a fingerprint to diagnose structural disorder. Both phases adopt the perovskite structure and disorder originates from the off-centre displacements of the Ti⁴⁺ cations toward a face of the octahedral coordination environment of O²⁻ anions via a second-order Jahn Teller distortion [Fig. 3.13(a)]. In a random decoration, each Ti⁴⁺ has a free choice of the eight $\langle 111 \rangle$ directions—*i.e.* toward each of the eight octahedral faces—in which it can displace. In this regime, relatively unstructured diffuse scattering is expected; however, the single crystal diffraction pattern shows highly structured features in the diffuse scattering indicating that there is strongly-correlated disorder in the material. The experimental diffraction behaviour is well represented by a model structure [Fig. 3.13] containing disorder correlations equivalent to the **C₃F** procrySTALLine network shown in Figure 3.4(p).

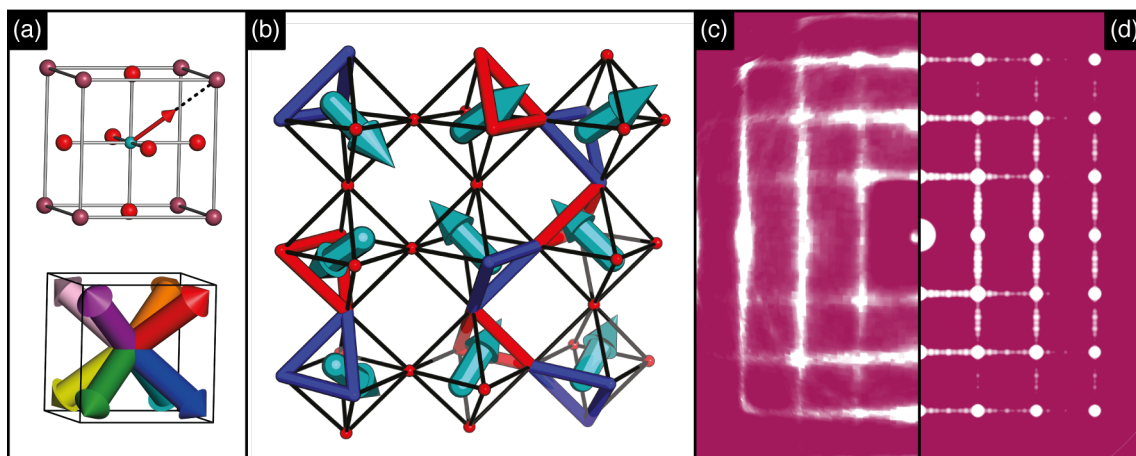


Figure 3.13: The procrySTALLine disorder in the cubic phase of BaTiO₃ and KNbO₃. (a) The Ti⁴⁺/Nb⁵⁺ cations displace toward one of the eight faces of their octahedral coordination environment which can be simply represented by a vector. [284] (b) The displacements occur in such a way that neighbouring cations displace in the same direction with respect to their interatomic vector. Correspondingly, the chosen $\langle 111 \rangle$ displacements alternate between replicating (red) and opposing (blue) the chosen octahedral face in the **C₃F** procrySTALLine network. (c) The experimental single crystal diffraction pattern of KNbO₃ (b) is adapted from Ref. [285]. Reproduced with permission of the International Union of Crystallography. (d) The highly structured diffuse scattering is reproduced by the simulated single crystal diffraction of the analogous structure based on **C₃F** procrySTALLine disorder.

The $\mathbf{C}_3\mathbf{F}$ model is a logical choice to represent the cubic phase of BaTiO_3 . Firstly, it is consistent with the cubic average structure; the average position of the Ti^{4+} cation is in the centre of the octahedron. Moreover, from chemical intuition it is expected that the orbitals of each oxygen ion are limited to involvement in the Jahn-Teller distortion of only one Ti^{4+} ion. In other words, a local bonding rule is formed: of the two neighbouring titanium cations of each oxygen anion, only one Ti^{4+} can displace toward it. Locally, this may seem a simple rule to satisfy, resulting in a highly disordered arrangement, but in reality, this imposes strict one-dimensional order, much like that found in square ice, and the very same to that found in the $\mathbf{C}_3\mathbf{F}$ procrySTALLINE phase.

The low-dimensional order originates from a combination of the two requirements: (i) titanium displacement in a $\langle 111 \rangle$ direction; (ii) the local restriction that an oxygen anion can only be involved in the Jahn-Teller distortion of one Ti^{4+} cation. If a given titanium ion at (x, y, z) displaces in the (111) direction for instance, the oxygen anions at $(x + \frac{1}{2}\mathbf{a}, y, z)$, $(x, y + \frac{1}{2}\mathbf{b}, z)$ and $(x, y, z + \frac{1}{2}\mathbf{c})$, directions are all engaged in this Jahn-Teller distortion. As such, the neighbouring Ti^{4+} ion situated at $(x + \mathbf{a}, y, z)$ cannot displace toward the O^{2-} at $(x + \frac{1}{2}\mathbf{a}, y, z)$. Yet, each Ti^{4+} ion must still displace in one of the $\langle 111 \rangle$ directions, so necessarily one of the four that move the cation away from the O^{2-} anion at $(x + \frac{1}{2}\mathbf{a}, y, z)$ —*i.e.* (111) , $(1\bar{1}1)$, $(11\bar{1})$, $(1\bar{1}\bar{1})$. This has a knock-on effect, in any single chain of unit cells of BaTiO_3 along the cartesian axes, the cations must always move in the same direction along the chain. However, in the cubic phase there are no correlations between chains, so similarly to square ice, while a single chain is ordered, the direction adopted by each chain—left and right for chains along $\mathbf{a}$, up and down for chains along $\mathbf{b}$ and in an out for chains along $\mathbf{c}$ —is random.

3.3.8 The phase behaviour of BaTiO₃ and KNbO₃

Upon cooling, BaTiO₃ and KNbO₃ undergo three sequential transitions from the high temperature cubic phase to a tetragonal, orthorhombic and finally rhombohedral phase, respectively. So can these forms also be understood in terms of the procrySTALLine formalism? The correlated displacements of the Ti⁴⁺ cations in each of the four phases of BaTiO₃ were recently determined from neutron pair distribution function measurements by Senn *et al.* [261]. In this work, the correlated disorder in the disordered cubic phase is equivalent to that described in the previous section—along each of the cartesian axes, chains of Ti⁴⁺ ions displace in the same direction along the chain but with no correlations from chain to chain. In this way, all of the displacements of the cations in a $N \times N \times N$ supercell can be represented by the $3N^2$ displacement vectors either along or against, but parallel to, the cartesian axes. The PDF refinements reveal that for each successive phase transition, the displacements along a single cartesian axis establish ferroelectric order, such that on decreasing temperature the cubic, tetragonal, orthorhombic and rhombohedral phases exhibit ordering of the chains along zero, one, two and three of the cartesian directions [Fig. 3.14].

Importantly, each of these models conforms with their respective experimental data: the average structure, the PDFs and the structured single crystal diffuse scattering. In the high temperature structure, the disordered chains along all three axes result in a cubic average structure with the titanium cation sitting at the centre of the unit cell. Successive orderings of chains along each axis also give the tetragonal, orthorhombic and rhombohedral average structures with the average displacements of Ti⁴⁺ along the [100], [110] and [111] axes respectively. The ordering is further reflected in the single crystal diffuse scattering. In the high temperature cubic phase the diffuse scattering is exhibited as three intersecting sets of orthogonal planes of diffuse scattering, where each plane is parallel to one of the {100} planes. The

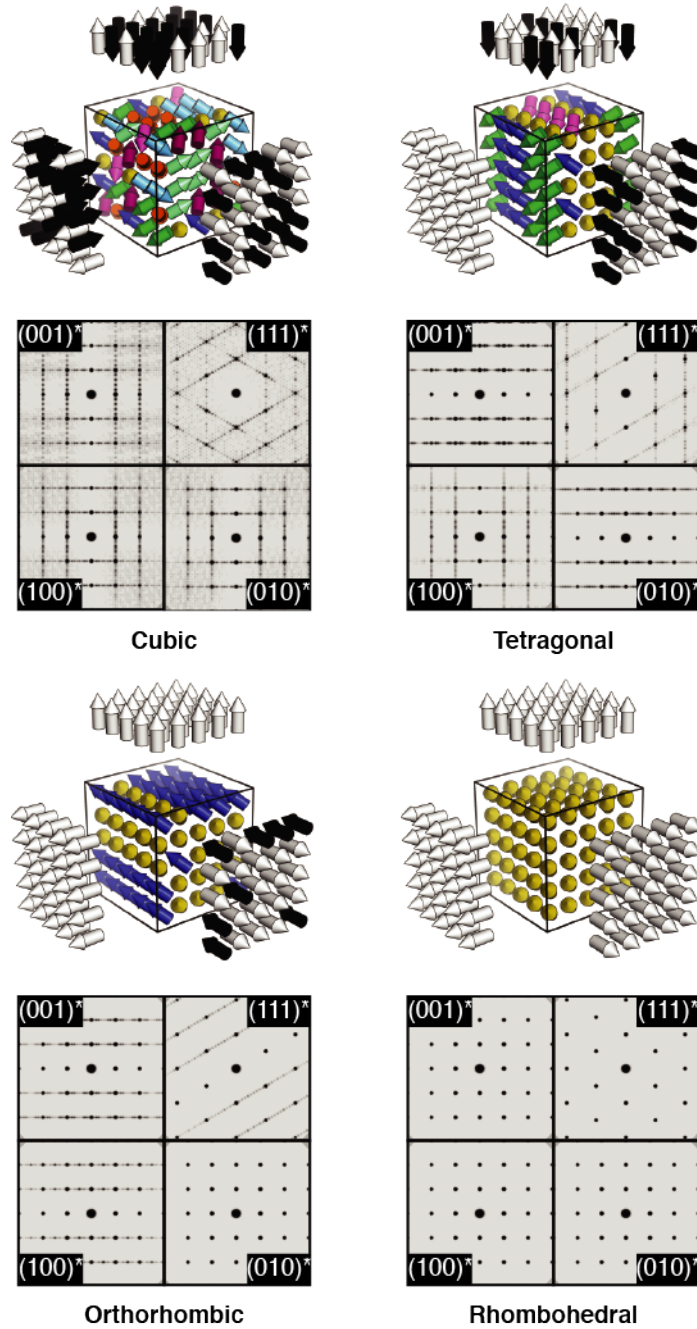


Figure 3.14: The phase behaviour of BaTiO₃. On decreasing temperature, the cubic phase of BaTiO₃ (top-left) proceeds through three phase transitions to the tetragonal (top-right), orthorhombic (bottom-left) and rhombohedral (bottom-right) phases. Each subsequent phase transition is associated with a ferroelectric ordering of the displacements of the Ti⁴⁺ ions—represented by coloured vectors—along a single cartesian axis as highlighted by the planes of black and white vectors representing the collective chain displacement along the three axes. Furthermore, each transition is characterised by a loss of a set of planes of diffuse scattering parallel to a {100} plane. Reprinted figure with permission from M. Senn, D. A. Keen, T. C. A. Lucas, J. A. Hriljac and A. L. Goodwin, *Phys. Rev. Lett.*, **116**, 207602, 2016 [261]. Copyright 2016 by the American Physical Society.

single crystal data reveals that over each phase transition that further orders the structure, a set of planes parallel to a $\{100\}$ plane is lost, an effect reproduced by the structural models [Fig. 3.14].

So how do these phases compare to procrySTALLINE phases? As discussed, the model for the cubic phase is equivalent to the $\mathbf{C}_3\mathbf{F}$ phase as discussed in Section 3.3.7. Correspondingly, the tetragonal, orthorhombic and rhombohedral phases merely represent subsets of the same $\mathbf{C}_3\mathbf{F}$ procrySTALLINE phase in which the chain displacements have been ordered along one, two and three axes respectively. Indeed, the rhombohedral phase is a unique subset of this procrySTALLINE phase—the fully ordered procrySTALLINE phase that represents all titanium displacements occurring along $[111]$.

It is clear that procrySTALLINITY alone cannot drive the ferroelectric phase transition (cubic $\rightarrow$ tetragonal). While all the possible realisations of the cubic and tetragonal phases fall under the procrySTALLINE definition, they are all energetically degenerate. Furthermore, the tetragonal phases are statistically unlikely realisations of the $\mathbf{C}_3\mathbf{F}$ state, where the likelihood of the polarised tetragonal state in a cubic $N \times N \times N$ supercell is equivalent to

$$P = \frac{2 \times 2^{N^4}}{2^{N^6}} = 2^{-(N^6 - N^4 - 1)}. \quad (3.8)$$

The derivation of the probability P is simple. In a given configuration each chain of Ti displacements independently takes one of two states—along or against the chain axis—and in total there are N^2 chains lying down each of the three cartesian axes such that there are $2^{N^2 \cdot 3} = 2^{N^6}$ degenerate ground states. In the tetragonal phase, chains parallel to two of the cartesian axis retain their uncorrelated orientations, while the displacements of the chains along the third axis all ferroelectrically align into one of two states, along or against the chain axis, hence $2 \times 2^{N^4}$ states. Consequently, the disorder exhibited in the tetragonal phase represents a subset of the

$\mathbf{C}_3\mathbf{F}$ procrySTALLine state which, in the absence of any driving forces, are therefore statistically unlikely realisations. Indeed, the comparatively ordered nature of the tetragonal phases in comparison to the cubic phases of BaTiO_3 is well accounted for by the reduction in entropy across the phase transition when cooling [286]. Moreover, given the subextensive nature of the disorder in the $\mathbf{C}_3\mathbf{F}$ configurations, the entropy change across the phase transition would be expected to depend on the size of the domain/crystallite, which is consistent with the spread in entropy values which have been measured [286].

3.4 Discussion

The reticular approach presented in Section 3.1.3 suggests multiple routes for realising crystal structures with procrySTALLine disorder. Metal-organic frameworks (MOFs) present themselves as an obvious candidate. The energetics of these structures rely on local interactions and as such they offer excellent control over the building-unit geometry [264]. Although procrySTALLinity in these particular systems is unlikely to affect collective properties, such as electronic states or vibrational band structure, in a meaningful way, the percolation of the porous network will certainly be alterable by disorder, and as such offer a method of changing their well-studied sorption and storage properties. In more conventional systems, the local symmetry lowering required for procrySTALLine disorder is possible through first- or second-order Jahn–Teller distortions (*e.g.* BaTiO_3 [261]), local bonding motifs (*e.g.* SrNbO_2N [254, 255]), or via a change of coordination environment such as in the pressure-induced amorphisation of ZrW_2O_8 [58]. Furthermore, this reticular approach is sufficiently general that it can also be applied to disordered structures found in electronic and magnetic states, or even on the macroscopic scale wherein correlated disorder has been used in the design of materials with large photonic band gaps [216, 217].

Indeed, in recent complementary research, the procrySTALLine class of disorder has

been suggested to play a key role in the ferroelectric phase transitions of materials such as BaTiO_3 [284]. In this work, the ferroelectric phase transition of BaTiO_3 has been linked to local driving forces including that which generates procrySTALLine disorder. Moreover, this work has revealed a generalised design strategy for creating ferroelectric materials through simple consideration of two local interactions. In doing so, this research has shown the potential importance of procrySTALLine disorder to the functional responses of materials. The work presented in the remainder of this thesis aims to develop further disorder–property relationships, as it is anticipated that correlated disorder will also alter the band structure of materials. So the following question provides the focus of the subsequent studies presented in this thesis: to what extent might the collective mechanical, electronic and photonic properties be altered and controlled by procrySTALLine disorder?

Chapter 4

Supercell lattice dynamics

Structural periodicity is fundamental to the calculation of phononic band structure. As such, there is a lack of suitable approaches to study the effect of disorder on the vibrational behaviour of materials. In its most general form, disorder is known to induce phonon broadening, but the impact of different disorder correlations and origins—*e.g.* bond strength, mass, bond length—remains poorly understood. This chapter is adapted from the publication “Phonon broadening from supercell lattice dynamics: Random and correlated disorder” [287] and presents the supercell lattice dynamical (SCLD) method. This approach enables the full phonon dispersion curves of disordered configurations to be calculated. As such, an understanding of the factors that effect disorder-induced phonon broadening can be determined.

This chapter begins by discussing the importance of understanding disorder-induced phonon broadening, especially for the design of high performance thermoelectrics. In Section 4.2, the SCLD methodology is summarised and the approach benchmarked against lattice dynamical calculations of ordered structures. A variety of case studies are then presented, revealing the impact different disorder types and correlations can have on the phonon band structure. The versatility of the SCLD method is demonstrated by tackling an assortment of different types and correlations of disorder, where in all cases the resulting disorder-phonon coupling can be ascertained, and finally the implications of the method are discussed. The SCLD method was developed in collaboration with Dr Arkadiy Simonov.

4.1 Introduction

Phonon broadening plays a key role in the thermal conductivity of solids, and as such it is an important factor to consider in the design of functional materials in which

thermal transport is of significance [73, 288–290]. By way of example, in the field of thermoelectrics, low thermal conductivity is desired such that a high temperature gradient is maintained for the material to generate voltage [68, 291]. The conversion efficiency of thermoelectric materials is limited by the figure of merit:

$$zT = \frac{S^2 \sigma T}{\kappa_L + \kappa_E} . \quad (4.1)$$

Here, the Seebeck coefficient (or thermoelectric power), S , represents the magnitude of electrical voltage generated by a given temperature gradient, σ is the electrical conductivity and κ_L and κ_E are the thermal conductivities due to lattice and electronic contributions respectively. In this way, the ideal strategy for designing efficient thermoelectrics, maximises the thermoelectric power and electrical conductivity, while reducing the thermal conductivity. However, these transport parameters are intercorrelated in such a way as to hinder the optimisation of zT , *e.g.* increasing the thermoelectric power often decreases σ , and κ_E is directly related to the electrical conductivity by the Wiedemann-Franz law:

$$\kappa_E = LT\sigma , \quad (4.2)$$

where the constant L is the Lorenz number [69, 292]. Optimisation of the lattice thermal conductivity, κ_L , relies upon increasing phonon broadening. While, reduction of the phonon lifetimes is independent of the other terms in the figure of merit, it is notoriously difficult to achieve without unintended consequences in, for instance, the electrical conductivity. As such, there is significant interest in understanding how phonon broadening might be introduced into a material in a controlled manner.

There are two main effects that contribute to phonon broadening—anharmonic phonon–phonon coupling and static disorder. Anharmonicity acts by increasing the rate of phonon scattering and so reducing the phonon lifetimes. The corresponding effect on the thermal conductivity is enhanced through the involvement of heavy

atoms, which will predominantly broaden the low frequency phonon bands responsible for thermal transport. This effect often occurs in systems with electron–phonon coupling and/or ferroelectric instabilities [293]. Indeed, it is anharmonic phonon–phonon coupling which is thought to be responsible for the high thermoelectric efficiency of PbTe, where a portion of a phonon band broadens dramatically in energy, which has been called the ‘waterfall’ effect [73]. The static disorder contribution to phonon broadening refers to structural changes that are long lived in comparison to the phonon lifetime. While compositional disorder is an obvious example, other less common realisations may include Jahn–Teller distortions, electronically driven structural changes and charge localisation. Moreover, aperiodic atomic arrangements such as quasicrystalline phases might be thought of in the same terms to reduce the lattice thermal conductivity [294]. In the field of thermoelectric design, there is a potential for using disorder as a design feature to decrease κ_L and hence optimise thermoelectric efficiency in, for instance, Heusler and half-Heusler alloys [295–299].

The relationship between structural disorder and vibrational properties has been well characterised for important cases, such as the presence of defect atoms and compositional disorder in binary alloys. In the case of the former, the inclusion of defects results in localised modes which can be mathematically solved in the harmonic limit through the use of Green’s functions [262, 300, 301]. These localised modes can be directly observed in, for instance, infra-red absorption spectra [302] with the effect being particularly noticeable if the mass and/or bonds strengths associated with the defect atom are considerably different from that of the atoms in the host crystal [303]. For example, a tightly bound, light atom defect will produce localised vibrational modes which split off at the top of the phonon spectra and density of states of the host crystal. However, studies into the vibrational behaviour of non-dilute disorder, such as that found in binary (AB) alloys, have made use of the coherent potential approximation (CPA) [262, 303, 304]. Here, an

approximation of the vibrational density of states can be obtained by considering the concentration of the two components A and B , and the ‘strength’ of the disorder *i.e.* the deviation of their masses and bond strengths from that of a representation of the average structure. The CPA approach produces good agreement with exact solutions when the concentrations of the two components are above the percolation threshold; however, at low concentrations of a single component, the details of the density of states for the localised modes are lost, and are approximated to be spread over a large range of frequencies [303, 304].

The atomic arrangements discussed in procrySTALLine arrangements contain both periodic and aperiodic features, where the disorder may be associated with specific periodicities [252]. Phonons represent collective vibrations within crystals, and are themselves associated a particular periodicity, described by the wave-vector, $\mathbf{k}$. As such, this presents an opportunity for selective disorder–phonon coupling, where certain disorder correlations might broaden specific phonon branches in particular regions of reciprocal space, while leaving others unaffected. Such an effect is desired for achieving the “holy grail” of thermoelectric design: a phonon–glass electron–crystal. Here, strongly–correlated disorder might be invoked to reduce thermal conductivity via phonon broadening in a narrow range of $\mathbf{k}$ –vectors while the material may conduct electricity in a separate, unaffected region of reciprocal space. Yet, despite its potential importance, the extent and nature of disorder-induced phonon broadening remains poorly understood, principally because translational periodicity is the fundamental cornerstone of lattice dynamical theory.

As a result, there is an obvious need for lattice dynamical approaches which can determine the effect of static disorder of different forms on the phonon band structure. The prevailing method is the virtual-crystal approximation (VCA), a computationally inexpensive approach which treats disorder by considering a unit cell of the average structure of the crystal within lattice dynamical calculations. As such, only the average effect of disorder on the band structure is determined. Phonon broad-

ening is then treated as a perturbation within the context of Klemens-Callaway theory [305–307], which holds well for low frequency phonon modes and low levels of disorder, but breaks down in more challenging cases [308, 309]. At the other limit of computational intensiveness, density functional theory (DFT) calculations have been employed to calculate excitation energies in specific atomic arrangements [310]. However, these calculations are extremely computationally expensive, and as such are limited the system sizes on the order of $\sim 10^2$ atoms.

Yet, there exists a potential compromise between these two extremes, wherein lattice dynamical calculations may be carried out upon large disordered supercell configurations representing the atomistic arrangement of interest. Here, each interaction within the supercell may effectively be parameterised, either within the quasi-harmonic limit or while accounting for anharmonicity [311], and implemented within well-established lattice dynamical software such as the General Utility Lattice Program (GULP) [249]. To date, this approach has been employed to explore the effects of substitutional and force-constant disorder on phonon density of states in simple alloys [311, 312]. Here, this supercell approach is extended such that the full phonon dispersion behaviour of disordered states can be determined. The key objective of this work is to emphasise the wide-ranging applicability of the supercell lattice dynamical approach and demonstrate the significance of this method in establishing a relationship between static disorder and phonon broadening.

4.2 The SCLD method

Lattice dynamical calculations of unit cell structures within GULP, make use of a force constant matrix, Φ :

$$\Phi_{\alpha\beta} \begin{pmatrix} j & j' \\ 0 & \ell' \end{pmatrix} = \frac{\partial^2 W}{\partial u_{j0}^\alpha \partial u_{j'\ell'}^\beta}, \quad (4.3)$$

which relates the lattice energy, W , to atomic displacements, u , to calculate the dynamical matrix $\mathbf{D}(\mathbf{k})$ at wave-vector, $\mathbf{k}$,

$$D_{\alpha j, \beta j'}(\mathbf{k}) = \frac{1}{(m_j m_{j'})^{1/2}} \sum_{\ell'} \left[\Phi_{\alpha\beta} \begin{pmatrix} j & j' \\ 0 & \ell' \end{pmatrix} \times \exp\{i\mathbf{k} \cdot [\mathbf{r}(j'\ell') - \mathbf{r}(j0)]\} \right]. \quad (4.4)$$

Here, j indexes an atom in unit cell ℓ positioned at $\mathbf{r}(j\ell)$ and α and β are the directions $\{x, y, z\}$ of the atomic displacements [30]. An important result of lattice dynamical theory is that the $3Z$ eigenvalues of $\mathbf{D}(\mathbf{k})$ —where Z is the number of atoms in a unit cell—give the squared normal mode frequencies, $\omega^2(\mathbf{k}, \nu)$, and the corresponding eigenvectors, $\mathbf{e}(\mathbf{k}, \nu)$, describe the atomic displacements for a given phonon mode, ν . A full set of phonon dispersion curves can then be constructed by evaluating $\mathbf{D}(\mathbf{k})$ at a suitably dense set of wave-vectors.

The SCLD method differs from conventional lattice dynamics in that rather than a single unit cell, a supercell containing N unit cells is implemented. Here, the atoms are indexed by j, l to track the position l of the unit cell within the supercell. Correspondingly, the mass of each atom can be assigned individual values, $m(jl)$, and the force constant matrix redefined as:

$$\Phi_{\alpha\beta} \begin{pmatrix} jl & j'l' \\ 0 & \ell' \end{pmatrix}. \quad (4.5)$$

The variability in $m(jl)$ and Φ necessitates that the supercell should be initially relaxed to minimise W and obtain the appropriate equilibrium atomic coordinates.

The resulting dynamical matrix contains $3ZN \times 3ZN$ entries and subsequent diagonalisation of $\mathbf{D}(\mathbf{k} = 0)$ yields the $3ZN$ squared normal mode frequencies ω^2 and

their corresponding eigenvectors $\mathbf{e}(\nu)$ of the supercell at Γ .^{*} The eigenvectors each contain $3ZN$ components, e_{jl}^α , each of which represent the displacement patterns of a single atom (of the ZN atoms in the supercell) in one of the three cartesian directions. The key step of the SCLD method involves projecting each of the $3ZN$ modes onto the allowable wave-vectors determined by the dimensions of the supercell. In a cubic supercell with cell length $L = \sqrt[3]{N}$ the allowed $\mathbf{k}$ -vectors are therefore

$$\mathbf{k} = 2\pi \left(\frac{n_1}{L}, \frac{n_2}{L}, \frac{n_3}{L} \right) ; n_i \in \{0, 1, \dots, L-1\}. \quad (4.6)$$

In this way a finer resolution in $\mathbf{k}$ can be obtained through the use of larger supercells. The projection, ρ , is determined for all ν at all $\mathbf{k}$ values commensurate with the supercell size by the following relation:

$$\rho(\mathbf{k}, \omega) = \sum_{\nu} \left\{ \frac{\delta[\omega - \omega(\nu)]}{N} \times \sum_{\alpha} \left| \sum_{jl} e_{jl}^\alpha(\nu) \exp[i\mathbf{k} \cdot \mathbf{r}(l)] \right|^2 \right\}, \quad (4.7)$$

where, $\mathbf{r}(jl)$ represents the position vector of atom jl within the supercell. The expression in Equation 4.7 is similar to the structure factor formalism (Equation 21 in Ref. [312]). In this way, the values of ρ represent the extent to which the eigenvector of a given phonon mode projects at each of the allowable $\mathbf{k}$ -points of the supercell. Here, $\rho = 1$ is the maximum value of the projection, in which the chosen $\mathbf{k}$ -vector fully describes the atomic motion of the phonon mode, whereas $\rho = 0$ represents an orthogonal relationship between the eigenvector and chosen $\mathbf{k}$ -vector.

Under the SCLD method, there is a requirement to average ρ over symmetry-equivalent $\mathbf{k}$ vectors; moreover, in disordered configurations the accuracy of the projection values can be further improved by averaging over multiple independent configurations. Throughout this thesis, all lattice dynamical simulations using the SCLD method are shown as the average of five independent configurations of the

^{*}For certain systems, particularly where LO/TO splitting is important, it may be necessary to calculate $\mathbf{D}(\mathbf{k} \rightarrow 0)$ —*i.e.* where $\mathbf{k}$ approaches Γ .

same size.

4.2.1 Unit cell lattice dynamical and SCLD approaches

An important sanity-check of the implementation of the SCLD method is to ensure that ordered supercells produce phonon dispersion curves consistent with those calculated for analogous unit cell representations. Here, a primitive cubic unit cell, with lattice parameter, a , containing a single atom with mass, m , is considered. Each atom interacts with its six nearest neighbours along the $\langle 100 \rangle$ directions through harmonic bond stretching and bond angle terms:

$$E_{\text{harm}} = \frac{1}{2} k_{\text{harm}} (r - r_0)^2, \quad (4.8)$$

$$E_{\text{angle}} = \frac{1}{2} k_{\text{angle}} (\theta - \theta_0)^2. \quad (4.9)$$

The exact parameter values were chosen to ensure elastic stability of the structure and a broad dispersion of phonon energies [Table 4.1].

The phonon dispersion curves for the corresponding SCLD calculations using $10 \times 10 \times 10$ and $20 \times 20 \times 20$ supercells closely match those obtained from a unit cell, which represents the average structure in further studies in this chapter [Fig. 4.1]. The obvious difference lies in the resolution, as the SCLD results are limited to a much coarser $\mathbf{k}$ -mesh. Yet, the phonon frequencies match those determined from the unit cell representation of the structure and the projection values, $\rho(\mathbf{k}, \omega)$, strictly take

Table 4.1: A summary of parameters used in the virtual-crystal approximation.

Parameter	VCA value
$a / \text{\AA}$	10
m / amu	60
$k_{\text{harm}} / \text{eV}\text{\AA}^{-2}$	10
$r_0 / \text{\AA}$	10
$k_{\text{angle}} / \text{eVrad}^{-2}$	10
$\theta_0 / ^\circ$	90

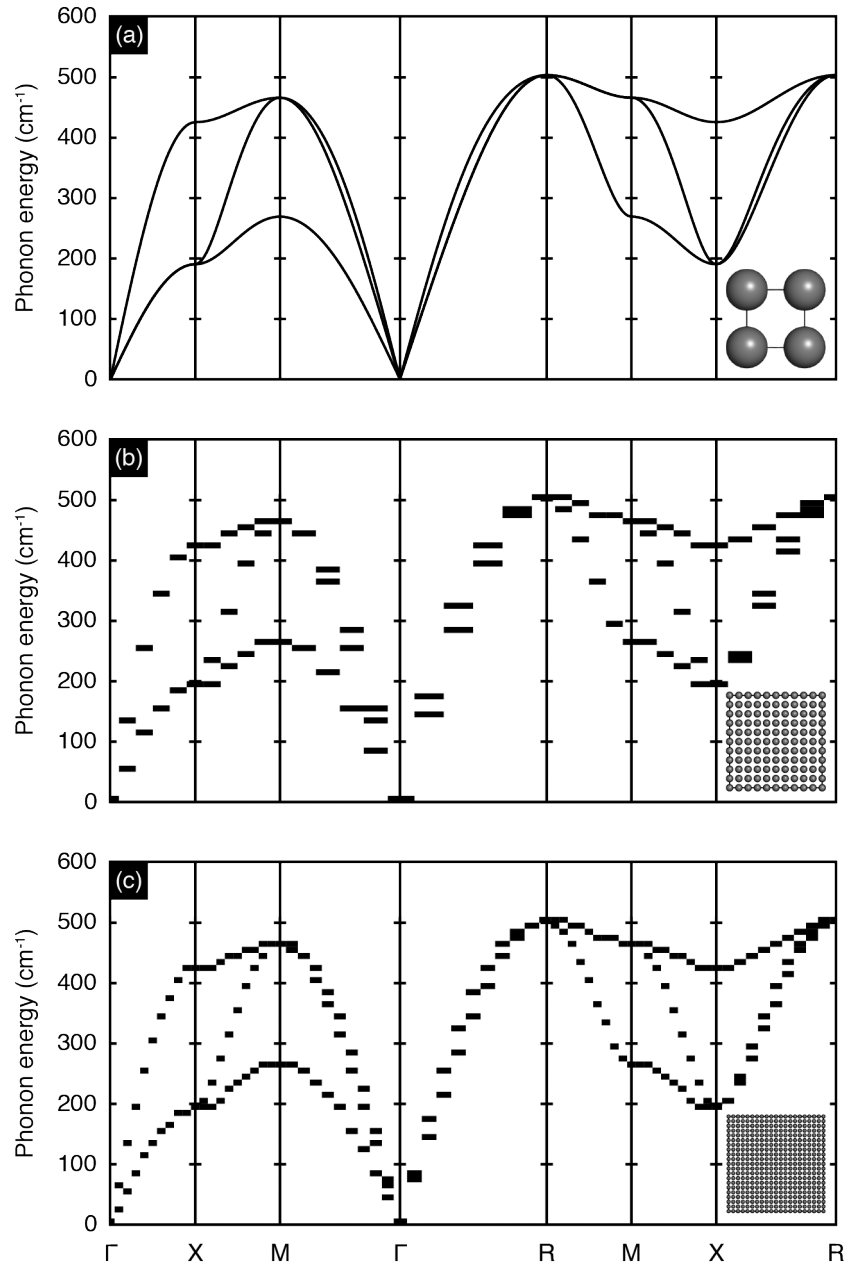


Figure 4.1: Consistency tests for the SCLD method using a periodic, primitive cubic model system. Phonon dispersion curves calculated from a unit cell representation as implemented in GULP [249] are shown in (a). The primitive unit cell contains a single atom, and as such, produces three phonon branches. Corresponding phonon dispersion curves calculated through the SCLD method are shown for a (b) $10 \times 10 \times 10$ and a (c) $20 \times 20 \times 20$ supercell which, aside from resolution effects, reproduce the results of (a). Representative configurations of the cells used in each lattice dynamical calculation are shown in the bottom right.

discrete integer values as the supercells contain no disorder. For future reference, this example corresponds to the VCA of the disordered binary alloy case studies which are the focus of the remainder of this chapter.

4.3 Case study 1: Random disorder

Having established that the SCLD method and VCA calculate equivalent phonon dispersion in the ordered limit, the effect of random static disorder on the phonon spectra is investigated in the following section. In this study, the disorder is embedded in one of two ways—a variation of either atomic mass, m , or the harmonic force constant, k_{harm} —within a simple cubic family of binary alloys (AB) whereby there are equal numbers of each of the two atom types.

4.3.1 Mass disorder

In the first example the effect of random mass disorder was considered, where the values of m_A and m_B were altered but the k_{harm} and k_{angle} terms were kept constant [Table 4.2]. Supercells of the primitive cubic alloy with dimensions $10 \times 10 \times 10$ were generated with a random decoration of A and B atoms, but with equal quantities. The phonon dispersion curves were obtained using the SCLD method and averaged across five configurations [Fig. 4.2(a)]. The presence of static disorder produces phonon broadening. This is observed through non-integer values of ρ creating a continuous widening of the phonon bands. Here, due to the presence of disorder, ρ can adopt intermediate values—in contrast to the integer values observed in the case of ordered supercells—which is represented by the use of a colour scale shown in Figure 4.2.

Yet, the spread in ρ values is more complex than a simple broadening term applied to each of the phonon bands. Indeed, the maximum phonon frequency increases—due to the presence of lighter atoms—and at the R point an additional branch

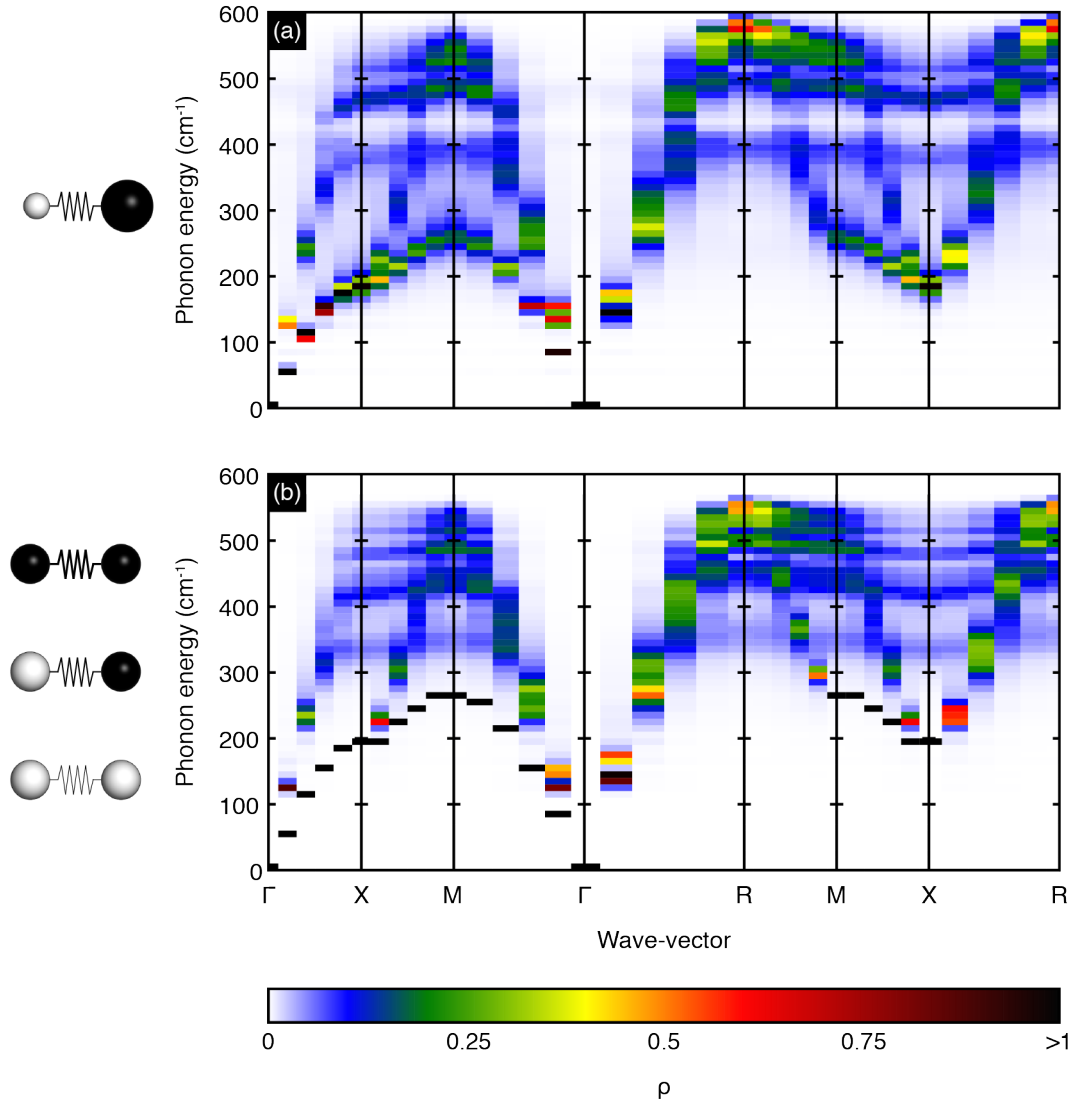


Figure 4.2: The vibrational effects of mass and bond-strength disorder. Investigation into the effect of (a) mass, m , and (b) bond strength, k_{harm} disorder on the vibrational behaviour of random binary alloys. The phonon dispersion curves were determined using $10 \times 10 \times 10$ supercells through the SCLD method. Disorder-induced phonon broadening is clearly evident through the non-integer values of ρ as represented by the colour scale (bottom) [Eqn. 4.7]. Yet, the disorder origins of (a) and (b) effect the phonon dispersion in different ways, with a small band gap emerging at 450 cm^{-1} due to mass disorder, but not bond strength disorder.

appears to emerge at 400 cm^{-1} . This demonstrates that the SCLD method is able to account for multiple effects simultaneously, distinguishing the approach from simple perturbation methods. Similar broadening effects are observed for different ratios of m_A/m_B . However, as expected, the magnitude of the broadening is affected by the extent to which the ratio deviates from $m_A/m_B = 1$.

4.3.2 Bond strength disorder

Equivalent calculations were carried out wherein, instead of the atomic masses, the harmonic bond stretching force constants were varied [Table 4.2]. The corresponding phonon spectrum determined using the SCLD approach is presented in Figure 4.2(b). The k_{harm} disorder reflects a stronger variation than that for the mass disorder case, but the overall extent of phonon broadening is similar. Nevertheless, there are clear differences between the broadening in these two cases. By way of example, bond strength disorder does not broaden the lowest frequency bands (the transverse acoustic branches) in specific regions of reciprocal space: $\Gamma \rightarrow X \rightarrow M \rightarrow \Gamma$. Here, the corresponding mode eigenvectors for these vibrations describe displacements that only vary bond angles and do not vary the distances between neighbours. Moreover, a small band gap appears to emerge at 450 cm^{-1} via mass disorder, whereas the phonon spectrum for bond strength disorder is gapless.

In both the case of mass and bond strength disorder, it is important to discuss the applicability of treating the vibrations as travelling waves. It is clear that in the low frequency limit, the phonon modes represent collective vibrations, as ρ approaches discrete integer values (0 or 1), especially for bond strength disorder. Contrastingly, higher frequency vibrations display broadening across $\mathbf{k}$ -space—although not uniformly—often with $0 < \rho < 0.15$ which indicates significant localisation of the these modes. As such, these simple model systems lie in the middle ground, displaying both collective and localised vibrations, where the suitability of describing the lattice vibrations as travelling waves is dependent upon both the frequency of the

phonon modes and the form of the disorder within the model. Indeed, this effect reflects the presence of both periodic and aperiodic components in structure.

The key result of this case study shows that different origins of disorder produce different phonon broadening effects. This is not entirely surprising; mass and force-constant disorder will affect the diagonal and off-diagonal components of the dynamical matrix to different extents. Moreover, it is interesting to note that broadening in the phonon spectrum is so sensitive to the type of disorder. However, when comparing to experimental data, subtle changes in ρ in both phonon frequency and $\mathbf{k}$ -space may be masked by the instrument resolution function, a factor not taken into account in these simulations.

4.4 Case study 2: Correlated disorder

But what of the effect of correlated disorder? Here, a simple occupational type disorder is considered wherein an avoidance of the same constituents on neighbouring sites is employed—*i.e.* A – A and B – B neighbours are disfavoured. This approach is similar to the Lowenstein rule of aluminium avoidance in zeolite chemistry, where Al – O – Al bonding motifs are forbidden [313]. In this study the extent of correlation within the supercell is determined by the order parameter:

$$\phi = \frac{N_{AB} - (N_{AA} + N_{BB})}{3ZN}, \quad (4.10)$$

Table 4.2: A summary of parameters used in case study 1.

Parameter	Mass disorder	Bond strength disorder
m_A / amu	40	60
m_B / amu	80	60
$k_{\text{harm}}(A-A)$ / $\text{eV}\text{\AA}^{-2}$	10	5
$k_{\text{harm}}(B-B)$ / $\text{eV}\text{\AA}^{-2}$	10	15
$k_{\text{harm}}(A-B)$ / $\text{eV}\text{\AA}^{-2}$	10	10

where N_{AB} , N_{AA} and N_{BB} are the number of nearest neighbouring pairs made up of atom types AB , AA , and BB respectively, Z represents the number of atoms in a single unit cell (one in this case) and N is equal to the number of unit cells in the supercell. However, the values of N_{AB} , N_{AA} and N_{BB} are not independent and must sum to $3ZN$, as such the expression for ϕ can be simplified to

$$\phi = \frac{2N_{AB}}{3ZN} - 1. \quad (4.11)$$

A statistical distribution of A and B atoms on the primitive lattice sites gives

$$N_{AA} = N_{BB} = 3N/4, \quad N_{AB} = 3N/2 \quad \therefore \quad \phi = 0. \quad (4.12)$$

By contrast if A - A and B - B nearest neighbour pairs are strictly avoided:

$$N_{AA} = N_{BB} = 0, \quad N_{AB} = 3N \quad \therefore \quad \phi = 1. \quad (4.13)$$

A decoration of the second type corresponds to the rocksalt structure, wherein the A and B atoms are ordered and occupy alternate sites.

A custom algorithm was used to generate $12 \times 12 \times 12$ supercells at each of the corresponding order parameter values: $\phi = 0, \frac{1}{4}, \frac{1}{2}, \frac{3}{4}, 1$. An initial supercell was generated with equal numbers of A and B atoms randomly distributed over the available sites. Swaps between random sites containing A and B atoms were then conducted until the desired ϕ value of the supercell was reached. To improve the statistics of this study, five configurations were prepared for each ϕ value except in the fully ordered limit of $\phi = 1$. Each configuration was examined for long range correlations through the correlation function $C(r)$, where

$$C(r) = \frac{1}{ZNz(r)} \sum_{i,j|r_{ij}=r} e(i)e(j). \quad (4.14)$$

Here, $z(r)$ represents the number of neighbours j of site i at a given distance r and the value of $e(i) = \pm 1$ is the site occupation of either an A or B atom respectively. The value of $C(r)$, averaged over the five independent configurations at each value of ϕ , is presented in Figure 4.3. As expected, this function shows that longer range correlations emerge as $\phi \rightarrow 1$.

Disorder in these configurations was realised through a variation of atomic mass only, with k_{harm} remaining fixed, and the parameters used were equivalent to those detailed in Table 4.2. As such, the form of the phonon dispersion of $\phi = 0$ is expected to closely resemble those determined for random mass disorder in Figure 4.2. The phonon dispersion curves for each configuration were determined using the SCLD approach, and then averaged over configurations with equivalent ϕ values. The phonon dispersion curves for each model were constructed along the following directions of the Brillouin zone:

$$\begin{aligned} \mathbf{k} = [0, 0, 0] \rightarrow \left[0, 0, \frac{1}{2}\right] \rightarrow \left[0, \frac{1}{2}, \frac{1}{2}\right] \rightarrow [0, 0, 0] \rightarrow \\ \left[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right] \rightarrow \left[0, \frac{1}{2}, \frac{1}{2}\right] \rightarrow \left[0, 0, \frac{1}{2}\right] \rightarrow \left[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right]. \end{aligned} \quad (4.15)$$

In the case of the primitive cubic cell, which represents the average structure of the $\phi = 0$ models, these directions correspond to a navigation of $\Gamma \rightarrow X \rightarrow M \rightarrow \Gamma \rightarrow R \rightarrow M \rightarrow X \rightarrow R$, shown at the top of Figure 4.3. However for the face-centred model observed in the ordered, $\phi = 1$, state the correct Bradley-Cracknell notation is instead represented by $\Gamma \rightarrow X \rightarrow X \rightarrow \Gamma \rightarrow \Gamma \rightarrow X \rightarrow X \rightarrow \Gamma$, which is shown at the bottom of Figure 4.3.

The corresponding averaged phonon dispersion curves for each ϕ value are presented in Figure 4.3. As expected, the disorder-phonon coupling observed in the $\phi = 0$ case is consistent with that observed for the mass disorder case study in Figure 4.2(a).

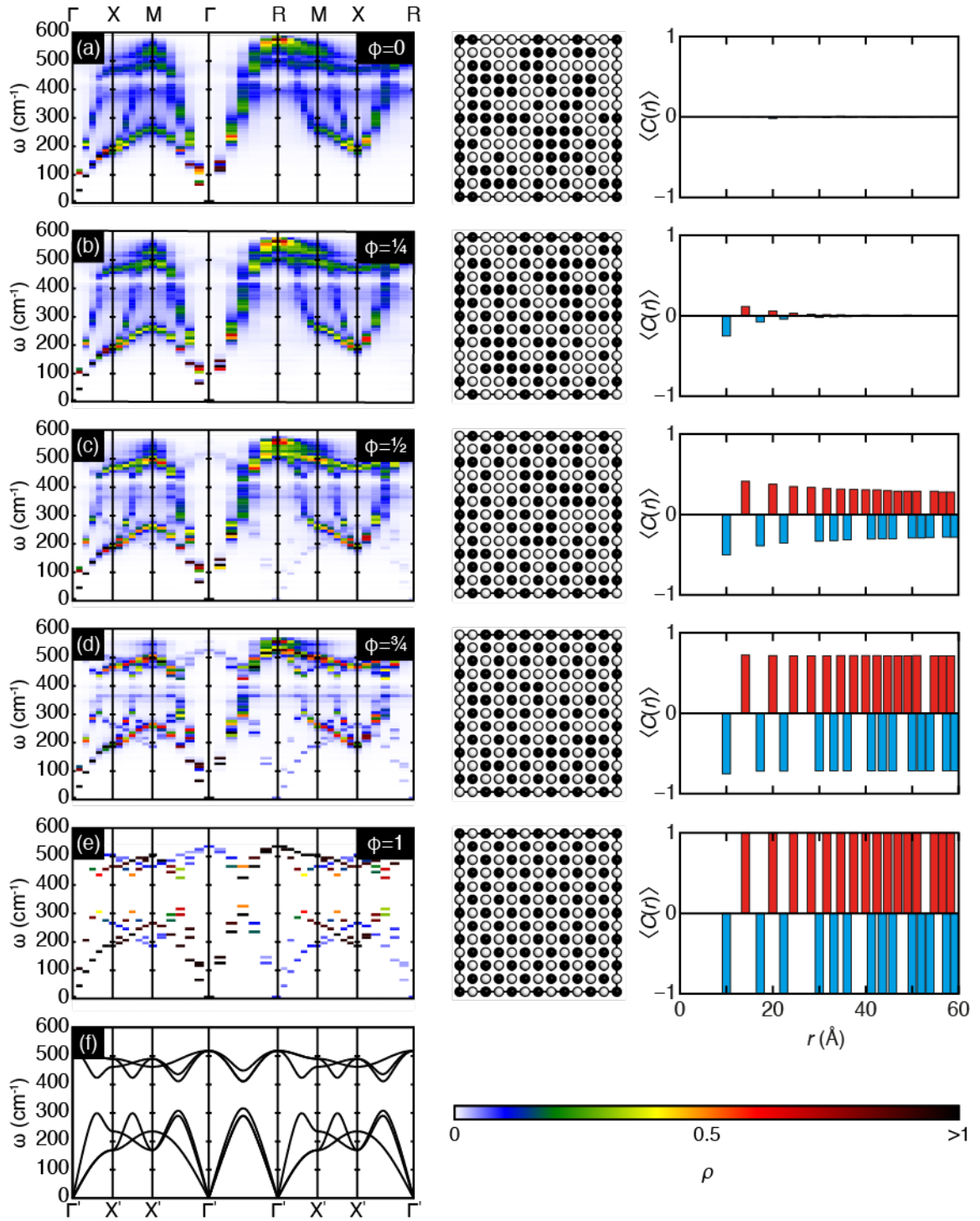


Figure 4.3: The impact of correlated disorder on phonon broadening. Phonon dispersion curves determined using the SCLD method are presented for alloys with mass disorder at ϕ values of (a) 0.00, (b) 0.25, (c) 0.50, (d) 0.75 and (e) 1.00. Panel (f) shows the phonon dispersion curves for the ordered limit ($\phi = 1.00$) determined through lattice dynamical calculations of a unit cell. The different wave vector labels shown at the top and bottom refer to the Brillouin zone of the primitive and face centred cell respectively. The centre column shows planes of a representative configuration with atom types A and B shown in black and white respectively. Average correlation functions $\langle C(r) \rangle$ are given for each ϕ value (right). Positive A–A and B–B correlations and negative A–B correlations are shown in blue and red respectively. Non-integer values of ρ are represented by the colour-bar (bottom-right).

Indeed, the main observable difference lies in the resolution of the two spectra as the $\mathbf{k}$ -mesh is slightly denser in Figure 4.3 due to the use of a larger supercell.

This case study serves as a test of the SCLD method, where the resulting spectra are consistent with intuition—the phonon broadening decreases with increasing ϕ , as order is introduced into the supercell. This effect is accompanied by an opening of a phononic band gap centred around 400 cm^{-1} . As such, it is anticipated that the density of states in a real binary alloy will be sensitive to the extent of site ordering.

Unsurprisingly, the largest difference is observed between the $\phi = 0$ and $\phi = 1$ cases. Besides the obvious change in phonon broadening, the underlying form of the phonon dispersion curves changes. As expected, in the ordered limit the original R point $\mathbf{k} = [\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$ is established as another zone centre labelled Γ' . Here, the $\phi = 1$ configuration has a face-centred cubic unit cell, constructed from a doubling of the primitive unit cell in all three axes. Correspondingly, the $\mathbf{k} = [\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$ point is now associated with a reciprocal lattice vector. Furthermore, the doubling of the unit cell also provides an explanation for the emergence of the band gap. Only acoustic modes are expected for the $\phi = 0$ case as there is only a single atom in the average unit cell. Conversely, for the $\phi = 1$ configuration, $Z > 1$, and hence both acoustic *and* optic modes are now expected. Therefore according to lattice dynamical theory, there is potential for a phononic band gap to be observed. Indeed, given that the $\phi = 1$ model is ordered, a unit cell can be used to calculate the exact phonon dispersion for the high symmetry directions attributed to the primitive unit cell case. As expected, these results match those obtained from the SCLD result exactly, except for the difference in resolution in the $\mathbf{k}$ -mesh of the two approaches [Fig. 4.3(f)].

The magnitude of the projection values for the $\phi = 1$ model have non-integer values despite the system being ordered. This effect arises from the sum of the projection magnitudes at each $\mathbf{k}$ -point being inherently restricted to $\sum \rho = 3$, as there is a

single atom in the parent unit cell. Yet, in the $\phi = 1$ case, there are more than three bands projecting at each $\mathbf{k}$ -point. In the remainder of this section, the values of ρ at Γ for the $\phi = 1$ model are derived.

An individual eigenvector for the supercell at the zone centre, e , describes the displacements of the two atom types with different masses, m_1 and m_2 . Hence, the eigenvector contains values describing the atomic displacements which are different for each atom type, e_1 and e_2 . The magnitudes of e_1 and e_2 are independent of bond strengths, but are dependent on the mass of the atoms in the ratio:

$$\frac{e_2}{e_1} = \frac{\sqrt{m_2}}{\sqrt{m_1}}. \quad (4.16)$$

Moreover, each supercell eigenvector is normalised such that

$$\frac{N}{2}e_1^2 + \frac{N}{2}e_2^2 = 1, \quad (4.17)$$

where N is the number of atoms in the supercell, equivalent in this case to the number of unit cells in the supercell. Subsequent combination of these two expressions yield

$$e_1^2 \left(1 + \frac{m_2}{m_1}\right) = \frac{2}{N}, \quad (4.18)$$

$$e_1^2 \left(1 + \frac{m_1}{m_2}\right) = \frac{2}{N}.$$

Rearrangement of Equations 4.18 give the values of e_1 and e_2 in terms of the atomic masses:

$$e_1 = \sqrt{\frac{2m_1}{N(m_1 + m_2)}}, \quad (4.19)$$

$$e_2 = \sqrt{\frac{2m_2}{N(m_1 + m_2)}}.$$

Given the phase of the atomic displacements at Γ , the projection values for the acoustic and optic modes are related to e_1 and e_2 in the following way:

$$\rho(\mathbf{k} = \mathbf{0}, \text{acoustic}) = \frac{1}{N} \left(\frac{N}{2} e_1 + \frac{N}{2} e_2 \right)^2, \quad (4.20)$$

$$\rho(\mathbf{k} = \mathbf{0}, \text{optic}) = \frac{1}{N} \left(\frac{N}{2} e_1 - \frac{N}{2} e_2 \right)^2.$$

Simple substitution of Equations 4.19 into Equations 4.20 yield the projection values for the acoustic and optic modes in terms of the atomic masses

$$\rho(\mathbf{k} = \mathbf{0}, \text{acoustic}) = \frac{1}{2} + \frac{\sqrt{m_1 m_2}}{m_1 + m_2}, \quad (4.21)$$

$$\rho(\mathbf{k} = \mathbf{0}, \text{optic}) = \frac{1}{2} - \frac{\sqrt{m_1 m_2}}{m_1 + m_2}.$$

In the case where the atomic masses are equivalent, only projection of the acoustic mode is observed which is consistent with the VCA phonon dispersion curves determined from SCLD in Figure 4.1. Yet, in the limit of large mass difference, $\rho \rightarrow \frac{1}{2}$ for both the acoustic and optic modes. In this second case study, the masses of the A and B atoms are 40 and 80 amu respectively, giving projection values of 97% and 3% for the acoustic and optical modes, respectively explaining the observations in Figure 4.3(e).

4.5 Discussion

The SCLD approach presented in this chapter provides a computationally efficient method to determine the phonon dispersion of disordered materials. In turn this offers up an attractive prospect for comparison of these simulations with experimental inelastic neutron/X-ray data. Here, both the atomic interactions and the structural disorder might act as refinable parameters, or contrastingly if one of these two factors is known, the SCLD method provides a potentially trivial way of determining the other. However, it is important to note that comparison with experimental data requires accurate characterisation of resolution function of the instrument along with correct treatment of the polarisation effects such as LO/TO splitting [30].

The two case studies presented in this chapter have revealed the existence of disorder-phonon coupling in the form of phonon broadening. This effect is particularly important in understanding the thermal transport behaviour of disordered materials. The broadening signatures represent a breaking down of the Bloch-wave description of vibrational states and so are not observable within the calculated phonon spectra of the average structure. As a result, the SCLD method represents an important step in accurately determining the effect of disorder on the thermal transport of solids.

This development is crucial in the design of new thermoelectric materials. Thus far, the desired phonon–glass electron–crystal state for efficient thermoelectric materials has remained elusive. Yet, the SCLD approach now provides a route to systematically develop an understanding of which types and correlations of disorder may, in principal, allow such a state to be achieved. In an ideal situation, correlated disorder would selectively broaden the low energy phonons in one region of reciprocal space, while leaving other areas unaffected for the conduction of electricity. Furthermore, the SCLD method facilitates investigation of the localisation of the broadened modes. Correspondingly, this study represents an important step in determining the

relationship between correlated disorder and thermal transport properties [312, 314].

Additionally, on the consideration of a large supercell, the SCLD method is essentially independent of any symmetry constraints. As such, this approach may in theory provide a pathway to investigate the, as yet unexplained, selection rule violations in the Raman/infrared spectra of disordered materials such as ice [315–317]. This avenue of study is particularly relevant as in Figure 4.3 the disordered configurations show appreciable projection values around 550 cm^{-1} at the Γ point; a phenomenon not predicted by the corresponding VCA calculations.

Chapter 5

Structure-property relationships in the procrySTALLine state

In this chapter, the work developed in Chapters 3 and 4, namely that of the procrySTALLine state and the supercell lattice dynamical (SCLD) method, are combined. Here two key questions are asked: (i) Is there a possibility that inelastic data might provide information of the disorder correlations, in keeping with the conclusions of Chapter 4? (ii) To what extent might band structure and related physical properties as a whole be impacted by procrySTALLine decorations of disorder?

This chapter begins with a discussion of disorder characterisation techniques and the potential role of inelastic data in this context. Subsequently, disorder models based upon the ReO_3 net, including those related to procrySTALLine decorations, are introduced. The details of the supercell lattice dynamical (SCLD) calculations, which allow the derivation of phonon dispersion curves for each of these different models, is presented. The phonon dispersion curves, densities of states, and mode localisation are then reported for each disorder model on the ReO_3 net and the relationship between the type of disorder present and form of the phonon spectra is established. A set of disorder models based on the simple α -Po net is then presented. These contain analogous disorder correlations to the original ReO_3 study, and again their corresponding dynamical behaviour is determined and discussed. In Sections 5.4 and 5.5, the impact of correlated disorder on other collective and experimentally observable properties, such as the electronic and photonic spectra, is then demonstrated. This chapter concludes with a complementary study revealing the changes in the vibrational and photonic band structure due to dimer decorations—*i.e.* the $\mathbf{C}_1$ and $\mathbf{S}_1$ state—followed by a discussion of the implications of the disorder-property

relationships established in this study.

5.1 Introduction

The characterisation of disorder in the solid state was recognised as an important challenge in early crystallographic studies [318, 319]. In recent years, research in this area has become more prominent and expanded [6, 208, 254] for two key reasons: (i) the development of higher quality detectors which enable the accurate collection of the weak intensity diffuse scattering features which act as signatures of disorder, while minimising the contribution of noise [320–322]; (ii) a vast improvement in computational performance allowing the characterisation of more complex systems and simulation of larger—and therefore more realistic—models of disordered materials [58, 165, 237]. The main scientific motivation for studying disorder is the central role it plays in the physics of functional materials including displacive disorder in high- T_c superconductors such as $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$ and $\text{HgBa}_2\text{CuO}_{4+\delta}$ [323, 324], dipolar disorder in ferroelectrics and thermoelectrics [10, 261], orbital disorder in unconventional spin glasses [325, 326], and orientational disorder in modern photovoltaics [327]. Yet the study of disordered materials remains challenging from many perspectives—theoretical, computational, and experimental—primarily as a result of the inherent complexity introduced as structural periodicity is lost. Consequently, there is much to be gained by establishing a broader understanding of the experimental signatures of different types of disorder—not only for characterising disordered states but ideally also to enable control over physical properties via manipulation of the type of disorder at play.

The most suitable experimental method for characterising disordered structures is elastic scattering, which includes total scattering / pair distribution function (PDF) [104, 328] and single-crystal diffuse-scattering measurements [102]. While many other experimental techniques are excellent probes of local structure in disordered materials (*e.g.* NMR [329–331], EXAFS [332], XANES [333], IR/Raman spec-

troscopy [334–336]), only scattering methods are sensitive to the manner in which local distortions correlate throughout a crystal lattice. For systems in which there is little energetic preference for disorder to correlate—*e.g.* the distribution of isotopes in a material*—this distinction can be less meaningful, but for the functional materials classes enumerated above, disorder is always present in a significantly correlated fashion, so scattering methods remain of key importance [6, 102, 233].

However, not all types of disorder are distinguishable using scattering methods alone, a consequence of the technique’s *indirect* sensitivity to three-body and higher-order correlations (Section 2.1.2). This problem is most noticable for amorphous systems (*e.g.* *a*-Si) [339, 340], but is also relevant for specific classes of disordered crystals [232]. Even in cases where two-body correlations should be sufficient to characterise disordered states, the interpretation of scattering measurements can be complicated by a number of factors. The underlying structural disorder may involve species with similar X-ray and/or neutron scattering strengths, such as in the common and important pairings (Al, Si) and (O, F) [341–343]. Single-crystal samples may be experimentally inaccessible, and the reduced information content of powder PDF measurements insufficient to identify unambiguously a particular disorder model [7, 344]. Moreover, even with access to high-quality PDF / single-crystal diffuse scattering data, the process of determining a meaningful disorder model remains difficult and far from routine [102, 237].

Given that disorder affects the vibrational behaviour of materials [30, 262], spectroscopic measurements are a natural complementary technique in the study of disordered systems. Indeed, spectroscopy may be expected to offer greater sensitivity to disorder than scattering methods, since the phonon spectrum is affected not only by static deviations from periodicity (composition, off-centering, *etc.*) but also vari-

*Isotopes have been shown to have a very weak preference for clumping in carbonate materials, where there is a higher proportion of ^{13}C – ^{18}O bonding motifs than expected from a random distribution. This effect is temperature dependent, a feature which has been used to analyse past climate patterns and to understand the physiology of extinct organisms *i.e.* body temperature [337, 338].

ations in interaction strengths [262, 345–347]. On the very simplest level, disorder changes the vibrational behaviour of crystalline materials by reducing phonon lifetimes, which is evident, for example, in the phonon broadening for high-temperature Cu_3Au [348]. In other systems, dilute and uncorrelated disorder leads to phonon localisation, which in turn results in the appearance of new dispersionless features in the phonon spectrum, which are often interpreted in the same ways as for molecular systems. Examples include oxygen interstitials in silicon [349], defects in alkali halides [301, 302] and mass-disordered binary alloys [350, 351]. In this picture, the phonon bandwidths for localised modes act as a semi-quantitative measure of defect concentration [352]. But what remains less clear is the intermediate case, where the structure is neither ordered or random, but the disorder propagates in a correlated fashion throughout the crystal such as in the procrySTALLINE state (Chapter 3) [252]. It has long been known that complex types of correlated disorder can result in non-trivial changes to the phonon spectrum that cannot be described in terms of simple effects of broadening or localisation [262]. It is precisely these complex correlated disordered states that are relevant to the various examples given above, and for which diffuse (elastic) scattering measurements might usually be employed. So one important focus of this chapter is to answer the straightforward question—to what extent might spectroscopic measurements offer sensitivity to the specific nature of correlated disordered states?

Fortunately, this is a question that can now be tackled computationally. Recent algorithmic developments including the SCLD approach detailed in Chapter 4 allow investigation of phonon broadening beyond the limitations of perturbation theory [305–307] to explore the dynamical properties of large atomistic supercells representing explicit descriptions of complex disordered states [252, 287, 312, 353–357]. To date, these methods have been applied principally to the problem of phonon broadening in thermoelectric materials, motivated by the desire to control thermal conductivity in subsequent materials design [252, 287, 290]. As such, there is now a

valuable opportunity to explore in more general terms the spectroscopic signature of correlated disorder in a wider variety of different systems.

Initially in this study, the dynamical behaviour of a series of systems related to the perovskite structure is calculated, with different models sharing identical average (long-range) structures but reflecting meaningfully-different types of disorder. This series is of conceptual importance to the ferroelectrics BaTiO_3 and KNbO_3 and colossal magnetoresistance (CMR) oxynitrides such as $\text{EuWO}_{1.5}\text{N}_{1.5}$ [254, 255]. These simulations find that random or weakly-correlated disorder results in phonon broadening and strong localisation (as anticipated), but that the presence of strongly-correlated disorder leads to the opening of phononic band gaps and a fundamentally different high-energy phonon spectrum to that of the corresponding random or virtual-crystal approximant models. From this result it is inferred that phonon density of states (DOS) measurements may in favourable cases aid in the identification of specific types of strongly-correlated disorder. This finding is likely to be most important in cases where the elastic scattering sensitivity of the disordered component in the material is low—*e.g.* in the transition metal oxyfluorides or oxynitrides [254, 343]. A complementary set of simulations are then conducted on analogous disorder models situated on the α -Po net. Here, a phononic band gap is only observed in the case of strongly-correlated disorder.

This chapter continues with a study into the electronic and photonic behaviour of analogously disordered materials. Here, it is revealed that similar relationships between disorder correlation and the emergence of gapped states can be established. The unusual phononic gapped behaviour associated with strongly-correlated disorder is expressed in two ways: (i) a reduction in the electronic density of states at the Fermi level; (ii) as a low frequency gap in the photonic spectrum on the consideration of a mesoscale system with embedded strongly-correlated disorder. A final preliminary study is conducted upon further procrySTALLINE states related to the dense decoration of dimers on a primitive/square lattice. Again these simulations

reveal the presence of both phononic and photonic band gaps, albeit with a different origin to the previous procrySTALLine models. Correspondingly, it is demonstrated that the emergence of gapped states is a generalisable, disorder-driven phenomenon. The development of these non-trivial disorder-property relationships is of considerable interest in the fields of hyperuniformity [217, 358], thermoelectrics [359], and disordered photonic materials [219, 263].

5.2 Methodology

5.2.1 Description of models

The models considered in this initial study of vibrational behaviour are closely related to the ReO_3 structure-type, which is itself an A -site deficient variant of the CaTiO_3 perovskite structure. The ReO_3 structure has $Pm\bar{3}m$ crystal symmetry with the Re atoms arranged on a primitive cubic lattice and each pair of neighbouring Re atoms connected by a single O atom. A general case is considered in which the Re site is occupied by a single atom type (labelled ‘ M ’), and the O site is occupied by equal fractions of two distinct atom types, which are labelled ‘ A ’ and ‘ B ’. Hence this system has empirical formula $MA_{1.5}B_{1.5}$ and average space group symmetry $Pm\bar{3}m$. The eventual goal is to establish how the relative arrangement of A and B atoms might affect the phonon spectrum of this system. The four models considered are summarised as follows:

- (i) *Virtual-Crystal Approximation (VCA)*: each O-atom site is occupied by a hybrid atom $(A/B) = A_{0.5}B_{0.5}$, with all interactions taken as the average of the individual interactions for A and B atoms.
- (ii) *Random (RND)*: each O-atom site is occupied by an A or B atom with equal probability, with the additional constraint that any supercell configuration contains equal numbers of A and B atoms.

- (iii) *Meridional local order ($\mathbf{C}_3\mathbf{M}$)*: A and B atoms are distributed on O-atom sites such that each M atom is coordinated by three A atoms and three B atoms, with each set disposed in a meridional arrangement.
- (iv) *Facial local order ($\mathbf{C}_3\mathbf{F}$)*: A and B atoms are distributed on O-atom sites such that each M atom is coordinated by three A atoms and three B atoms, with each set disposed in a facial arrangement.

Illustrations of these four models are given in Fig. 5.1, where the similarities and differences in both local coordination and configurational degrees of freedom are highlighted. A crucial point is that the four models are represented by the same average structure, and so from a crystallographic viewpoint give rise to identical Bragg diffraction patterns. It should be noted that the $\mathbf{C}_3\mathbf{M}$ and $\mathbf{C}_3\mathbf{F}$ procrySTALLine models [Fig. 3.4(o),(p)] represent the only two possible ways of arranging equal numbers of A and B atoms in ReO_3 -type $MA_{1.5}B_{1.5}$ systems subject to the constraint that all M atoms share identical coordination environments [252]. In real materials, this constraint often follows naturally from chemical bonding considerations [360]; moreover the $\mathbf{C}_3\mathbf{F}$ model is considered relevant to both $\text{EuWO}_{1.5}\text{N}_{1.5}$ and BaTiO_3 [261, 285, 361]. While there are 12 equivalent arrangements of the *mer*- MA_3B_3 unit, there are just eight of the *fac*- MA_3B_3 unit. This reduced configurational degeneracy, highlighted by a lower Pauling number (Section 3.2.3), when combined with the implicit occupational correlation between neighbouring units at their shared vertex, results in a state with sub-extensive configurational entropy [252]. In other words, the $\mathbf{C}_3\mathbf{F}$ model is different from the other models as it contains distinct features which are easily observable from the strictly-alternating $-A-M-B-M-$ arrangements highlighted in red in Fig. 5.1.

5.2.2 Generation of models of correlated disordered states

The VCA model represents the average structure of the system, and as such, the corresponding phonon dispersion curves can be determined from a unit cell repre-

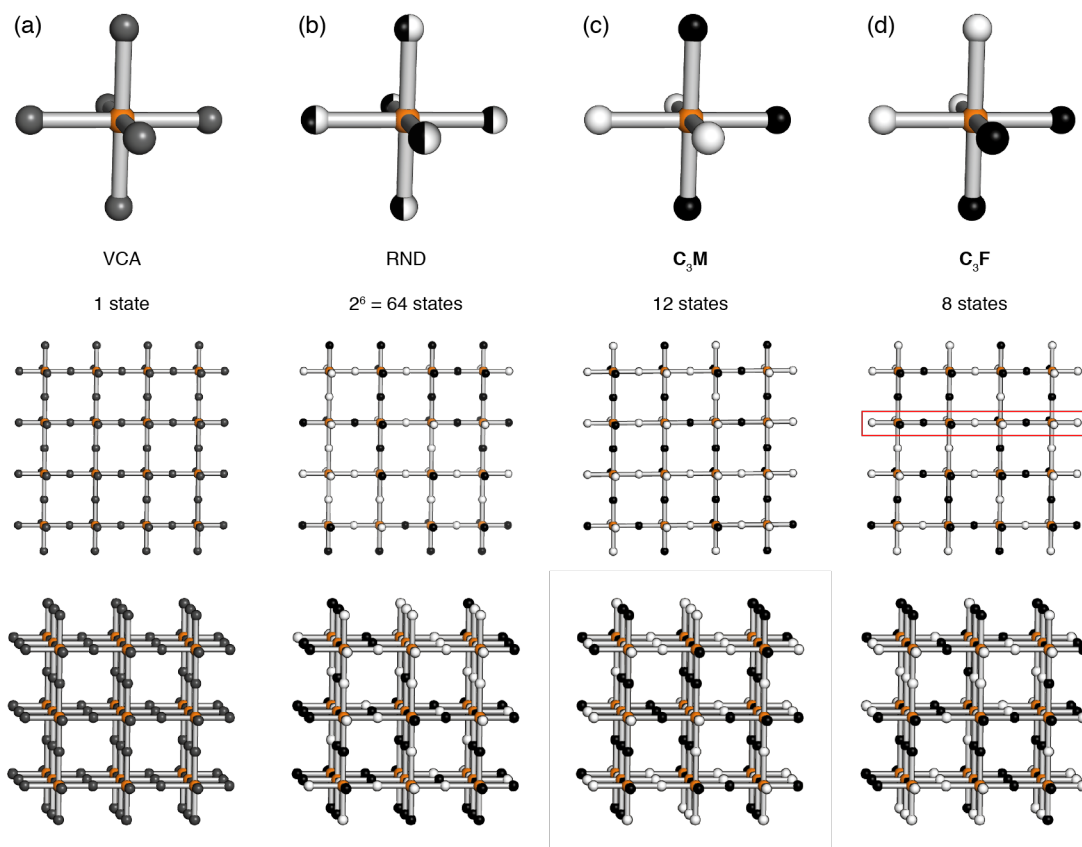


Figure 5.1: The ReO_3 disorder models. A representative depiction of the (a) virtual-crystal approximant [VCA], (b) random disorder [RND], (c) locally meridional [C_3M] and (d) locally facial [C_3F] models employed in this study. The local environment (top) shows the first coordination shell of the M atom (orange), surrounded by A (black), B (white) or A/B hybrid (grey) linker atoms. Individual planar (middle) and volumnar (bottom) sections depict the disorder correlations in each structure. Within the C_3F configuration (d) distinct features of alternating $-A-M-B-M-$ arrangements are highlighted in red. Also given is the number of possible local linker arrangements for each model.

sentation [30]. By contrast, the RND, $\mathbf{C}_3\mathbf{M}$, and $\mathbf{C}_3\mathbf{F}$ models all require explicit atomistic realisations, representing large supercells of the average-structure unit cell. Supercell configurations for the RND model were simply constructed by decorating each of the linker sites randomly with either an A or B atom with the only constraint being that in total the two linker types were present in equal numbers.

Atomistic configurations corresponding to the $\mathbf{C}_3\mathbf{F}$ and $\mathbf{C}_3\mathbf{M}$ models however, were generated using the Monte Carlo (MC) approach previously employed in Ref. [252] and Chapter 3. The MC variables represent the chemical occupation of each O-atom site of an ReO_3 supercell, and periodic boundary conditions are applied. The MC parameters are assigned values of $\epsilon = +1$ and -1 to A and B states, respectively. The configurational energy is calculated as a sum across all nodes of the ReO_3 lattice:

$$E = \sum_{i \in \text{nodes}} [E_{i1} + \delta(E_{i1})E_{i2}] , \quad (5.1)$$

where δ is the delta-function

$$\delta(x) = \begin{cases} 1 & x = 0 \\ 0 & x \neq 0 \end{cases} , \quad (5.2)$$

and E_{i1} and E_{i2} are functions of the number and geometry, respectively, of A and B atoms in the coordination environment of node i . The terms are given explicitly by

$$E_{i1} = \left[\sum_j \epsilon_j \right]^2 , \quad (5.3)$$

where the sum is taken over vertices j of node i , and

$$E_{i2} = \pm \frac{1}{2} \sum_{j,j'} (\epsilon_j + \epsilon_{j'})^2 , \quad (5.4)$$

where the sum is taken over opposite pairs of vertices j, j' of node i and the leading sign is positive for $\mathbf{C}_3\mathbf{F}$ (energy minimised for unlike atoms as opposing vertices)

and negative for $\mathbf{C}_3\mathbf{M}$ (favouring like atoms as opposing vertices). Note that E_{i1} is minimised for configurations in which the six O-type neighbours of node i include three A atoms and three B atoms. In this way, the ground state of Equation 5.1 corresponds to a homogeneously disordered $\mathbf{C}_3\mathbf{F}$ or $\mathbf{C}_3\mathbf{M}$ configuration, according to the leading sign in Equation 5.4. A custom simulated-annealing MC algorithm was used to generate an ensemble of ground state configurations of each model type.

5.2.3 The VCA model

In order to determine the harmonic phonon frequencies for the VCA model described above, a dynamical matrix approach was used, as implemented in the General Utility Lattice Program (GULP) [249]. The lattice dynamical model was made elastically stable by employing three interaction potentials: a harmonic pairwise stretching potential between M atoms and each of their six hybrid A/B neighbours,

$$E_{\text{harm}} = \frac{1}{2}k_{\text{harm}}(r - r_0)^2, \quad (5.5)$$

and two harmonic bond-bending potentials applied to the linear $M-(A/B)-M$,

$$E_{\text{lin}} = k_{\text{lin}}[1 + \cos(\phi)], \quad (5.6)$$

and 90° $(A/B)-M-(A/B)$ angles, respectively,

$$E_{\perp} = \frac{1}{2}k_{\perp}(\theta - \theta_0)^2. \quad (5.7)$$

Here, k_{harm} , $k_{\perp}$ and k_{lin} are the force constants for bond-stretching, $M-(A/B)-M$ bond-bending and $(A/B)-M-(A/B)$ bond-bending potentials, and r_0 and θ_0 are the equilibrium values for the $M-(A/B)$ bond length and $(A/B)-M-(A/B)$ bond angles. The variables r , θ and ϕ correspond in turn to the observed $M-(A/B)$ bond length, $(A/B)-M-(A/B)$ bond angle, and $M-(A/B)-M$ bond angle.

The actual values of the parameters used in these calculations are given in Table 5.1. These were chosen through trial-and-error and tuned to ensure elastic stability and to give a broad dispersion in the phonon frequencies across the Brillouin zone (BZ). In all of the studies the chosen parameter values for the virtual crystal approximant gave $C_{12} = 0$ GPa.

5.2.4 Supercell lattice dynamical calculations

For the three models of disorder that require large supercell descriptions (*i.e.* RND, C_3M , and C_3F), the phonon frequencies were determined using the SCLD method described in Ref. [287] and Chapter 4. The relevant parameters are given in Table 5.1; in this study only the relative strengths of the M - A and M - B pairwise bond-stretching terms are varied. In all of the SCLD simulations in this study, phonon dispersion curves were generated from $10 \times 10 \times 10$ supercells, which represent a good compromise between computational efficiency and $\mathbf{k}$ -mesh resolution.

The phonon density of states, $g(\omega)$, is usually given by integration of the eigenvectors over the entire Brillouin zone. However, given that the calculation of eigenvectors is restricted to a discrete $\mathbf{k}$ -mesh in the SCLD method, the density of states is instead

Table 5.1: A summary of the parameter values used in the ReO_3 lattice dynamical calculations, both for the VCA and disordered supercells.

Parameter	VCA	RND/ C_3M / C_3F
a / Å	10	10
m_M / amu	60	60
$m_A = m_B$ / amu	60	60
$k_{\text{harm}}(M-A)$ / $\text{eV}\text{\AA}^{-2}$	50	70.7
$k_{\text{harm}}(M-B)$ / $\text{eV}\text{\AA}^{-2}$	50	35.4
$k_{\perp}(X-M-X)$ / eVrad^{-2}	50	50
$k_{\text{lin}}(M-X-M)$ / eV	50	50
$r_0(M-X)$ / Å	5	5
$\theta_0(X-M-X)$ / °	90	90

determined by a summation of the ρ values:

$$g(\omega) = \frac{1}{3ZN} \sum_{\mathbf{k} \in \text{BZ}} \rho(\omega, \mathbf{k}). \quad (5.8)$$

When plotting the phononic DOS, the frequency-space bin-width was set to 30 cm^{-1} .

5.3 Phononic behaviour

5.3.1 ReO_3 decoration

The starting point of this study involves the phonon dispersion relation of the average structure, as calculated using both lattice dynamical calculations of the unit cell model and through the SCLD method. In the spirit of Ref. [287] and Chapter 4, this comparison serves to validate the use of the SCLD approach for the more complex disorder models that are eventually considered. In the VCA limit the SCLD method produces phonon dispersion curves which, except for the finite $\mathbf{k}$ -mesh, are identical to those calculated from a unit cell of the average structure [Fig. 5.2(a)]. The difference in resolution between the two methods is a direct consequence of the size of the supercell employed in the SCLD calculations, as demonstrated previously in Ref. [287]. For this particular interaction model, the phonon spectrum contains a single gap, which covers phonon frequencies between *ca.* 700 and 750 cm^{-1} . This gap in phonon energies occurs between two sets of modes: (i) the higher energy vibrations, in which motion of the A/B hybrid atom is parallel to the $M-A/B-M$ vector—i.e. longitudinal motion; (ii) the lower energy vibrations, where the motion of the A/B hybrid atom is perpendicular to the $M-A/B-M$ vector—i.e. transverse motion.

The phonon dispersion relations for each of the RND, $\mathbf{C}_3\mathbf{M}$, and $\mathbf{C}_3\mathbf{F}$ models are shown in Figure 5.2(b-d). Firstly, the similarities and differences between the RND and VCA models are discussed, since neither one of these simple models takes into

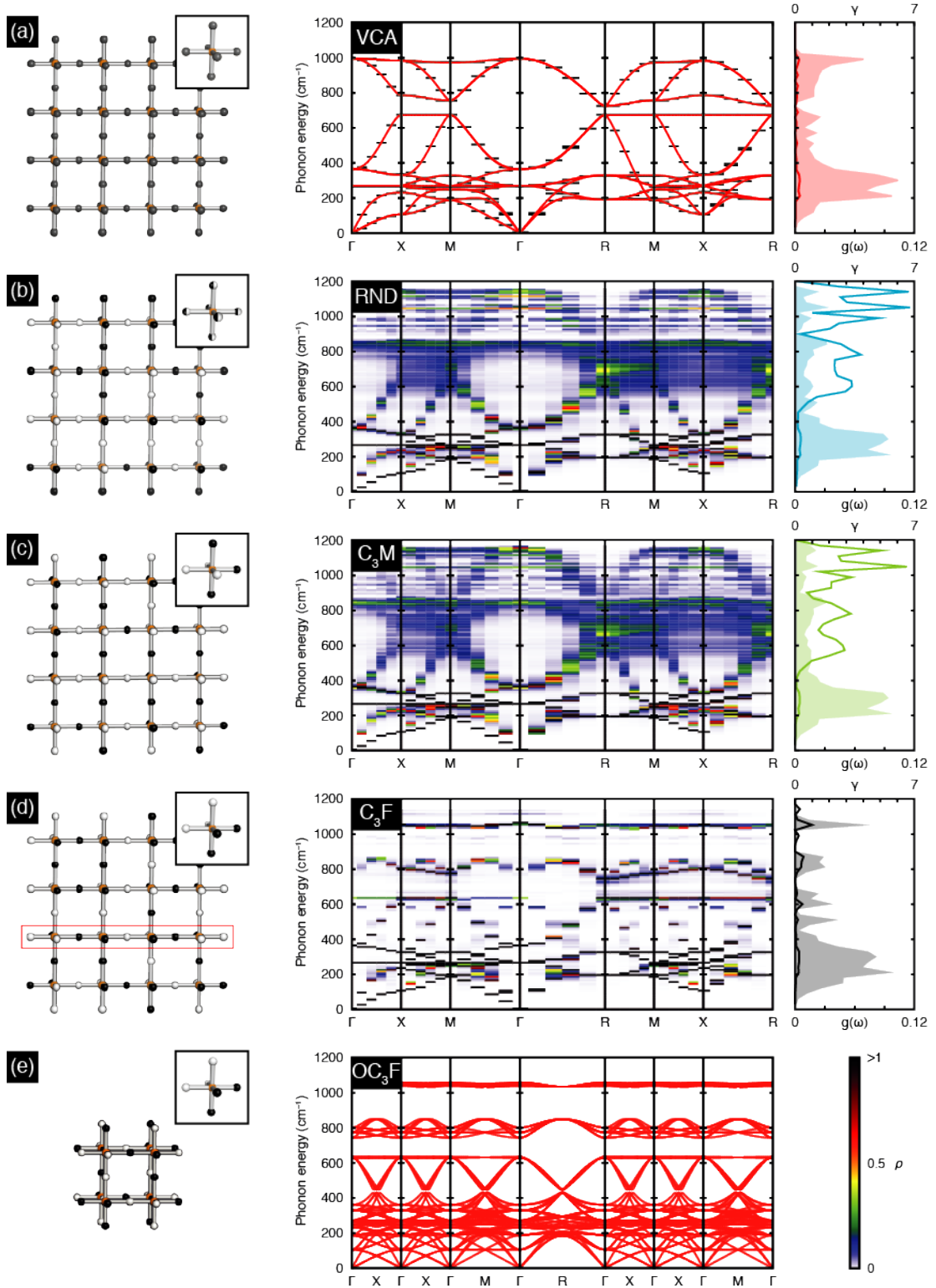


Figure 5.2: The impact of disorder on phonon spectra on the ReO_3 net. In descending order, representative local and planar depictions (left) of the (a) virtual-crystal approximant [VCA], (b) random disorder [RND], (c) locally meridional [C_3M], (d) locally facial [C_3F] and (e) ordered locally facial [OC_3F] models employed in this study. The phonon spectra (right)—presented as red lines and coloured bars (see bottom-right for details) in conventional and SCLD simulations respectively—and phonon density of states (right - shaded area) are shown alongside the localisation γ (right - bold lines). These reveal the presence of two phononic band gaps only in the C_3F case, associated with delocalised modes—*i.e.* low γ .

account any correlations in A/B site disorder. An obvious difference between the two is that the projections, ρ , do not assume integer values for the SCLD calculations; indeed it is this property that allows any intrinsic disorder-driven phonon broadening to be observed. At low frequencies, both RND and VCA models give very similar phonon frequencies and dispersions: the extent of phonon broadening in the RND model is low in this regime, since low energy modes tend not to involve the stretching of bonds. At high frequencies, however, where many of the phonon branches are associated with bond-stretching vibrations, two key differences emerge. First, the highest-frequency bands of the VCA phonon dispersion ($\sim 800\text{--}1000\text{ cm}^{-1}$) are split into two components: one spanning the frequency range $600\text{--}850\text{ cm}^{-1}$, and the other spanning the range $\sim 850\text{--}1150\text{ cm}^{-1}$. Inspection of the individual eigenvectors shows these to be associated with stretching of the weaker $M\text{--}B$ and stronger $M\text{--}A$ bonds, respectively. The second difference is the broadening of phonon branches in k -space for frequencies above 600 cm^{-1} , which is strongly reminiscent of the behaviour noted in Refs. [252, 287] and reflects severe mode localisation.

This type of comparison—between VCA and explicit models of random disorder—has been carried out previously for a number of different systems and under various guises; these results are entirely consistent with these earlier studies [362, 363]. The key point is that random bond disorder broadens the phonon dispersion and has the greatest impact at high frequencies [287].

Perhaps unexpectedly, the $\mathbf{C}_3\mathbf{M}$ model gives rise to a phonon spectrum that is remarkably similar to the random case. These two models are profoundly different in real-space: each M atom in the $\mathbf{C}_3\mathbf{M}$ model finds itself in the same local bonding arrangement, whereas there are a total of 10 chemically-distinct local environments in the RND model. And yet, in the phonon spectra, the excitations of the two systems are essentially indistinguishable: the same partitioning of the $M\text{--}A$ and $M\text{--}B$ stretches are found, together with the same phonon broadening. At face value, this similarity in dynamical behaviour might be attributed to the disordered

nature of the arrangements of A and B atoms upon the periodic sites in both RND and $\mathbf{C}_3\mathbf{M}$ models.

For the high frequency domain of the phonon spectrum, the behaviour of the $\mathbf{C}_3\mathbf{F}$ model is fundamentally different to that of either RND or $\mathbf{C}_3\mathbf{M}$ cases in a number of important ways. First, there is remarkably little intrinsic phonon broadening in the $\mathbf{C}_3\mathbf{F}$ case. Second, the primary distinction from the VCA phonon spectrum is a perceived mirroring of the dispersion such that the zone corners behave as if they were new zone boundaries. This leads to features that resemble the anti-crossing behaviour of the two $M-A$ and $M-B$ stretching phonon bands observed in the ordered variant of the $\mathbf{C}_3\mathbf{F}$ model [Fig. 5.2(e)] and the opening of a phonon gap between 900 and 1050 cm^{-1} . Third, analysis of the associated eigenvectors reveals that the gap-edge states involve contributions from both A and B atom displacements, rather than partitioning into separate $M-A$ and $M-B$ stretching modes. This observation points to collective behaviour, rather than mode localisation. Hence, certain types of local order (*i.e.* $\mathbf{C}_3\mathbf{F}$ *vs* $\mathbf{C}_3\mathbf{M}$) can lead to substantial differences in the phonon spectrum—both relative to the virtual-crystal approximant (VCA) and to that of random disorder (RND).

Importantly, this contrast in vibrational behaviour is evident not only in the full phonon dispersion spectrum but also in the phononic DOS functions, which are more straightforwardly probed in, for instance, inelastic neutron scattering (INS) measurements of polycrystalline samples [30]. The phononic DOS was calculated for each of the four models; the resulting functions are shown as shaded regions in Figure 5.2. In comparing models in the same order as above, the RND spectrum is qualitatively similar to that of the virtual-crystal approximant, but with broadening of the high-frequency features and filling of the 700–750 cm^{-1} gap. The phononic DOS functions for $\mathbf{C}_3\mathbf{M}$ and RND models are essentially indistinguishable. By contrast, the $\mathbf{C}_3\mathbf{F}$ model has a unique density of states that is characteristic of its particular form of local bond order. The new 900–1050 cm^{-1} gap is especially

obvious; correspondingly, it is argued that this feature should aid the identification of $\mathbf{C}_3\mathbf{F}$ -type local order from the other models even in the absence of conclusive evidence from elastic scattering measurements. There is scope even for discriminating sensitivity with infrared and/or Raman spectroscopy, given that the zone-centre mode frequencies and broadening are different for the $\mathbf{C}_3\mathbf{F}$ model, on the one hand, and the $\mathbf{C}_3\mathbf{M}$ /RND models, on the other hand—in particular, the presence of a signature Γ -point excitation at 625 cm^{-1} for $\mathbf{C}_3\mathbf{F}$ that is absent in all other models.

But what is the origin of this varied vibrational behaviour? The greatest differences are clearly in the high-frequency region of the phonon spectrum, which is associated with M - A and M - B stretching deformations. Stretches of this type affect bond distances within individual chains $-(A/B)-M-(A/B)-M-$ but one peculiarity of the ReO_3 structure is that, within the harmonic approximation, longitudinal displacements of neighbouring chains are effectively decoupled. Consequently, the extent of phonon broadening within this regime might be expected to depend only on the degree of bond order within individual chains rather than the presence or otherwise of 3D long-range order. This is precisely the distinction between the $\mathbf{C}_3\mathbf{F}$ and $\mathbf{C}_3\mathbf{M}$ /RND models: it is only in former case that individual chains are ordered, with strictly-alternating $-A-M-B-M-$ bonds.

The data presented in Figure 5.2(d),(e) also allow the phonon dispersion behaviour of disordered and ordered variants of the $\mathbf{C}_3\mathbf{F}$ model ($\mathbf{OC}_3\mathbf{F}$) to be compared. Here the ordered state corresponds to in-phase decoration of neighbouring $-A-M-B-M-$ chains along all three crystal axes, which gives a periodic structure with volume eight times larger than that of the parent ReO_3 structure (*i.e.* $2 \times 2 \times 2$ supercell). This cell-doubling in real-space means that the Brillouin zone corners for the parent cell correspond to zone centres for the ordered daughter cell. Hence, the phonon dispersion is folded along high-symmetry directions, precisely as observed for the high-frequency component of the disordered $\mathbf{C}_3\mathbf{F}$ phonon spectrum. It is this band folding, together with the feature that resemble the anti-crossing of symmetry-

related branches, that results in the opening of new phononic gaps. In this way, the phonon spectrum of the $\mathbf{C}_3\mathbf{F}$ model [Fig. 5.2(d)] can be related to that of the VCA model at low frequencies [Fig. 5.2(a)], and the $\mathbf{OC}_3\mathbf{F}$ (ordered $\mathbf{C}_3\mathbf{F}$) model at high frequencies [Fig. 5.2(e)]. Preliminary results have also found that an analogous effect occurs in systems with strongly-correlated mass disorder—*i.e.* where A and B atoms with different masses, rather than bond strengths, are included within the $\mathbf{C}_3\mathbf{F}$ model—except that in such cases the entire phonon spectrum is affected rather than just the high-frequency domain.

The existence or absence of bond order within chains also affects the localisation of the phonon modes. An idea has already been flagged within this thesis that excitations in these systems may, in principle, be localised or collective (phonon-like). This point is demonstrated by calculating the weighted inverse participation ratio, which is able to determine which aspects of the excitation spectrum might be understood in each of these two contexts. The weighted inverse participation ratio, $\gamma(\omega)$, for the phononic DOS of each of the four models is similar to the inverse participation ratios which have been calculated for electronic states [314]:

$$\gamma(\omega) = g(\omega) \langle \sigma^{-1} \rangle, \quad (5.9)$$

where the average is taken over all phonon branches ν for modes with frequency ω (the same $\Delta\omega$ bin-width of 30 cm^{-1} used in the phononic DOS calculations). The participation ratio $\sigma(\nu)$ for each such mode is given as [262, 345]:

$$\sigma(\nu) = \frac{\langle |u_{jl}(\nu)|^2 \rangle^2}{\langle |u_{jl}(\nu)|^4 \rangle}, \quad (5.10)$$

where $u_{jl}(\nu)$ is the displacement amplitude of atom j in unit cell l for the phonon mode labelled by ν . Collective modes are characterised by the participation ratio $\sigma = 1$, giving the minimum value of $\gamma = g(\omega)$, whereas for localised modes $\sigma \rightarrow 0$, resulting in $\gamma \gg g(\omega)$. Hence, $\gamma(\omega)$ can be interpreted as the number of

localised modes with frequencies close to ω . The functions of $\gamma(\omega)$ for all four of the models are shown in Figure 5.2. Strong phonon localisation is evident at high frequencies in both RND and $\mathbf{C}_3\mathbf{M}$ models, whereas localisation is weak for both $\mathbf{C}_3\mathbf{F}$ and VCA models. This observation is consistent with the understanding that the differences in vibrational behaviour originate from the presence of the distinct features—highlighted in red in Figure 5.1—in the $\mathbf{C}_3\mathbf{F}$ configurations.

One key conclusion of this study is the potential—in favourable cases—for phonon density of states measurements to identify unambiguously the presence of a particular form of strongly-correlated disorder. It is expected that this result will be of greatest importance in cases where disorder is associated with the distribution of two or more species for which conventional scattering measurements offer only weak discriminating ability. An important example is the O/N distributions in ‘open order’ oxynitrides, such as the colossal magnetoresistance system $\text{EuWO}_{1.5}\text{N}_{1.5}$ [361]. strongly-correlated bond disorder is also implicated in disordered dimer states (or valence-bond solids) [12], including the spin glass $\text{Y}_2\text{Mo}_2\text{O}_7$ [326], and may even be relevant to the fluctuating trimeron state of magnetite Fe_3O_4 [256]. Yet, this study also highlights an important caveat: namely that certain types of correlated disorder affect lattice dynamics in a manner that is essentially indistinguishable from the random-disorder case. Consequently, the presence of strong local rules in disordered systems does not ensure any substantive effect on vibrational behaviour, even if in some cases its consequences can be very profound.

5.3.2 α -Po decoration

The $\mathbf{C}_3\mathbf{F}$ decoration on the ReO_3 net has been found responsible for the emergence of a gapped state due to the presence alternating bond strengths as shown in Figure 5.1. So, if the gapped state is truly driven by the local ‘building-unit’ geometry, is it possible that analogous $\mathbf{C}_3\mathbf{F}$ decorations on other primitive cubic nets will produce the same effect?

Conveniently, it is possible to simplify the ReO_3 models by considering the α -Po structure type instead. Here, each unit cell contains a single M atom which is directly bonded to its six neighbouring M atoms. As such, rather than the disorder being reflected in the strength of the bonds between each central M atom and its six linking A/B neighbours (as in the ReO_3 structure type), the disorder in the α -Po models lies in the variation of the M - M bond strengths [Fig. 5.3]. In this study, the dynamical behaviour of the α -Po based VCA, RND and C_3F states was determined using the same model generation and SCLD methods detailed previously (Sections 5.2). The GULP parameters employed in this work are summarised in Table 5.2. Here, the ratio of deviation of k_{harm} is equivalent to that of the ReO_3 ; however the absolute values of k_{harm} and k_{L} have been changed to ensure a reasonable separation of the phonon bands, particularly along the M- Γ -R directions.

Each of these models contain a single atom in the parent unit cell which according to lattice dynamical theory, will produce three continuous phonon bands. These bands are clearly visible within the phonon dispersion curves of VCA limit [Fig. 5.3(a)], determined both through lattice dynamical calculations on a unit cell representation and SCLD methods. As expected, the corresponding phonon dispersion for the RND model, where weak and strong M - M bonds are distributed randomly throughout the configuration, reveal strikingly similar band structure to the VCA [Fig. 5.3(b)]. Again, disorder-induced phonon broadening is only apparent in the higher energy

Table 5.2: A summary of the parameter values used in the α -Po lattice dynamical calculations for both the VCA and disordered supercell representations.

Parameter	VCA	RND/ C_3F
$a / \text{\AA}$	20	20
m_M / amu	60	60
$k_{\text{harm}}(M-M, \text{strong}) / \text{eV}\text{\AA}^{-2}$	100	141.4
$k_{\text{harm}}(M-M, \text{weak}) / \text{eV}\text{\AA}^{-2}$	100	70.7
$k_{\text{L}}(M-M-M) / \text{eVrad}^{-2}$	1000	1000
$r_0(M-M) / \text{\AA}$	20	20
$\theta_0(M-M-M) / ^\circ$	90	90

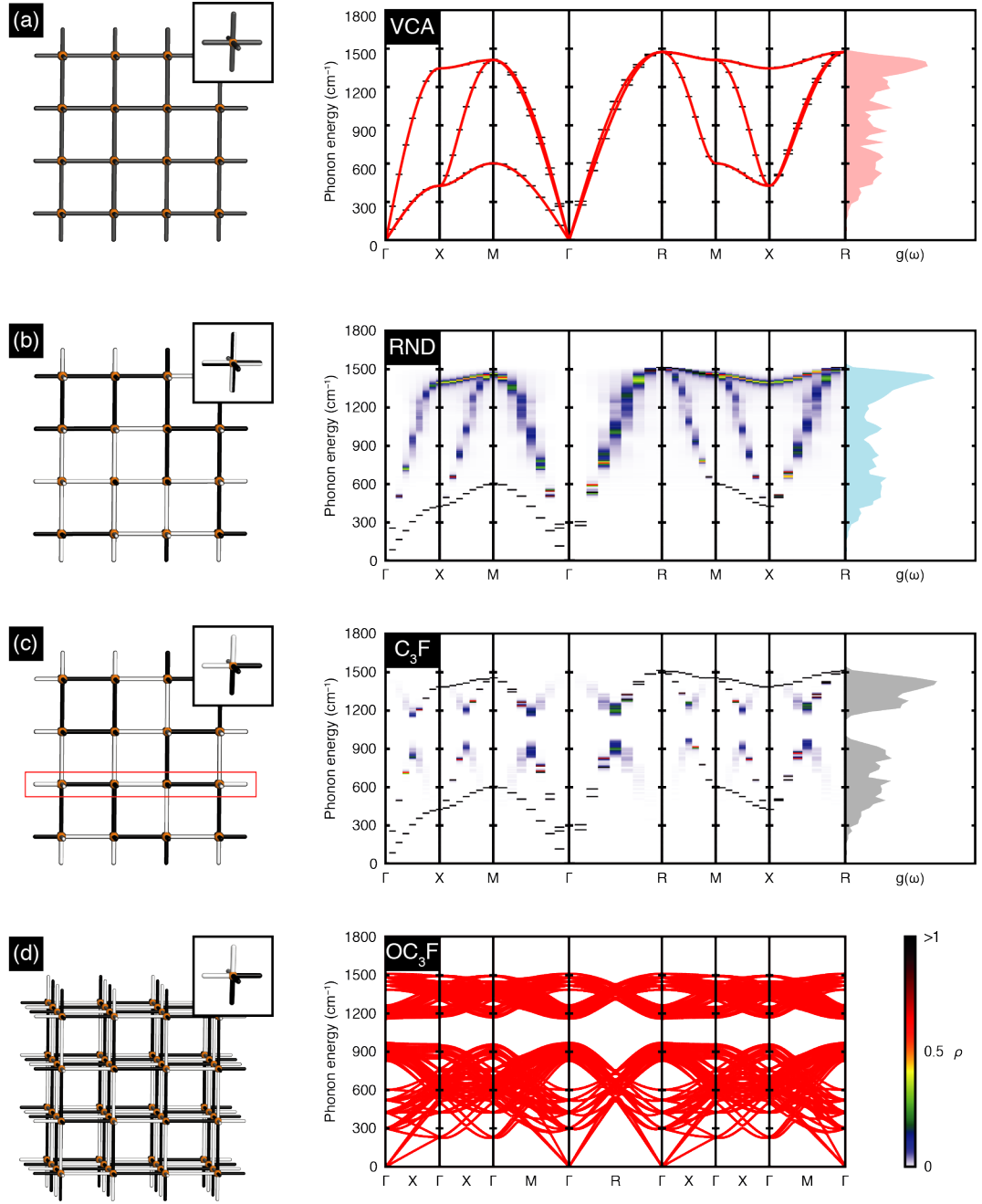


Figure 5.3: The impact of disorder on phonon spectra on the α -Po net. In descending order, representative local and planar depictions (left) of the (a) virtual-crystal approximant [VCA], (b) random disorder [RND], (c) locally facial [C_3F] and (d) $4 \times 4 \times 4$ ordered locally facial [OC_3F] models employed in this study. Within the C_3F configuration long-range correlations are present within 1D chains, highlighted in red. The phonon spectra (middle) is presented as red lines and coloured bars (see bottom-right) in lattice dynamical calculations of a unit cell representation and SCLD simulations, respectively. The associated phonon density of states (right) reveal the presence of an unconventional phononic band gap in the C_3F case, due to a discontinuity in the acoustic modes.

bands where the vibrations correspond to significant bond stretching. However, in this case these effects are heavily damped in comparison to the previous study as the high energy bands do not split into $M-A$ and $M-B$ vibrations, respectively.

Yet, the vibrational behaviour of the $\mathbf{C}_3\mathbf{F}$ model provides a stark contrast to both the VCA and the RND configurations [Fig. 5.3(c)]. The most obvious feature is the appearance of a phononic band gap, analogous to that found in the ReO_3 study. Again this occurs due to the underlying distinct features contained within the system whereby each chain of bonds alternate weak–strong–weak–strong. The subsequent band-folding due to the alternating bond strengths is shown clearly in the phonon dispersion curves of the $4 \times 4 \times 4$ ordered $\mathbf{C}_3\mathbf{F}$ model in Figure 5.3(d). The key result here is that in the $\mathbf{C}_3\mathbf{F}$ case, crystallographic methods would reveal that the average structure contains a single atom (*i.e.* equivalent to the $1 \times 1 \times 1$ cell of the VCA model), yet a gap still emerges in the phonon spectrum. Indeed, in a similar fashion to the ReO_3 models, the phonon spectrum of the $\mathbf{C}_3\mathbf{F}$ model [Fig. 5.3(c)] can be related to both that of the VCA for the low frequency modes [Fig. 5.3(a)] and $\mathbf{OC}_3\mathbf{F}$ (ordered $\mathbf{C}_3\mathbf{F}$) for the high frequency modes [Fig. 5.3(d)].

The observation of a phononic band gap in this system has two important implications. Firstly, it is clear that the arrangement of bond strength disorder in the $\mathbf{C}_3\mathbf{F}$ configuration directly drives the formation of a band gap irrespective of the net onto which it is imprinted. Secondly, the vibrational spectra are substantially different to that of the average structure—*i.e.* a primitive cubic unit cell containing a single atom. Here, any system with a single atom in the unit cell should result in three *continuous* acoustic phonon bands, each of which has a vibrational energy of zero at the Γ point. As such, lattice dynamical theory shows there can be no band-gap in the case of an ordered crystal with a unit cell containing a single atom. Correspondingly, $\mathbf{C}_3\mathbf{F}$ disorder presents different vibrational behaviour, showing a broadened vibrational spectra similar to that of the $4 \times 4 \times 4$ ordered $\mathbf{C}_3\mathbf{F}$ model, while still retaining the single atom in the average unit cell.

5.4 Electronic behaviour

There are strong conceptual parallels between the phononic band structures of solids and their electronic and photonic counterparts. In each case, conventional band structure calculations are derived from Bloch wave approaches, where the energy of certain states are determined with respect to a given wave-vector within the first Brillouin zone. Therefore, the study of the vibrational behaviour detailed in Section 5.3 implies that analogous systems with $\mathbf{C}_3\mathbf{F}$ -type disorder might exhibit electronic and photonic band gaps.

In this study, the electronic density of states were determined through density functional theory (DFT) calculations within the ABINIT software package [364] performed by Dr Carl Romao. The projector augmented wave (PAW) method [?] and local density approximation (LDA) exchange-correlations [?] were used in this study to improve computational efficiency. The local density approximation is the simplest exchange-correlation, but it is commonly used for calculations in solids because of its low computational cost and reasonable accuracy. This method tends to overbind, *i.e.* bond energies are predicted as being higher than experimental values; however, this error tends to be systematic and predictable. In each simulation, the cell parameters were initially relaxed with the atomic positions remaining fixed, using an $85 \text{ \AA}^{-1}$ spacing for the $\mathbf{k}$ -point mesh, and a 24 Ha cutoff. The subsequent calculation of the electronic density of states was established using a $20 \times 20 \times 20$ $\mathbf{k}$ -point grid. The convergence criteria for these simulations consisted of a tolerance of 1 part in 10^{10} in the residual of the potential for the self-consistent minimisation and 1 part in 10^7 in the stresses for the structural relaxation.

Here, an average structure pertaining to a simple cubic array of bismuth atoms was considered. This proof of concept study was performed on $2 \times 2 \times 2$ supercells, *i.e.* containing eight bismuth atoms. Bismuth was specifically chosen for two reasons: (i) each of the valence p -orbitals contains a single electron, so each atom can potentially

form a single σ -like bond along each of the cartesian axes; (ii) of the elements in group XV, bismuth has the largest valence p -orbitals, enabling maximum overlap, and so the largest effect on the electronic states.

Only two disorder models—VCA and $\mathbf{C}_3\mathbf{F}$ —were considered in this study, due to the difficulty in evaluating the electronic band structure of large supercells. As before, the VCA configuration was equivalent to the average structure—a simple cubic array of Bi atoms with a lattice parameter of 3.227 Å. A corresponding $\mathbf{C}_3\mathbf{F}$ model was constructed through the use of a $2 \times 2 \times 2$ supercell. Here, each of the Bi atoms was statically displaced in a $\langle 111 \rangle$ direction by 0.0358 Å. In relation to the $\mathbf{C}_3\mathbf{F}$ α -Po phonon model shown in Figure 5.3, each M/Bi atom is moved toward their neighbouring black bonds and therefore away from their white bonds. In this way, every Bi atom was situated closer to three of their six neighbours, effectively forming the alternating dimers along each chain highlighted in the $\mathbf{C}_3\mathbf{F}$ model in Figure 5.3.

The DFT calculations began with an initial relaxation of the unit cell parameters of each structure with the atomic positions fixed, details of which can be found in Appendix C. Subsequently, the electronic density of states were determined by establishing the energy of each electronic state on a $20 \times 20 \times 20$ k-point mesh. Here, the VCA configuration was found to exhibit a metallic state—*i.e.* a large density of states at the Fermi level—while the corresponding electronic density of states in the $\mathbf{C}_3\mathbf{F}$ model was markedly reduced, approaching semi-metal behaviour [Fig. 5.4]. Indeed, the beginnings of a gapped state in the $\mathbf{C}_3\mathbf{F}$ configuration is strongly reminiscent of a Peierls instability [86, 365], although in this case there is no long-range symmetry breaking. The implication for electronic states of conceptually related systems is that Peierls-type transitions may also be allowed to occur without any symmetry breaking, resulting instead in a disordered valence bond solid with a finite gap at the Fermi level.

5.5 Photonic behaviour

The effect of C_3F disorder on the photonic behaviour was explored through the supercell calculation approach using the MIT photonic bands (MPB) package [32, 251]. The supercell photonic band (SPB) method is similar to the SCLD approach described earlier; the photonic band frequencies are determined at the Γ point for a large supercell, allowing easy determination of the photonic DOS. Due to the proof of concept nature of this study, these investigations were constrained to two-dimensional structural analogues of the VCA, RND and C_3F models. Unfortunately, there is no direct two-dimensional analogue of C_3M type disorder; however a suit-

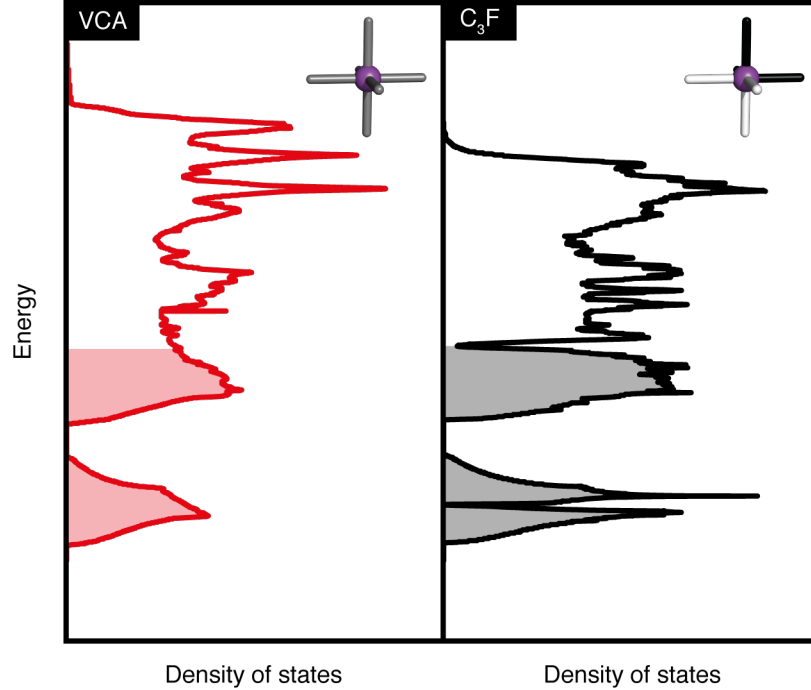


Figure 5.4: The effect of disorder on the energy of electronic states. The electronic density of states for a virtual-crystal approximant [VCA] (left) and locally facial decoration [C_3F] were determined using density functional theory calculations. The VCA structure consists of a $1 \times 1 \times 1$ cell of bismuth atoms in a primitive cubic array whereas the C_3F model is constructed upon a $2 \times 2 \times 2$ supercell with small displacements along the $\langle 111 \rangle$ directions—*i.e.* toward the black bonds. The subsequent simulations reveal a marked reduction in the electronic density of states at the Fermi level for the C_3F configuration. This effect is conceptually similar to a Peierls distortion both in terms of the effect on the crystal structure through chains of alternating dimers and in the opening of an electronic band gap.

able model is possible for $\mathbf{C}_3\mathbf{F}$ disorder—due to presence of the distinct features—in the form of the $\mathbf{S}_2\mathbf{C}$ procrySTALLINE state [Fig. 3.4(b)]. The unit cell in each of the structures consists of three fragment types with dielectric constants, ϵ_r , summarised in Table 5.3 [Fig. 5.5]:

A : one $0.64a \times 0.64a$ square with $\epsilon_r = \epsilon_1$.

B : four $0.18a \times 0.18a$ squares with $\epsilon_r = \epsilon_2$.

C : four $0.18a \times 0.64a$ oblongs with variable dielectric constants.

In the average photonic structure (VCA) the dielectric constant for fragment C is set as the intermediate value, ϵ_3 , whereas in the RND and $\mathbf{S}_2\mathbf{C}$ models the dielectric constant of C can only take one of two values, ϵ_1 or ϵ_2 . In the RND structure, as with the phononic models, there is no correlation to the dielectric value taken; however, there must be an equal number of $C(\epsilon_1)$ and $C(\epsilon_2)$ over the entire supercell. Contrastingly, the $\mathbf{S}_2\mathbf{C}$ model strictly contains unit cells with two $C(\epsilon_1)$ and two $C(\epsilon_2)$. The fragments with the same dielectric constants must be situated in a cis arrangement, and furthermore across neighbouring unit-cells, no two adjacent C may share the same value of ϵ_r . In this way, two-dimensional disorder correlations analogous to those in the $\mathbf{C}_3\mathbf{F}$ structure are observed, which includes the distinct alternating features along all rows and columns.

Here, 20×20 supercells were constructed for each of the models and their photonic DOS determined for the transverse-electric modes using the parameters summarised

Table 5.3: A summary of the parameter values employed within the photonic simulations in Section 5.5.

Parameter	VCA	RND/ $\mathbf{C}_3\mathbf{F}$
ϵ_1	1	1
ϵ_2	10	10
ϵ_3	5.5	—
d_1 / a	0.18	0.18
d_2 / a	0.64	0.64
MPB Resolution	16	16

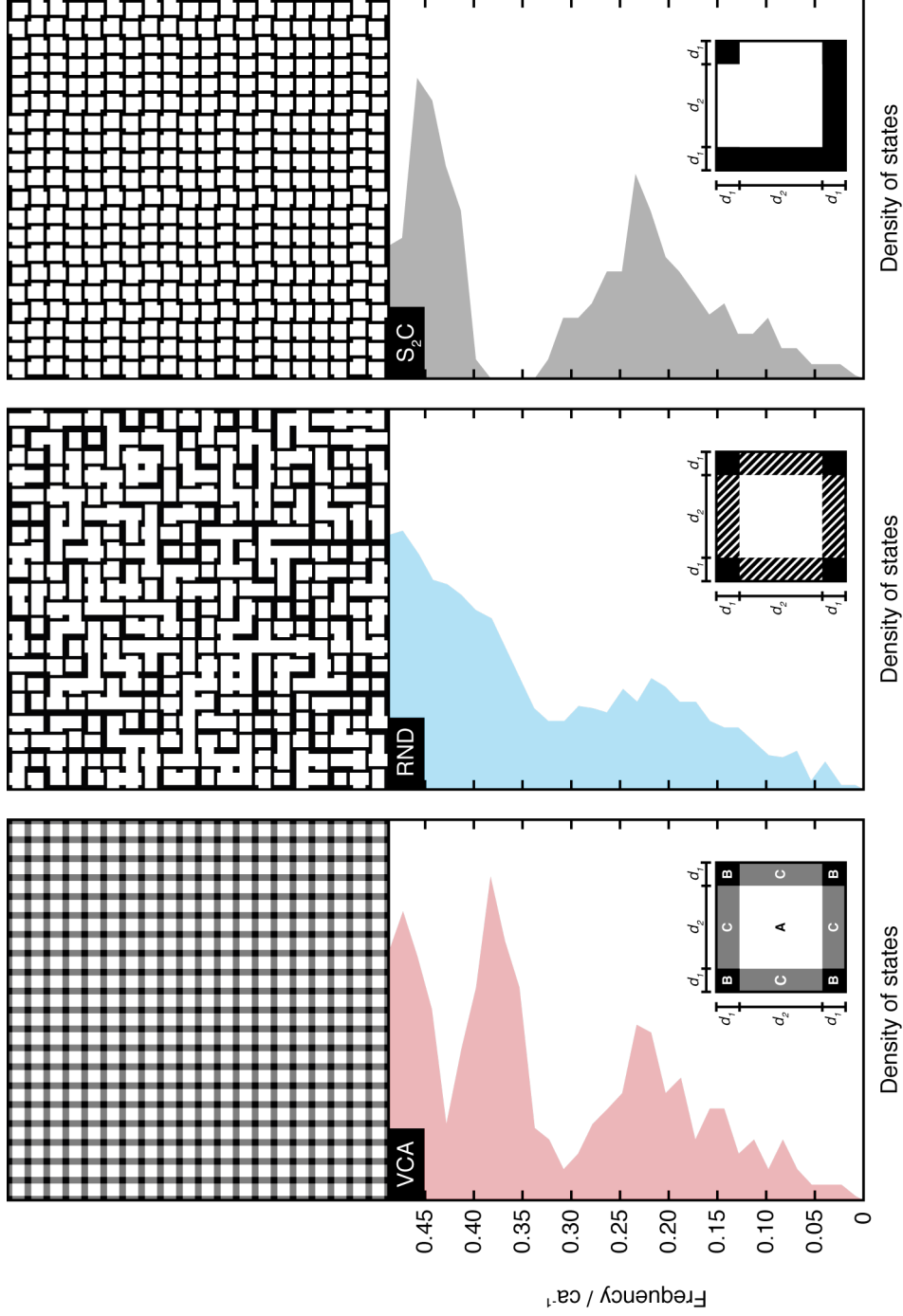


Figure 5.5: The effect of disorder on photonic behaviour. A representation of photonic crystals (top) for the average [VCA] (left), random [RND] (middle), and correlated disordered structures [S₂C] (right). Here, the structures are made from materials of with three different dielectric constants: low (ϵ_1) shown in white, high (ϵ_2) in black and intermediate (ϵ_3) in grey. The unit-cell building block for each model is shown (bottom-right), alongside the associated photonic density of states, calculated using the MPB package, (bottom) which reveals a photonic gap only in the case of correlated disorder. The mode frequencies are given in units of ca^{-1} —i.e. the speed of light, c , multiplied by the inverse unit cell length, a^{-1} .

in Table 5.3. When plotting the photonic DOS, bin-width of $0.015\text{ }ca^{-1}$ were used, where the units ca^{-1} refer to the speed of light, c , multiplied by the inverse unit cell length, a^{-1} . The principal result here reveals the existence of a photonic band gap ($0.34\text{--}0.38\text{ }ca^{-1}$) between the first and second lowest frequency bands in the structure containing correlated disorder ($\mathbf{S}_2\mathbf{C}$). By contrast, both the VCA and RND configurations display continuous band structures [Fig. 5.5]. Currently, there is strong interest in the microscopic origin of gapped spectra in states with complex forms of order and disorder, including hyperuniform systems [216, 217, 263], continuous random networks [366, 367], and quasicrystals [220, 368]. As such, the emergence of a photonic gapped state in the $\mathbf{S}_2\mathbf{C}$ model is of considerable importance. Much of the interest in the field is centred on the potential for designing wave-guides or materials with structural colour [369, 370], and also on the interpretation of meso-scale structures observed in nature [371, 372]. These results add to this discussion in two respects: on the one hand, a new type of complex order (the procrySTALLine state) is identified for the design of gapped photonic metamaterials, and on the other hand it is shown that strong local order is not by itself a sufficient condition for gap formation. Instead there appears to be a complex relationship between the type of correlated disorder and structure of the photonic bands that will surely reward further research.

5.6 Dimer decorations

In the knowledge that $\mathbf{C}_3\mathbf{F}$ disorder and its two-dimensional analogue, $\mathbf{S}_2\mathbf{C}$, drive the formation of gapped states, is it possible that other procrySTALLine phases might display the same behaviour? Obviously this effect cannot be true for all procrySTALLine systems, as it has already been shown that a decoration of $\mathbf{C}_3\mathbf{M}$ disorder replicates the ungapped behaviour of a random disorder decoration. Indeed, the phononic gapped behaviour exhibited by the $\mathbf{C}_3\mathbf{F}$ model was attributed to the features of alternating bond strengths. This feature is not present in any of the re-

maintaining procrystalline decorations of the primitive cubic or square nets, so it might be surmised that none of these systems can also present gapped behaviour.

In this section, a preliminary study of phononic and photonic behaviour of the $\mathbf{C}_1$ and $\mathbf{S}_1$ procrystalline states is presented [Fig. 3.4(a),(l)]. Of the remaining square and primitive cubic configurations, these arguably represent the most physically relevant procrystalline phases, as they are equivalent to a dense decoration of dimers described in Section 1.2.2. As such, they map onto well-established systems, including resonant valence bond states and polyhedral tilings. Indeed, one might anticipate that the $\mathbf{C}_1$ dimer decorations will produce dissimilar phononic behaviour to that of $\mathbf{C}_3\mathbf{F}$ and $\mathbf{C}_3\mathbf{M}$, simply because, in contrast to the previous study in Section 5.3, dimers are isolated structural features which will likely disrupt the collective vibrational states in a different manner.

5.6.1 Vibrational behaviour

So what of the phonon band structure? Here, the SCLD method was again employed to determine the phonon dispersion curves of a $10 \times 10 \times 10$ supercell of a $\mathbf{C}_1$ procrystalline decoration of bond strength disorder upon the α -Po net. In this case, each M atom was defined to be strongly bound to only one of its six neighbours, meaning that the corresponding VCA model would contain weaker bonds than that shown in Figure 5.3. However, the overall form of the VCA phonon dispersion will be qualitatively similar, in keeping with the vibrational behaviour of the alkali metals/noble solids discussed in Section 1.1.2. Initially, the GULP parameters were chosen to be equivalent to that of the RND/ $\mathbf{C}_3\mathbf{F}$ [Small Δk_{harm} , Table 5.4] such that a direct comparison can be made with the $\mathbf{C}_3\mathbf{F}$ phonon dispersion curves presented in Figure 5.3.

The corresponding vibrational spectra of the $\mathbf{C}_1$ state reveal a splitting of the highest energy modes along the $\text{R} \rightarrow \text{M} \rightarrow \text{X} \rightarrow \text{R}$ directions [Fig. 5.6(a)]. The two split bands share similar phonon dispersion behaviour, in contrast to the analogous $\mathbf{C}_3\mathbf{F}$

case. In this case, a complete phononic band gap is not observed—the two sets of high energy modes are extremely close in energy, and so with the additional effects of phonon broadening, they overlap. Unsurprisingly, the gap between the two bands is related to the contrast between the strong and weak $M-M$ bonds. Therefore, a secondary study was conducted with exactly the same disorder decoration, but with the stiff $M-M$ bond strength altered from 141.4 to 246.5 eVÅ⁻² to cause a larger change in the vibrational behaviour and an average bond strength in accordance with that of the VCA in Figure 5.3 [Large Δk_{harm} , Table 5.4]. The corresponding phonon dispersion curves and DOS show a large, complete phononic band gap centred around 1400 cm⁻¹ [Fig. 5.6(b)]. Here, the higher energy of the two bands has been shifted to higher frequency as it is associated with the bond stretching of the stiff $M-M$ bonds. Yet, the remainder of the phonon dispersion curves remain relatively undisturbed in comparison as these are derived from the much more prevalent weak $M-M$ bond strengths. Consequently, the value of k_{harm} for the strong $M-M$ bonds is an effective means of tuning the size of the unconventional band gap in a system with a single atom in the average unit cell.

5.6.2 Photonic behaviour

In this preliminary study, the photonic behaviour of the dimer state has also been investigated to determine whether the presence of a band gap in the dimer state is

Table 5.4: A summary of the parameter values employed within the dynamical simulations of the dimer state.

Parameter	Small Δk_{harm}	Large Δk_{harm}
a / Å	20	20
m_M / amu	60	60
$k_{\text{harm}}(M-M, \text{strong})$ / eVÅ ⁻²	141.4	246.5
$k_{\text{harm}}(M-M, \text{weak})$ / eVÅ ⁻²	70.7	70.7
$k_{\text{L}}(M-M-M)$ / eVrad ⁻²	1000	1000
$r_0(M-M)$ / Å	20	20
$\theta_0(M-M-M)$ / °	90	90

also a generalisable phenomenon. Again, unfortunately, photonic calculations for the large three-dimensional supercells of the $\mathbf{C}_1$ state are too computationally expensive. As such, an analogous two-dimensional photonic structure was constructed, which contained dimers on the square lattice—*i.e.* the $\mathbf{S}_1$ procristalline state. Here, the photonic crystal was made from a single building unit with three fragments [Fig. 5.5]:

A : one $0.74a \times 0.74a$ square with $\epsilon_r = \epsilon_1$.

B : four $0.13a \times 0.13a$ squares with $\epsilon_r = \epsilon_2$.

C : four $0.13a \times 0.74a$ oblongs with variable dielectric constants.

Within each building unit, three C fragments are assigned $\epsilon = \epsilon_2$ with the fourth

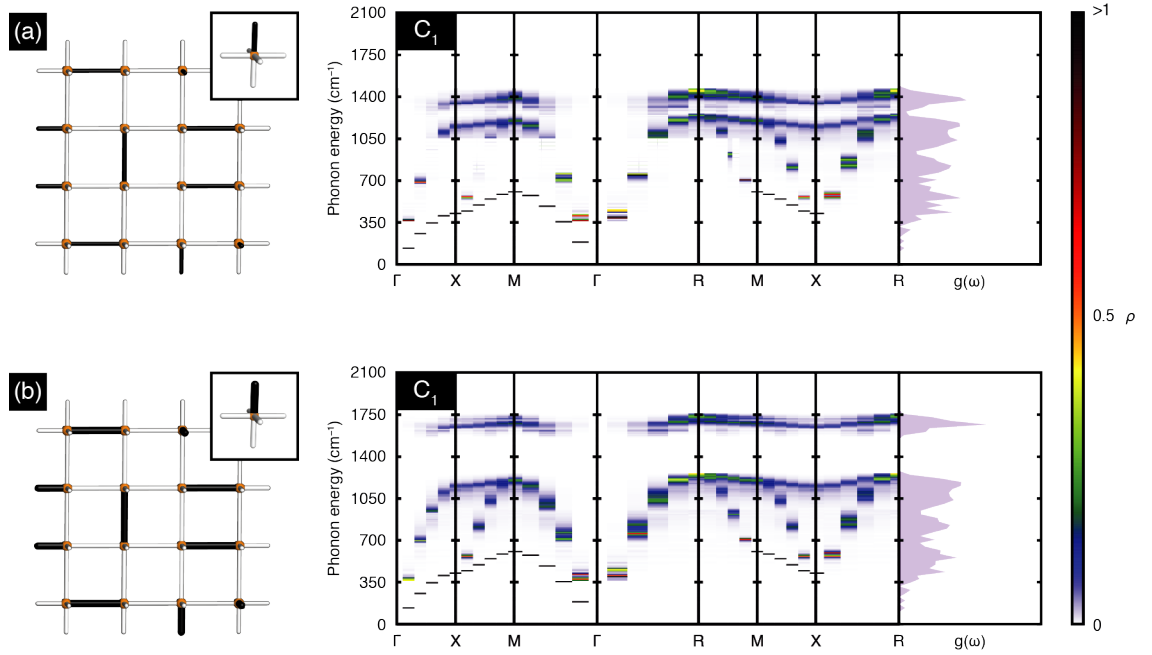


Figure 5.6: The effect of $\mathbf{C}_1$ bond strength disorder on the phonon spectra of the α -Po net. Representations of $\mathbf{C}_1$ bond strength disorder on the α -Po net are shown on the left, where each M atom (orange) is bonded to its neighbours with five ‘weak’ and one ‘strong’ bond. The two sets of phonon dispersion curves and densities of states correspond to different variations in the bond strengths: (a) k_{harm} (black) = $141.41 \text{ eV } \text{\AA}^{-2}$, k_{harm} (white) = $70.7 \text{ eV } \text{\AA}^{-2}$ and (b) k_{harm} (black) = $246.45 \text{ eV } \text{\AA}^{-2}$, k_{harm} (white) = $70.7 \text{ eV } \text{\AA}^{-2}$. While the smaller deviation in bond strength in (a) results in the splitting of the high frequency phonon bands, no band gap emerges, whereas the larger variation in (b) produces a phononic band gap centred about 1400 cm^{-1} as evident in the phonon dispersion curves and associated density of states (right).

fragment being comprised of a material with $\epsilon = \epsilon_1$, to form a domino-like tiling. This particular building unit was chosen such that the ratio of the areas of the two dielectric materials, ϵ_1 and ϵ_2 , remained consistent with that of the photonic crystals in Section 5.5. However, the contrast in the dielectric constant of the two materials was increased to accentuate the effect of $\mathbf{S}_1$ disorder on the photonic properties of the crystal. These parameters, along with other details of the MPB simulations, are summarised in Table 5.5.

The subsequent calculation of the photonic density of states of a 20×20 supercell of the $\mathbf{S}_1$ state reveals a band gap centred around $0.20 \text{ } ca^{-1}$ [Fig. 5.7]. Consequently, this further strengthens the assertion that procrySTALLinity may be used as a feature in the design of wave-guides with isotropic band gaps, the same functional materials targeted in the complementary study of hyperuniform photonic structures [216, 217].

Given the preliminary status of this study, the origin of the gapped states in the $\mathbf{C}_1$ and $\mathbf{S}_1$ decorations is yet to be fully understood. Nevertheless, it is anticipated these effects may be caused by the localised nature of the individual dimers. This assertion is supported by the vibrational behaviour where the strong $M-M$ bonds produce a fairly dispersionless set of high energy modes. Overall, this study reinforces the previous conclusions of this chapter that procrySTALLINE disorder can be used to cause a generalisable impact on the band structure of materials—*i.e.* both the phononic and photonic states. Moreover, this work also reveals that the presence of band gaps in procrySTALLINE phases is not dependent on the presence of the distinct features

Table 5.5: A summary of the parameter values used in the MPB simulations to determine the photonic states of the $\mathbf{S}_1$ arrangement of dielectric media.

Parameter	$\mathbf{S}_1$
ϵ_1	1
ϵ_2	20
d_1 / a	0.13
d_2 / a	0.74
MPB Resolution	16

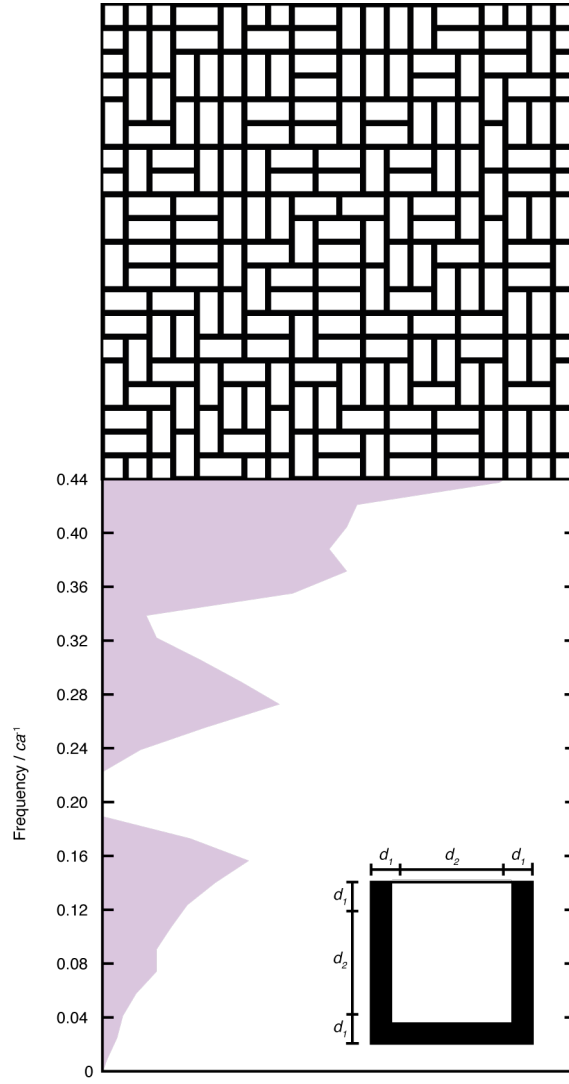


Figure 5.7: The optical properties of a photonic crystal containing dimer disorder. A model representation of the S_1 photonic crystal (top) is constructed from materials with two different dielectric constants: low (ϵ_1) shown in white, high (ϵ_2) in black. The unit-cell building block for each model is shown (bottom-right), with the associated photonic density of states (bottom) which reveals a photonic band gap centred around $0.20 \text{ } ca^{-1}$.

shown in Figure 5.1, and so crucially is not limited to the $\mathbf{C}_3\mathbf{F}$ and $\mathbf{S}_2\mathbf{C}$ states.

5.7 Discussion

The work in this chapter has demonstrated that the peculiar gapped behaviour of the correlated disorder models is a direct consequence of particular types of procrystalline disorder. In the phononic studies, the $\mathbf{C}_3\mathbf{F}$ and $\mathbf{C}_1$ states have been shown to display a mixture of localised and extensive vibrational behaviour and, in the case of the $\mathbf{C}_3\mathbf{F}$ state, features that resemble anti-crossing behaviour of ordered variants. As such, this raises the interesting point of the interplay between disorder and apparent preservation of symmetry relationships in their dynamical behaviour.

Furthermore, these studies have demonstrated that strongly-correlated disorder is an important consideration in understanding the collective properties of materials. This is particularly clear in the determination of the electronic properties where the consideration of procrystalline disorder has been shown to alter the electronic density of states. Oftentimes a mismatch in the experimental and simulated electronic properties of the average structure is attributed to electron localisation such as in Mott-Hubbard insulators [373, 374]. Yet, these results suggest that atomic displacements in a strongly-correlated manner may also be responsible for a similar effect. Furthermore, this work also suggests that functional procrystalline systems may be easily achievable. The simulated optical properties shown to exist for procrystalline arrangements of dielectric media may be exploited across multiple length scales, with well-established lithographic methods or 3D printing providing routes for the manipulation of visible light and microwaves respectively.

Chapter 6

Extreme mechanical responses in disordered fibre entanglements

The existence of strongly-correlated disorder has been shown to have a significant effect on the vibrational, electronic and photonic properties of materials. However, the relationship between the degree of disorder and the corresponding physical behaviour remains an open and important question. In this work, the mechanical properties associated with packings of one-dimensional fibres are of interest, specifically their swelling capacities. Previous work has shown that the swelling capacity is linked to the arrangement of fibres, with some ordered packings unable to swell and others displaying extreme responses. However, to date, the underlying cause of the complex relationship between structure and swelling is not well-understood. So here a simple question is asked: what effect can topological disorder, such as an entangling of the fibres, have on the subsequent swelling response?

The arrangement of one-dimensional (1D) objects in three-dimensional (3D) space is a non-trivial problem of relevance to a wide variety of both naturally occurring and synthetic materials including carbohydrates [375], synthetic polymers [376], deoxyribonucleic acid (DNA) [377], ribonucleic acid (RNA) [378], carbon nanotubes [379, 380], biomaterials [381–383], liquid crystals [384, 385], skymion magnets [386], metal-organic framework materials [387], superconductors [388] and lipid assemblies [389]. The topological diversity of these structures is of particular interest as it has direct implications on their physical characteristics including phase behaviour and mechanical properties.

This chapter is focussed on the work published in “Extreme cooperative swelling in topologically disordered fibre entanglements” [390], beginning with an enumeration

of the ordered packings of one-dimensional cylinders and their relation to structures in crystallography. It is followed by a discussion of the swelling capacity of such structures, including a summary of the previous methods used to determine the magnitude of this mechanical response. The approaches used in this study are then detailed including the process of generating quantifiable disordered topologies of one-dimensional objects and the procedures employed to determine their swelling capacities. Finally, the swelling behaviour of disordered entanglements is reported along with a discussion of the wider implications for understanding the unusual mechanical responses in amorphous media and developing broad relationships between disordered topology and physical properties. The work presented in the chapter originated from preliminary studies conducted by Raj Pandya and the methodology to determine the swelling ratios of fibrous materials was developed in collaboration with Dr Arkadiy Simonov.

6.1 Rod packings

The simplest arrangements of one-dimensional objects are the rod packings. [391–397]. Here, rods are defined as non-intersecting, uniform, straight cylinders. The initial enumeration of rod packings drew parallels from the early approaches to understand the dense packings of spheres *e.g.* hexagonal and cubic close packings. Correspondingly, the arrangements of rods are defined crystallographically, with an associated space group for each packing. In other words, the orientation and position of the rods are related to one another by the symmetry operations of the crystallographic space group. In real physical and chemical systems a single rod within the packing may be represented by any linear or straight zig-zagging chain of *e.g.* atoms, polyhedra, bundles of cylinders, or simply void space in a structure. While fundamental in nature, the interest in rod arrangements has found application in the mechanical and photonic properties of fibrous structures [398, 399], while also developing insights into the atomic arrangements in crystals [391].

Broadly speaking, the rod packings can be universally categorised into three groups by dimensionality: (i) bundles (one-dimensional), (ii) layered arrangements (two-dimensional) and (iii) interlaced packings (three-dimensional).

6.1.1 1D bundles

In the bundled arrangements all rods lie parallel to a single axis and, as such, map onto the problem of covering a plane with circles [400]. The two simplest arrangements are honeycomb, otherwise referred to as hexagonal (which also corresponds to the triangular net), and the square packing [Fig. 6.1]. These are observed frequently in physical systems including the arrangement of skyrmions [401], superconducting vortices [388], the elemental structure of selenium and tellurium [85] and channels formed by peptide assemblies [402].

6.1.2 2D layered arrangements

Contrastingly, the set of layered systems refer to rod packings in which the rod axes, rather than lying parallel to a common axis, are arranged in planes. The distinction here being that each plane of rods can lie parallel to a different common

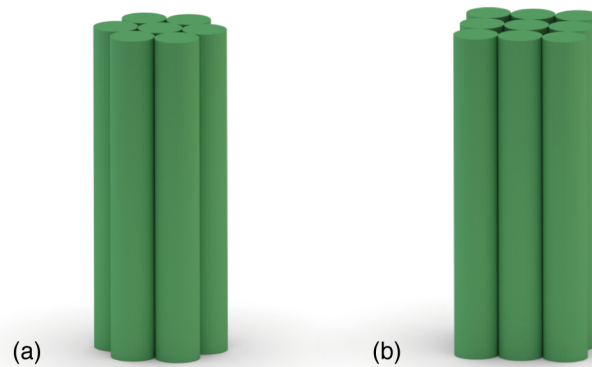


Figure 6.1: Representations of one-dimensional rod packings. (a) A hexagonal and (b) a square arrangement.

axis (perpendicular to the stacking direction) and can also be translated within the plane, perpendicular to the rod axes. The simplest packing is a tetragonal, two-layer (ABAB...) stacking shown in Figure 6.2(a). This arrangement is uncommon in crystallography, seemingly only observed in the chains of square planar coordinated Pt ions in, for example, PtO, PtS, CaPt_2O_4 and $\text{Na}_x\text{Pt}_3\text{O}_4$. A related four-layer packing (ABA'B'...) can be constructed through a translation of every third and fourth layer by 0.5ϕ —where ϕ is the distance between the centre of each rod or more plainly the diameter of touching cylinders in the structure—in the direction perpendicular to the rod axis within the layer plane [Fig. 6.2(b)]. This arrangement is much more common within crystal structures, being related to the chains of Hg atoms in $\text{Hg}_{2.186}\text{AsF}_6$ (alchemist's gold) [403], and the proposed structure of laminar sulphur ($\omega_2\text{-S}$) [404]. The final simple laminar structure is a hexagonal three layer packing (ABC...), where adjacent layers are staggered by 60° [Fig. 6.2(c)]. Analogous arrangements can be found in the structures of β -quartz [405] and $\text{NaHg}_2\text{O}_2\text{I}$ [406], where the rods are composed of zig-zagging lines of O atoms and $-\text{O}-\text{Hg}-\text{O}-$ respectively.

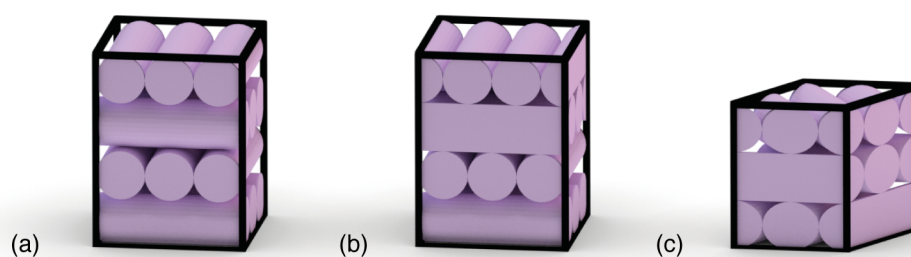


Figure 6.2: Three common layered rod packings. (a) A tetragonal, two layer (ABAB...) arrangements stacked twice in the stacking direction, (b) a tetragonal, body centered four layer (ABA'B'...) packing of cylinders and (c) a hexagonal, three layer (ABC...) packing of rods.

6.1.3 3D interlaced packings

The final set of rod packings refer to those in which the rods are not coplanar. These arrangements are much more varied, complex and, as such, immediately less intuitive. Due to the large variety of rod packings in this class, only the most crystallographically relevant examples of the cubic rod packings will be discussed here.

The nomenclature used to refer to specific interlaced rod packings can be particularly troublesome as multiple versions exist. The three most common are: (i) Greek letter notation where superscripts denote single enantiomorphs (*e.g.* Π^+/Π^-) or doubly interpenetrated networks (*e.g.* Π^*); (ii) equivalent fibrous topologies derived from tiling on minimal surfaces[†] (*e.g.* $G_{118}^+(1)$); (iii) the crystallographic description—*i.e.* the space group and occupied Wyckoff position(s) used to construct the rods—for example $Pn3m$, 12(g). This thesis will make use of the Greek letter notation wherever possible. A summary of relevant nomenclature conversions is available in Appendix D.

The simplest family of cubic interlaced packings contain rods lying along $\langle 100 \rangle$ directions, known by the descriptor Π . There are two sets to consider within the Π family: (i) Π^+/Π^- [Fig. 6.3(a)], which are enantiomorphic structures with $I4_132$ symmetry, and which, when rods are comprised of chains of face-sharing tetrahedra, map onto the structure of β -Mn [410]; (ii) Π^* [Fig. 6.3(b)], which exists in the $Pm\bar{3}n$ space group and describes the structure of β -W [411]. Here, the interpenetration of the Π^+ and Π^- arrangements yields the doubly interpenetrated Π^* packing.

Further families of cubic rod packings— Γ , Σ , and Ω —are made up of rods lying parallel to the $\langle 111 \rangle$ directions. The Γ packing exhibits $Ia\bar{3}d$ and is the densest cubic

[†]Here the initial letter gives the surface (G(yroid), D-surface, H-surface). The superscript denotes the enantiomorph if applicable (+/−) [407]. The subscript number gives the hyperbolic group number from Ref. [408, 409]. Finally the number in parentheses refers to the hyperbolic pattern within that group.

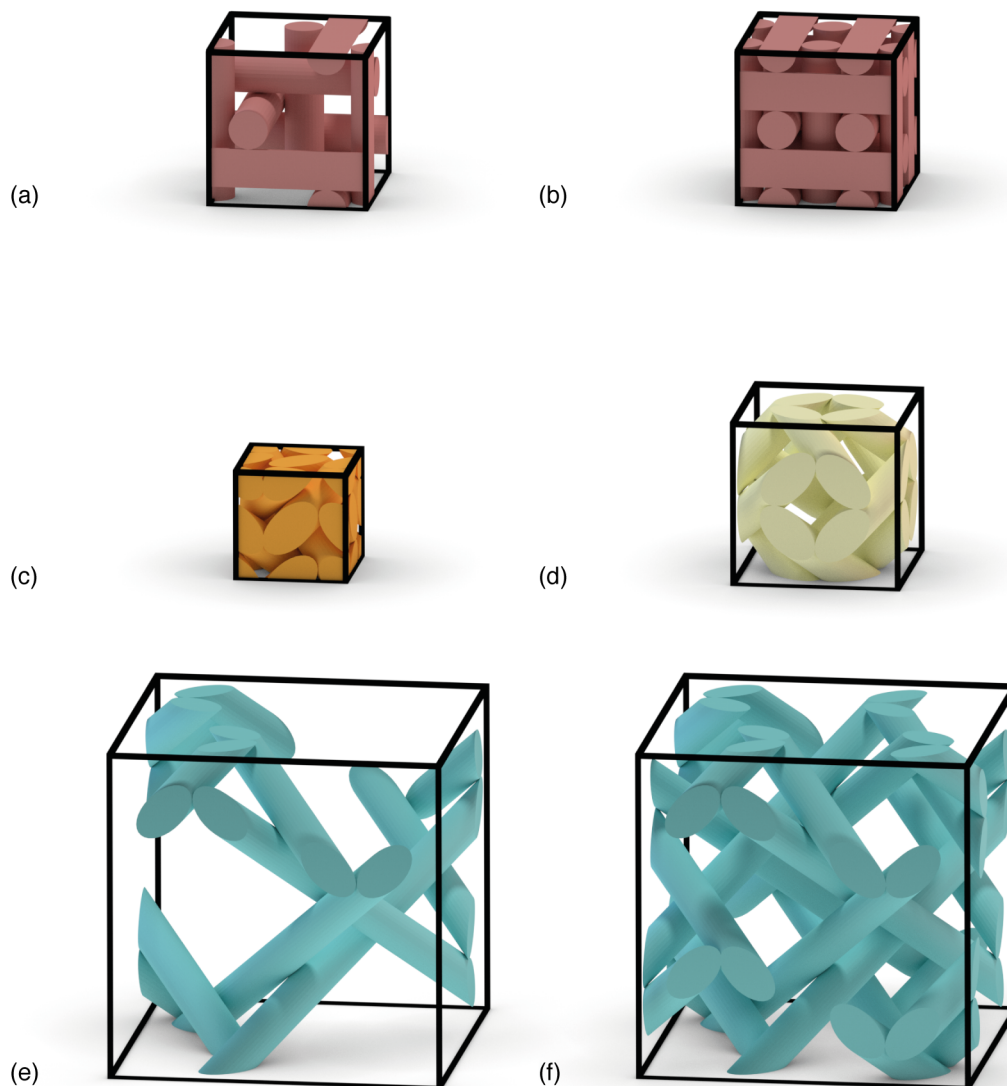


Figure 6.3: A representation of the well-studied cubic three-dimensional interlaced rod packings. (a) Π^+ , (b) Π^* , (c) Γ , (d) Ω^+ , (e) Σ^+ , (f) Σ^* . The unit cell sizes vary to accommodate touching rods of same diameter. Here colour is used to illustrate the topological family to which each packing belongs: Π (red), Γ (orange), Ω (yellow), and Σ (teal).

arrangement of rods with a packing fraction of 68% [Fig. 6.3(c)]. This packing, like the Π^+ topology described above, is also related to the β -Mn structure; however, in this case the rods are comprised of metaprisms and tetrahedra aligned along the four three-fold axes of the cubic cell [412].

The Ω family of rod packings can exist as one of two enantiomorphs (Ω^+/Ω^-) in the $I432$ space group [Fig. 6.3(d)]; however, no interpenetrated packing (Ω^*) is possible as the rods of the two enantiomorphs intersect. In this case no crystal structures are known to map onto the Ω rod packing, in large part due to the rarity of crystal structures in the $I432$ space group or its cubic subgroups.

The final family, Σ can exist as either a single enantiomorph (Σ^+/Σ^-) [Fig. 6.3(e)]—a packing with $I4_132$ symmetry related to the structure of SrSi_2 [413]—or a doubly interpenetrated network Σ^* [Fig. 6.3(f)]—exhibiting $Ia\bar{3}d$ symmetry and mapping onto the structure of γ -Si [414].

6.2 Swelling

By definition, rods have no curvature, but fibres may. The introduction of curvature into the rod packings transforms them into periodic ‘weavings’ of fibres, with identical topologies. These fibre weavings are able to accommodate a range of packing densities. A collective change in fibre curvature while retaining configurational topology has the possibility of varying the porosity, and hence the density of a structure. The ability of a particular weaving to swell is defined by the ratio:

$$\tau = V_{\text{max}}/V_{\text{min}} , \quad (6.1)$$

where V_{max} and V_{min} represent the most porous (max) and densest (min) configurations adopted by a given entanglement. This transformation reflects the mechanism by which physical processes that affect curvature—such as hydration [376] or thermal

treatment [383]—are able to alter the volume of fibre assemblies without requiring changes in topology such as the breaking of chemical bonds.

6.2.1 Swelling of ordered topologies

The swelling ratio, τ , of periodic fibre weavings has previously been established by Evans *et al.* [399, 415]. Their approach to determine the swelling capacity begins with the generation of the weaving topology—line patterns in the Hyperbolic plane are projected onto triply-periodic cubic minimal surfaces in the Euclidean plane (*i.e.* the primitive, gyroid and diamond membranes) [Fig. 6.4] [416]. These line weavings are then decorated by filaments with uniform diameter. The topology of the weaving is maintained by treating the filaments as hard objects—*i.e.* the closest approach of two filaments is never smaller than the diameter ϕ and filaments are unable to pass through one another upon configurational relaxation.

The least swollen configuration ($V_{\min}$) is obtained by initially decorating the weaving with filaments of a very small diameter. Fibres are then incrementally tightened (by reducing the total length of fibre in the unit cell using the Shrink-On-No-Overlaps (SONO) algorithm [417]) and thickened until further optimisation is not possible. The resulting configuration with the thickest possible array of tightened fibres therefore represents the densest packing of fibres ($V_{\min}$).

The extended, porous state, $V_{\max}$, is then derived from the dense configuration. The fibres within the dense configuration ($V_{\min}$) are kept at constant ϕ while the unit cell undergoes incremental homothetic expansion, with a tightening procedure applied at each stage. In general, this sequence results in a gradual straightening of the fibres. The extended terminal configuration $V_{\max}$ of the swelling mechanism is then determined at the point at which further expansion of the unit cell results in the loss of inter-fibre contacts.

A key result of the research of Evans *et al.* found that the magnitude of the swelling

response is a function of weaving topology [399, 415]. The ubiquitous hexagonal fibre packing cannot swell; *i.e.* $\tau = 1$. The same is true for the Γ and Π^* topologies. In contrast, Π^+ and Σ^+ arrangements of fibres can swell but to different extents, with swelling ratios, τ , of 2.247 and 5.429, respectively. Put more simply, while the variation of fibre curvature can cause a five-fold decrease in volume of the Σ^+ arrangement, the same process has no effect on other topologies such as the Π^* packing.

6.3 Mechanical responses of disordered structures

The distinct relationship between topology and swelling strongly implies that the magnitude of τ must also be sensitive to the presence of topological disorder. This

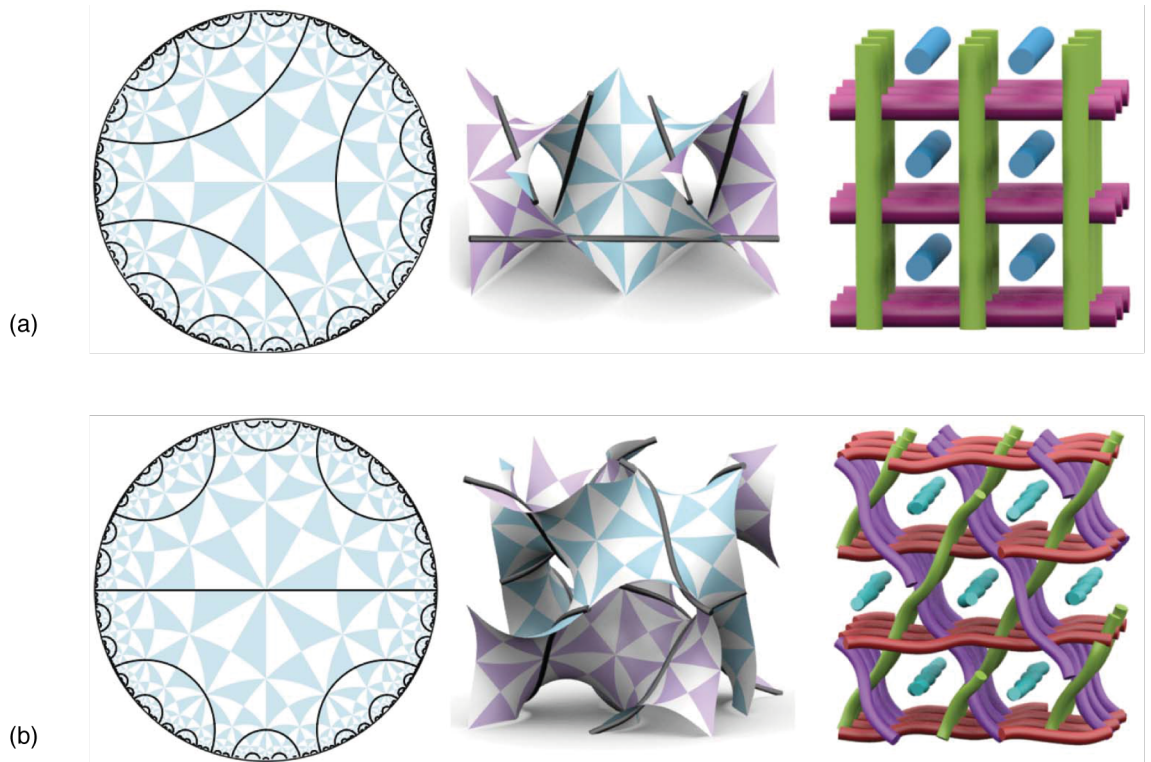


Figure 6.4: The conversion of line patterns in the Hyperbolic plane to minimal surfaces in the three-dimensional Euclidean plane. Line patterns in $\mathbb{H}^2$ (left) mapped onto minimal surfaces in $\mathbb{E}^3$ (middle) creating rod packing topologies (right). The diamond and gyroid minimal surfaces in $\mathbb{E}^3$ gives the (a) Π^* and (b) Γ rod packing topologies respectively. Adapted from Ref. [416]. Reproduced with permission of the International Union of Crystallography.

statement is entirely consistent with intuition: the collective mechanisms responsible for swelling responses in ordered structures will become interrupted as disorder introduces knots, perhaps even at low concentrations [399].

Optical microscopy of both natural and synthetic packings reveals the widespread presence of entangled disordered states made up of curved fibres [Fig. 6.5]. This is not unexpected: curved fibres exhibit substantially more topological diversity than straight rods—by way of analogy the packing of dried spaghetti strands is considerably simpler than the entangled weavings formed in its cooked, curved state. Nevertheless, despite the clear evidence of complex entangled states, modelling techniques often use topological simplifications. Common approaches include (i) interpretation of entanglements as ordered arrangements of fibres [383, 399, 415] or (ii) modelling these structures in terms of two independent components, a random-coil fraction surrounded by an ordered weaving containing the local structural motifs present in the structure [418]. As such, there is a fundamental disconnect between our understanding that mechanical response is topologically dependent, and the oversimplifications used in modelling real systems. Furthermore, the existence of reversible dilatancy in ‘randomly’ coiled materials [419] and the auxetic behaviour of amorphous foams [259, 420]—an effect also found in entangled wires [421]—clearly demonstrates that complex disordered topologies are capable of exhibiting complex mechanical behaviour. As such this chapter aims to answer the following important question: to what extent does topological disorder affect cooperative mechanical responses such as swelling?

In this chapter, the relationship between topological disorder and swelling response will be studied using a combination of geometrical and structural relaxation approaches. A key challenge here is to devise a methodology which allows topological disorder to be controlled systematically. A common parent structure of the Π^* and Σ^* weavings is identified, which allows the generation of intermediate entanglements of quantifiable, yet arbitrary, degrees of topological disorder. Importantly,

the swelling capabilities of the bounding topologies are very different—extremely large in the case of Σ^* and zero for Π^* —and as such τ must vary across the topological continuum. The magnitude of τ is measured using structural relaxation approaches and the method verified against the ordered weaving topologies. This study shows that the mechanism responsible for the extreme swelling capacity of the Σ^* topology is sensitive to topological disorder, but the introduction of small quantities of disorder into the Π^* structure does not induce a large change in τ . The key result; however, finds that specific disordered entanglements allow extreme swelling behaviour even greater than that of Σ^* ($\tau > 6$). The work in this chapter definitively shows that topological order is not a prerequisite for large swelling responses observed in fibrous materials. Indeed, disordered entanglements are capable of supporting collective mechanisms to allow extreme swelling behaviour.

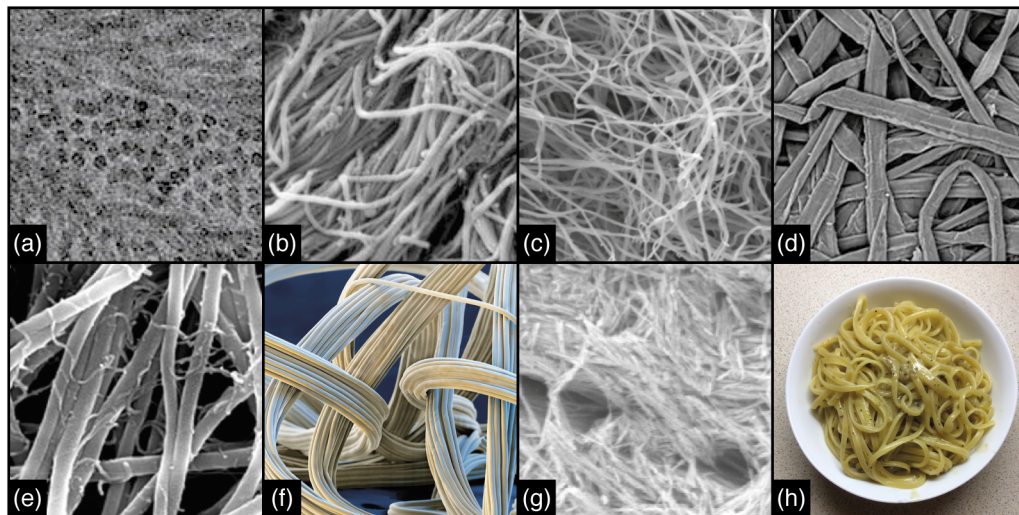


Figure 6.5: Images of fibre entanglements found both in natural and synthetic systems. (a) Keratin, reprinted from *J. Invest. Dermatol.*, **123**, L. Norlén and A. Al-Amoudi, Stratum Corneum Keratin Structure, Function, and Formation: The Cubic Rod-Packing and Membrane Templating Model, 715–732, copyright 2004, with permission from Elsevier [383]. (b) Collagen, adapted from Ref. [422]. (c) Fibrin, reprinted from *Matrix Biol.*, **60**, O. V. Kim, R. I. Litvinov, J. Chen, D. Z. Chen, J. W. Weisel and M. S. Alber, Compression induced structural and mechanical changes of fibrin collagen composites, 141–156, copyright 2017, with permission from Elsevier [423]. (d) Cellulose, adapted from Ref. [424]. (e) Carbon nanotubes, adapted from Ref. [425]. (f) Elastane, adapted from Ref. [426]. (g) Chrysotile—otherwise known as white asbestos—adapted from Ref. [427]. (h) Fresh spaghetti.

6.4 Generation of fibre entanglements

6.4.1 Parent structure

Each weaving topology is originally derived from a unit cell of $Ia\bar{3}d$ symmetry with nodes situated on the 48g Wyckoff sites. These are connected by two symmetry-inequivalent types of linker between 2nd and 3rd nearest neighbour nodes (red and teal). Four linkers meet at each node, two of each type [Fig. 6.6(a)]. Entanglements are obtained by partitioning linkers into equal sets in which exactly two linkers meet at each node. In this way a linker set describes a decoration of self-avoiding one-dimensional pathways which is dense with respect to the coverage of the nodes.

6.4.2 Topological continuum of states

Each entanglement can be described by the variable x , which represents the constituent fraction of teal linkers within a given linker set. Accordingly, the trivial sets bounding the topological continuum, *i.e.* only red ($x = 0$) or only teal ($x = 1$) linkers, produce structures topologically identical to the Π^* and Σ^* rod packings respectively [Fig 6.7(b-c)]. Entanglements corresponding to intermediate values of x represent disordered states with a mixture of teal and red linkers [Fig. 6.7(d)].



Figure 6.6: The local arrangement of linkers. (a) The local environment of each node within the parent cell. (b-d) The allowed arrangements of linkers around each node in a given fibre entanglement. (e) Entanglements containing nodes with this arrangement of linkers are discounted from this study as the tight binding angle causes the formation of small rings over one-dimensional chains.

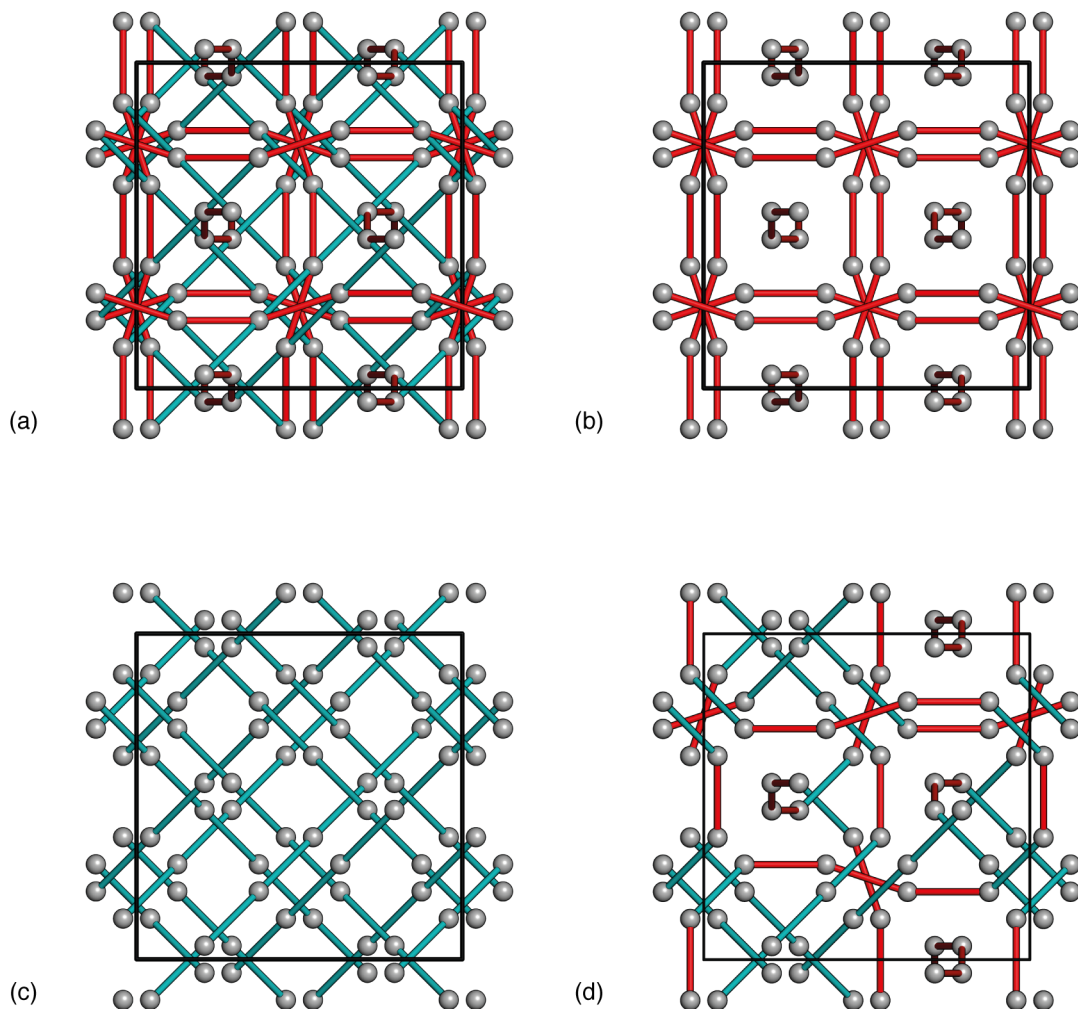


Figure 6.7: The construction of disordered fibre entanglements. (a) A representation of the parent $Ia\bar{3}d$ network from which the entanglements are derived. Nodes occupy the 48g Wyckoff sites and are shown as grey spheres. They are connected to one another by two symmetrically distinct types of linker shown in teal and red. The trivial partitionings give the (b) Π^* and (c) Σ^* topologies corresponding to the use of only red ($x = 0$) and only teal ($x = 1$) linkers respectively. Linker sets combining both red and teal linkers predominantly give disordered entanglements of one-dimensional objects as shown in (d).

6.4.3 Consideration of local structure

Locally there are four possible arrangements of two linkers around a given node [Fig. 6.6(b-e)]. One of these local structures, shown in Figure 6.6(e), is precluded from the appearing in entanglements. In this arrangement the small angle between the occupied linkers (43°) promotes the formation of small rings instead of the one-dimensional fibres which are the focus of this study.

6.4.4 Creating disordered entanglements

Disordered entanglements ($0 < x < 1$) were generated using custom Monte Carlo code. Periodic boundary conditions were applied to the parent unit cell and linkers were randomly assigned one of two initial states: $a = \pm 1$, which denote whether a linker is occupied (+1) or vacant (-1). A fictitious configuration energy was then calculated:

$$E = Q + \bar{a}\delta(Q) , \quad (6.2)$$

where

$$Q = \sum_{i \in \text{nodes}} \left| \left(\sum_{j \in \text{linkers}} a_{ij} \right) \right|^2 , \quad (6.3)$$

and

$$\bar{a} = \begin{cases} 4, & \theta < \frac{\pi}{2} \\ 0, & \theta \geq \frac{\pi}{2} \end{cases} . \quad (6.4)$$

where a_{ij} is the state of the j^{th} linker surrounding the i^{th} node, δ is the Kronecker delta function, and θ represents the angle between the two occupied linkers. Here, the term in Equation 6.3 is minimised when two linkers surround each node in the configuration. Equation 6.4 prevents small rings from being formed by applying an energy penalty to local linker arrangements with tight binding angles. The configurational energy penalty for the presence of nodes with local linker arrangements equivalent to those shown in Figure 6.6(e) was chosen as 4, so as to be equal to that

of an arrangement of three or one occupied linker sites around a single node *i.e.* on the same scale as other disfavoured local arrangements.

Monte Carlo minimisation proceeded via the Metropolis algorithm [245] wherein a single move consisted of the switch $a_{ij} \rightarrow -a_{ij}$. This study is focussed on the swelling behaviour of non-defective entanglements of one-dimensional fibres, and as such, simulations were terminated at $E = 0$ and the constituent fraction of teal linkers x determined. The resulting disordered topologies were then converted into analogous atomistic representations fibres for use in the structural relaxation procedure by decorating each node with one atom and each linker with five equidistant atoms [Fig. 6.8]—a compromise between resolution of the fibrous structure and computational efficiency.

6.5 Identification of swelling behaviour

In this study, structural relaxation approaches are used to determine the swelling behaviour of the disordered entanglements generated from the methodology of Section 6.4. The ultimate goal here is to characterise the function $\tau(x)$, where $0 \leq x \leq 1$. Before presenting the results, the basic approach used to determine τ for a given generalised entanglement is given.

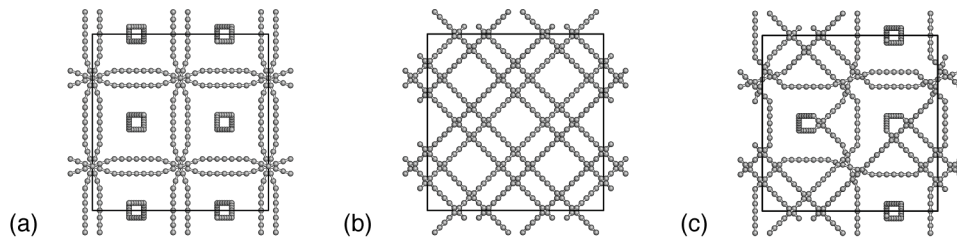


Figure 6.8: Atomistic representations of fibre packings. (a) Π^* , (b) Σ^* and (c) the disordered entanglement shown in Figure 6.7(d) for use in the structural relaxations.

6.5.1 Initial structure relaxation

Each entanglement was first subjected to structural relaxation using the General Utility Lattice Program (GULP) [Fig. 6.9] [249]. Two potentials were employed in this study: (i) a coulomb repulsion between fibres (requiring Ewald summation techniques [250]), with each fibre being negatively charged and confined with a cell of fixed lattice parameter; (ii) a harmonic bond potential between nearest neighbours (1–2) and 3rd nearest neighbours (1–4) within each fibres. The harmonic potential of the form

$$E_{\text{harm}} = \frac{1}{2}k(r - r_0)^2 \quad (6.5)$$

acts to maintain the fibre connectivity. Each atom was given the same charge, 0.5 e, and as such the coulomb potential

$$E_{\text{elec}} = \frac{q_1 q_2}{r_{12}} \quad (6.6)$$

maximises fibre separation as the fibres repel each other within the confined unit cell. Correspondingly, both terms act to maintain the topology of the initial entanglement set during linker partitioning by maintaining the connectivity of a single chain and discouraging fibres from passing through one another. A summary of the parameters used during relaxation is presented in Table 6.1. These values were chosen such that entanglement topology was maintained while allowing fibre curvature. Sample GULP input files can be found in Appendix F.

6.5.2 Determination of the most porous structure

For each entanglement the relaxed configuration was subjected to isotropic expansion and contraction of the GULP lattice parameter $d = 50 \text{ \AA}$ in $0.1 \text{ \AA}$ increments. After each increment of the isotropic expansion/contraction a structural relaxation is applied using the same parameters listed in Table 6.1 with the exception of d . At

each stage the maximum r_{12} distance—*i.e.* the largest distance between neighbouring atoms within a single fibre—is calculated. A plot showing the variation of $\max r_{12}$ as a function of d reveals two clear regimes—(i) where all fibres are unstretched and contain curvature; (ii) where at least one fibre is taut and being overextended. In the latter regime the elastic properties of the fibre itself are being probed, which is not relevant to the swelling of the entanglement itself, so the most swollen configuration is defined as the boundary between the two regimes, at which a fibre is at the point of stretching.

The exact configuration is determined by calculating the intercept lines of best fit for each of the two regimes (using linear regression) [Fig. 6.10]. In order to avoid probing the elastic properties of the fibres themselves, the most porous configuration is taken as that with the value of d rounded down to the nearest 0.1 Å.

6.5.3 Determination of the densest arrangement

The next step in the methodology to determine swelling behaviour is to calculate the configuration with the densest arrangement of fibres. This is achieved by subjecting the most porous configuration of the entanglement to isotropic contraction with d

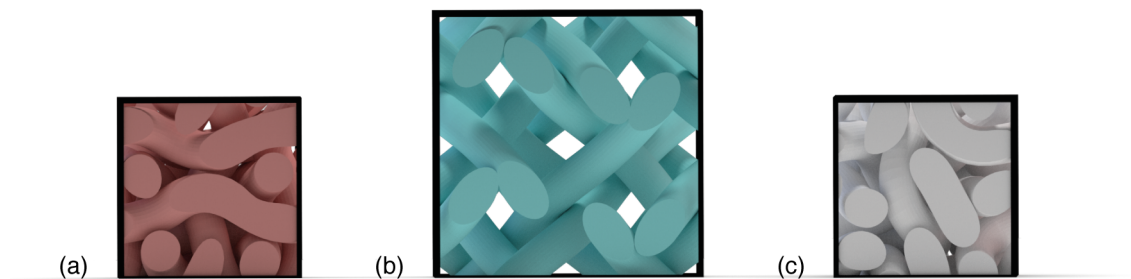


Figure 6.9: Relaxed arrangements of fibres. (a) Π^* , (b) Σ^* and (c) a disordered entanglement. The structural relaxations are performed upon the atomistic representations in Figure 6.8. The unit cells vary in size—and hence porosity—to accommodate touching fibres of unit diameter.

decreasing in 0.1 Å increments. Again, a structural relaxation was applied at each stage. To establish which configuration is the densest, a rescaled lattice parameter, L , is calculated for each configuration,

$$L = \frac{d}{r_f}, \quad (6.7)$$

where r_f is the closest approach of fibres within the cell. Here, a representation of the structure with a cell parameter altered to that of the rescaled lattice parameter, L , produces a configuration in which the closest approach of the centres of fibres of unit diameter is equal to the fibre diameter itself—*i.e.* the fibres are at the point of touching. The configuration in which L is at a minimum therefore corresponds to the densest configuration. The closest approach of fibres can be obtained by the proximity of two separate fibres, or a single fibre curving around and passing close to itself. In the event of the latter, caution must be taken to avoid r_f representing the short distances between neighbours directly along a straight chain, so the closest contact is defined to take place between 13th nearest neighbours along the fibre or greater. The densest arrangement of fibres is then determined as the point at which L is at a minimum. Further compression in d from this configuration results in an increase in L due to inflationary coiling [Fig. 6.11].

Table 6.1: The parameter values used within the structural relaxation procedure.

Parameter	Value
$d / \text{\AA}$	50
$r_{12} / \text{\AA}$	2.406
$r_{14} / \text{\AA}$	7.218
q / e	0.50
$k_{12} / \text{eV}\text{\AA}^{-2}$	100
$k_{14} / \text{eV}\text{\AA}^{-2}$	50

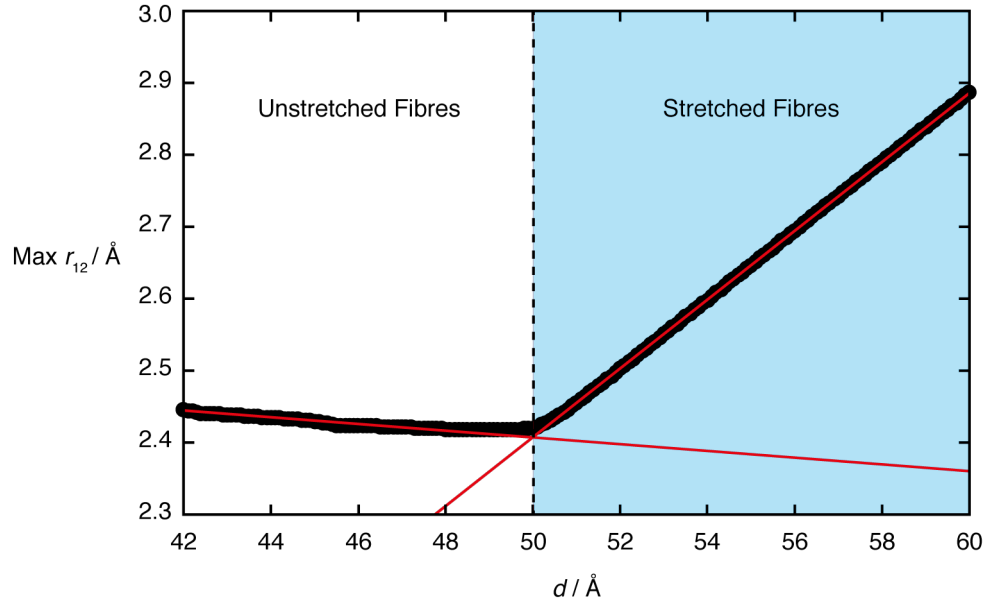


Figure 6.10: Isotropic expansion of fibre arrangements. A plot showing the effect of isotropic expansion and compression of d on the maximum r_{12} distance within a fibre in the Σ^* configuration. The stretch point is determined by the intercept of two lines of best fit (red), each determined for the two distinct regimes—where all fibres are curved (white) and where a fibre is being stretched (blue).

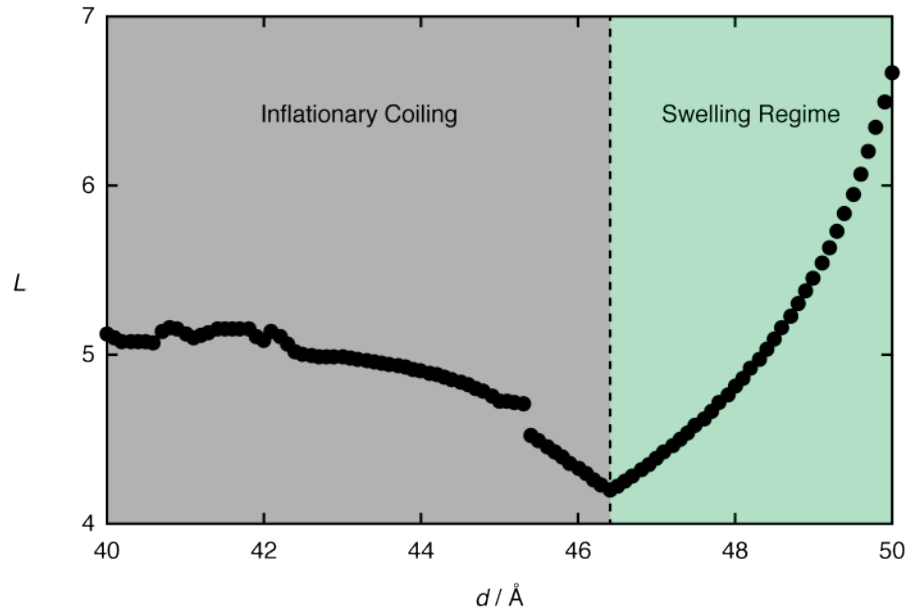


Figure 6.11: Isotropic compression of fibre arrangements. A plot detailing the effect of isotropic compression of d from the most porous structure on the rescaled cell length, L , in the Σ^* configuration. The configuration of lowest porosity is defined as the point at which L reaches a minimum. This point marks the switch between the swelling regime (green) and inflationary coiling (grey).

6.5.4 Calculation of the swelling capacity

The range of L values accessible by a given entanglement can be obtained by defining the bounds of the swelling response between these two configurations. Use of the rescaled lattice parameter, L , ensures that fibres of unit diameter are kept in constant contact throughout the swelling mechanism such that the swelling capacity can be determined as the simple ratio between the relative volumes of the dense ($V_{\min}$) and open pore ($V_{\max}$) forms of the entanglement:

$$\tau = \frac{(L_{\max})^3}{(L_{\min})^3}, \quad (6.8)$$

where $L_{\min}$ and $L_{\max}$ refer to the rescaled lattice parameters of the dense and open pore structures respectively. In this way, a topology in which open pore and dense form coincide within the same configuration will yield $\tau = 1$ —*i.e.* the structure cannot swell as there is no mechanism to increase the density of the open pore form without stretching the fibres themselves.

6.5.5 Topological stability

One of the crucial challenges of the structural relaxation methodology is to retain the topology of the fibre entanglement throughout the multiple structural relaxation phases while, allowing the fibres to slip and slide over one other. This approach makes use of harmonic and coulomb potentials to maintain fibre connectivity and maximise fibre separation respectively and in doing so, preserve the entanglement topology. Nevertheless, there remains a possibility for fibres to pass through each another, changing the entanglement topology—known as a phantom move in Ref. [399]—upon structural relaxation. Phantom moves are made all the more probable due to the variation in the lattice parameter, d , when exploring the swelling landscape. Observation of topology changes occurred most often on the expansion of the cell as the fibres are being pulled against each other. In this study each entan-

gement was visualised both before and after every structural relaxation to establish whether a phantom move had taken place.

Phantom moves often produce a characteristic signal when plotting the maximum r_{12} distance against d . Upon a topological change, two distinctive regimes are evident (i) a increase in maximum r_{12} of a polynomial form in d as two fibres pull against one-another, stretching the intra-fibre harmonic bonds; (ii) a sharp drop in the maximum r_{12} distance back down to the original value as the two fibres undergo a phantom move and the atoms within each fibre relax back toward the r_0 value [Fig. 6.12]. These phantom moves are almost exclusively observed during isotropic expansion of the cell when determining the most porous configuration.

In theory it would be possible to ascertain the most porous structure of entanglements containing a phantom move. At low values of d , before the phantom move, the treatment would remain the same *i.e.* fitting to a linear line of best fit; however in the regime where the fibres are being pulled taut against each other a polynomial fitting would need to be employed. This approach presents a problem as the configuration of highest porosity (at the point of stretching fibres) would become very

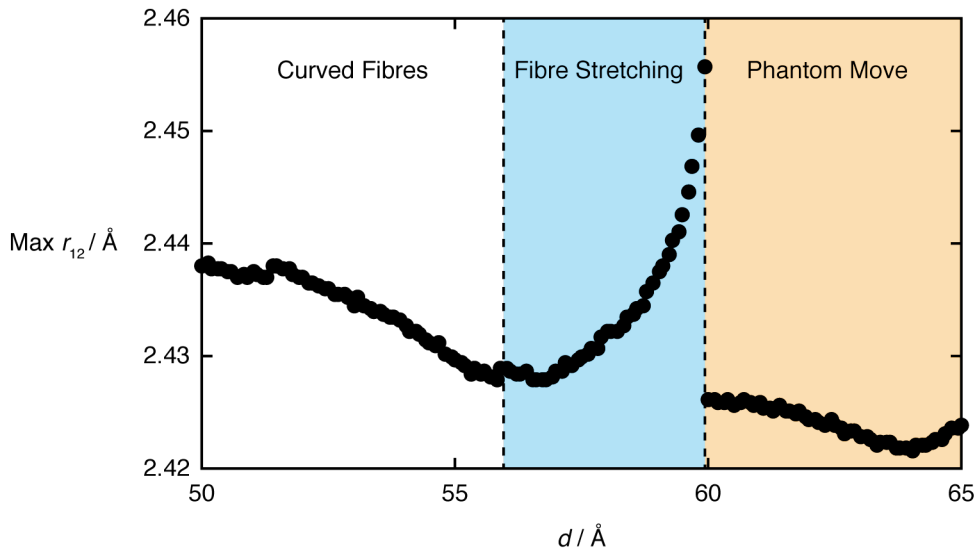


Figure 6.12: The characteristic evidence of a phantom move. An increase of maximum r_{12} with increasing d followed by a sharp drop indicating that a change in topology has taken place.

difficult to accurately ascertain as the polynomial fitting itself would greatly alter the position of the intercept. Unfortunately, the increased error in determining d for the most porous structure will result in large variations in the resulting value of $L_{\max}$ and therefore τ [Fig. 6.11]. Consequently, in the cases where a phantom move was observed, the entanglement was discarded from the study and a replacement configuration generated.

6.6 Results

6.6.1 Swelling ratio of ordered end members

The structural relaxation methodology was first benchmarked against the known swelling behaviour of the Π^* and Σ^* topologies [399]. In the case of Π^* ($x = 0$) only a small range of L states can be accessed where $L \simeq 4$. Consequently $L_{\min} \simeq L_{\max}$ and, as such, $\tau(0) = 1.04 \simeq 1$ [Fig. 6.13(a)]. In contrast, the Σ^* topology can accommodate a large range of L states with $4.20 \leq L \leq 6.67$, resulting in $\tau(1) = 4.00$ [Fig. 6.13(b)]. The collective rearrangement of fibres during swelling of the Σ^* weaving is similar to that found Ref. [399] and is presented in Figure 6.13(c) (an animation of the same mechanism can be found in Appendix F). Crucially, in both cases the swelling ratio determined by the structural relaxation approach—described in Section 6.5—provides a good qualitative match to the exact values— $\tau(0) = 0$ and $\tau(1) = 5.429$ [399]—and a slightly better result to that found in similar simulations— $\tau(1) = 3.9$ [415].

6.6.2 Swelling ratio of disordered intermediate states

Crucially, the structural relaxation approach for determining swelling capacities is general in nature and so can be applied to disordered entanglements where $0 \leq x \leq 1$ —allowing the form of the function $\tau(x)$ to be determined. Ten entanglements at each of the following intermediate x values were generated—0.125, 0.25, 0.375,

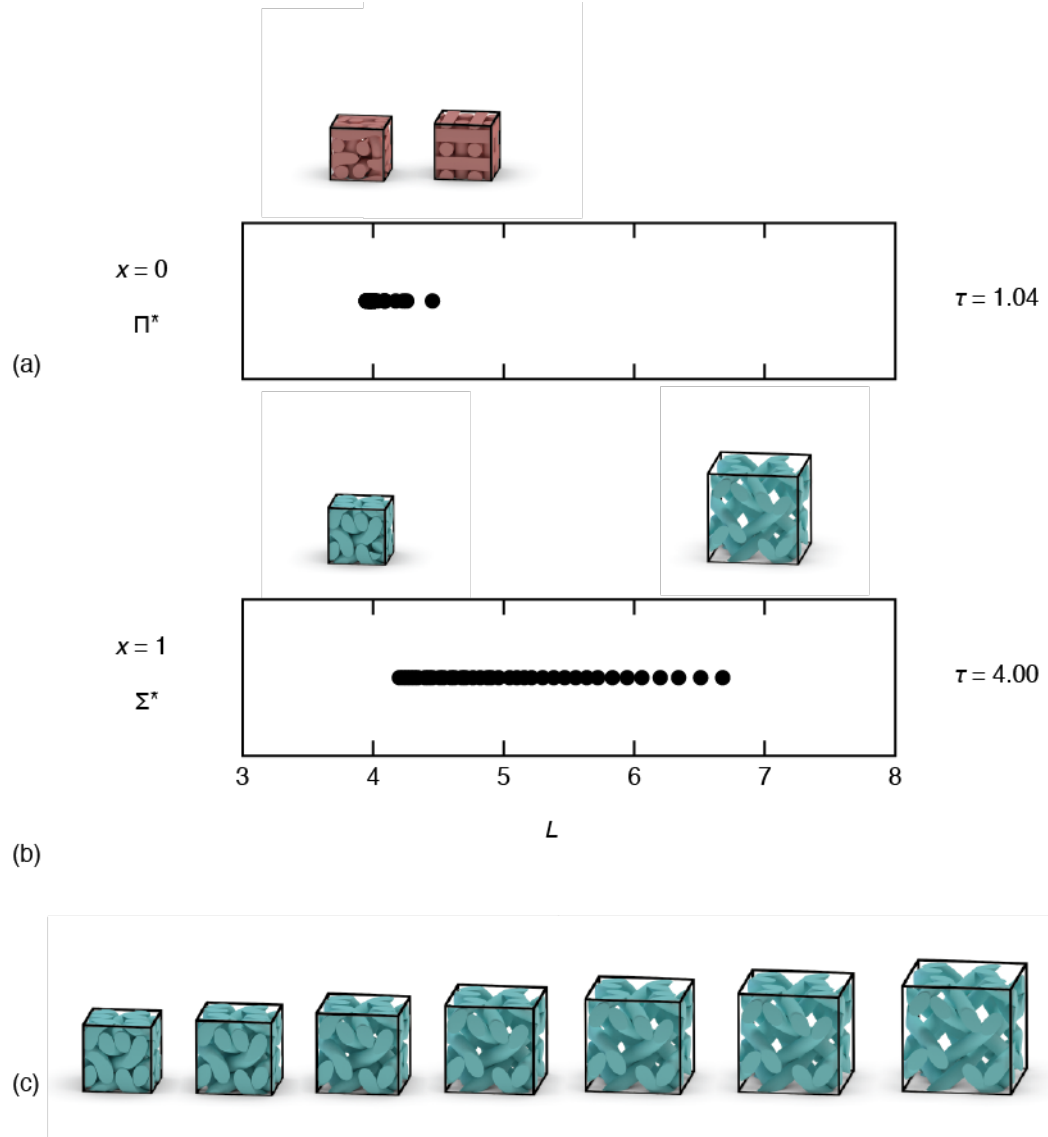


Figure 6.13: The swelling of ordered fibre packings. Plots showing the allowed L states for the (a) Π^* and (b) Σ^* topologies. These bounding values are used to determine the swelling ratios of 1.04 and 4.00 respectively. A representation of the swelling mechanism for the Σ^* topology is presented in (c). A movie of the analogous rearrangement can be found in Appendix F.

0.5, 0.625, 0.75 and 0.875—providing sensible resolution in x while also allowing a representative spread of topologies at a given x value. The results for the disordered entanglements reveal a highly complex relationship between swelling capacity and topology indicating that two contrasting effects are at play [Figs. 6.14 and 6.15]. On the one hand there is a continuum of intermediate states which favours $\tau \rightarrow 1$ as $x \rightarrow 0$, *i.e.* there is a tendency for the swelling capacity to be quickly quenched as disorder is introduced into the Σ^* topology. This make intuitive sense as low levels of disorder introduced into the Σ^* weaving will result in a disruption of the collective swelling mechanism of the ordered state. Yet, on the other hand there are a small handful of disordered entanglements which exhibit a large swelling ratio, defying the original trend. Collectively, these effects mean that at a given intermediate value of x , some fibre entanglements show very small swelling effects, while other topologies will exhibit extreme swelling capacities—highlighted by the allowed L states shown in Figure 6.14(a),(b) for two $x = 0.5$ configurations. Furthermore, these results show that the swelling ratio of disordered entanglements can exceed the extreme response of the ordered Σ^* weaving. The swelling mechanism of these disordered entanglements reveals a strongly cooperative rearrangement of fibres comparable, but clearly different to that for the ordered Σ^* topology [Fig. 6.14(c)].

6.6.3 Robustness of the structural relaxation method

Reversibility

The reproducibility of the structural relaxation methodology was demonstrated by evaluating the swelling ratio upon a repeated swelling cycle. The starting configuration was taken as the densest configuration ($V_{\min}$) of the selected entanglement *i.e.* the end point of the initial cycle. The entanglement was then (i) expanded isotropically in d , (ii) the most porous structure determined, (iii) isotropically compressed in d , (iv) the densest configuration obtained and finally (v) the swelling ratio calculated. This repeated cycle was applied to selected entanglements from

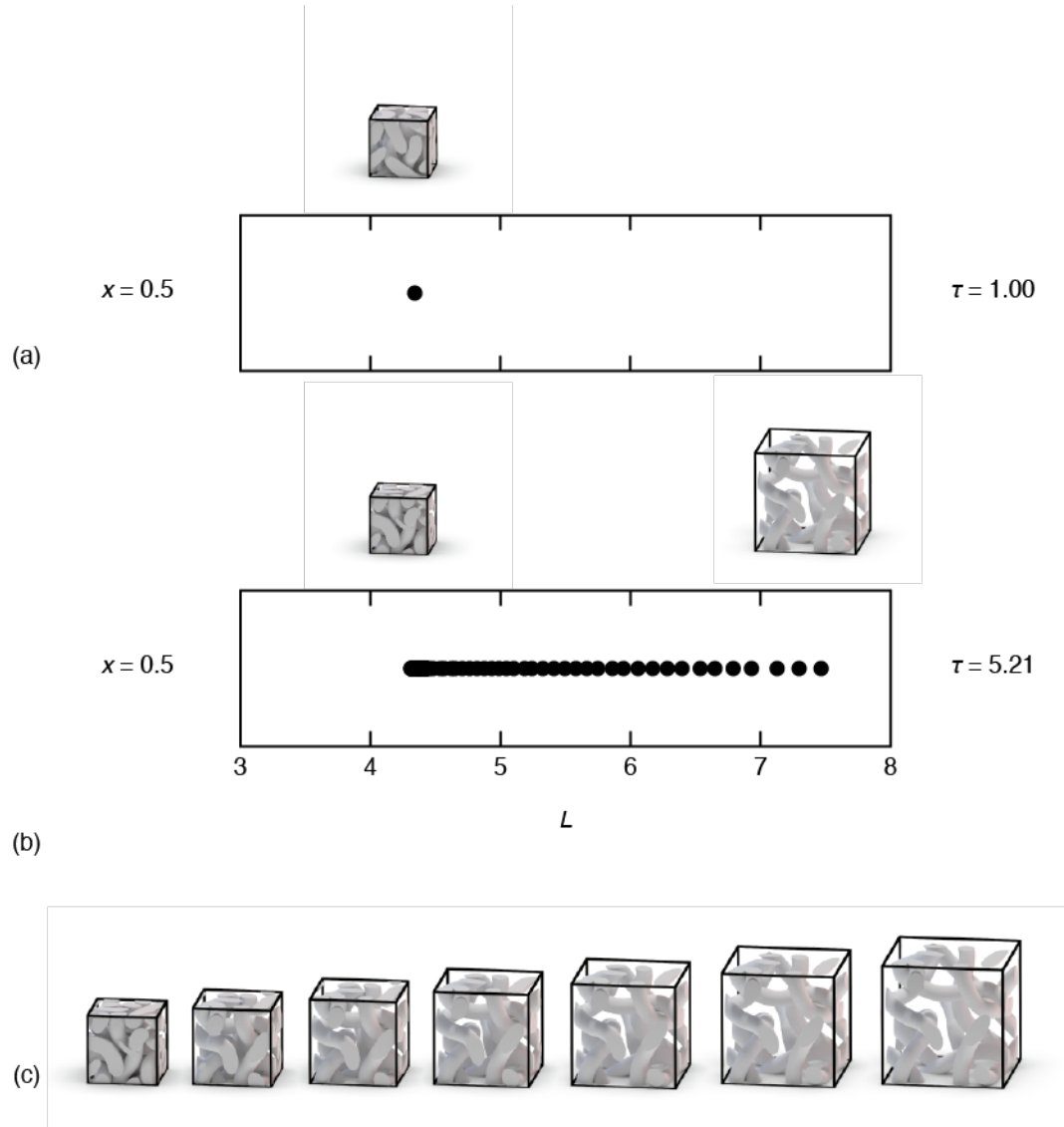


Figure 6.14: The swelling of disordered fibre entanglements. Plots showing the allowed L states for two disordered entanglements ($x = 0.5$). These data reveal (a) minimal swelling behaviour and (b) an extreme swelling capacity. The collective mechanism for the swelling response in (b) is shown in (c) wherein rearrangements of touching fibres with equal diameter are able to vary the pore volume of the cell. An animation of the swelling response can be found in Appendix F.

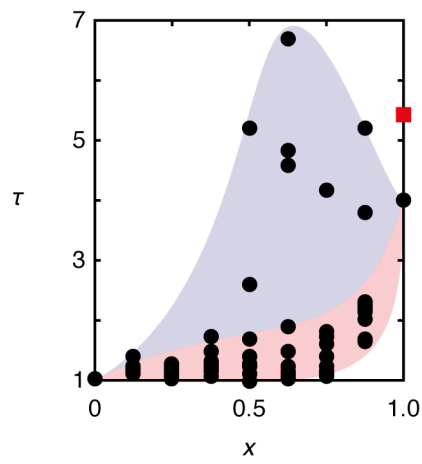


Figure 6.15: The impact of topological disorder on the swelling behaviour of fibre entanglements. A plot showing the form of the function $\tau(x)$ —*i.e.* the effect of topological disorder on the swelling capacity of fibre entanglements. The value $\tau(1)$ is given both from this study (black circle) and the exact value of Ref. [399] (red square). Two regimes are evident which are highlighted by the background colour to guide reader: (i) the swelling capacity being quenched as disorder is introduced (red background); (ii) disordered topologies with extreme swelling ratios (blue background).

the original study spanning a range of both x and τ values. Upon a further swelling cycle the original swelling ratios (τ_1) when remeasured (τ_2) are recovered to good agreement, demonstrating that not only is the swelling mechanism reversible, as expected, but also that magnitude of the swelling ratio is well-recovered by the structural relaxation methodology [Fig. 6.16].

Sensitivity to GULP parameters

Ideally the GULP parameter values chosen to conduct the entanglement relaxations (Table 6.1) would have no effect on the obtained swelling ratios. To establish the sensitivity of τ to the GULP parameter values perturbations were applied to each value in turn [Table 6.2]. The ten new sets of relaxation conditions (A–J) were individually applied over the entire structural relaxation procedure detailed in Section 6.5 to four key entanglement topologies (i) Π^* ($x = 0$), (ii) Σ^* ($x = 1$) (iii) a disordered entanglement where $x = 0.5$ with a minimal swelling ratio under the original relaxation conditions ($\tau = 1.000$) and (iv) a disordered entanglement where $x = 0.5$ with an extreme swelling ratio under the original relaxation conditions

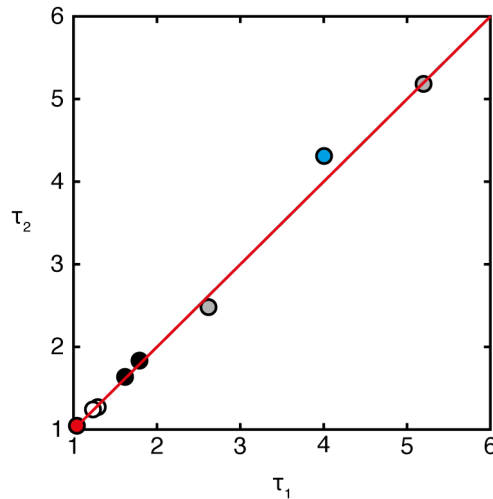


Figure 6.16: The reversibility of the swelling mechanism. Good agreement is found between the initial swelling ratio (τ_1) and that calculated after a repeated swelling cycle (τ_2). Entanglements at $x = 0$ (red), 0.25 (white), 0.5 (grey), 0.75 (black) and 1 (blue) were selected to demonstrate the reversibility of swelling using the structural relaxation method. Ideal reversibility ($\tau_1 = \tau_2$) is shown as a red line.

($\tau = 5.205$).

The subsequent swelling capacities for each simulation are summarised in Figure 6.17. These data show clearly that, while the swelling ratio undergoes minor fluctuations under different relaxation conditions, the magnitude of τ remains relatively constant. Fundamentally, these simulations demonstrate that the structural relaxation method is capable of robustly distinguishing between entanglements with extreme and minimal swelling ratios, irrespective of the particular chosen GULP parameter values.

6.7 Discussion

The key result of this study reveals that large swelling capacities are accessible to disordered entanglements. There is no obvious rationale for the observed variance in τ due to topological disorder; however, this is somewhat to be expected as the relationship between swelling response and topology is poorly-understood even in the limit of ordered weavings. In light of these results, there are a number of important considerations to mention. First and foremost, an intermediate value of x does not itself ensure the generation of a disordered entanglement. By way of example,

Table 6.2: Perturbations in parameters values for the structural relaxations implemented to explore the sensitivity of the swelling capacity.

Parameter	Original	A	B	C	D	E
$r_{12} / \text{\AA}$	2.406	2.506	2.306	2.406	2.406	2.406
$r_{14} / \text{\AA}$	7.218	7.218	7.218	7.318	7.118	7.218
q / e	0.50	0.50	0.50	0.50	0.50	1.00
$k_{12} / \text{eV}\text{\AA}^{-2}$	100	100	100	100	100	100
$k_{14} / \text{eV}\text{\AA}^{-2}$	50	50	50	50	50	50
Parameter	Original	F	G	H	I	J
$r_{12} / \text{\AA}$	2.406	2.406	2.406	2.406	2.406	2.406
$r_{14} / \text{\AA}$	7.218	7.218	7.218	7.218	7.218	7.218
q / e	0.50	0.25	0.50	0.50	0.50	0.50
$k_{12} / \text{eV}\text{\AA}^{-2}$	100	100	200	50	100	100
$k_{14} / \text{eV}\text{\AA}^{-2}$	50	50	50	50	100	25

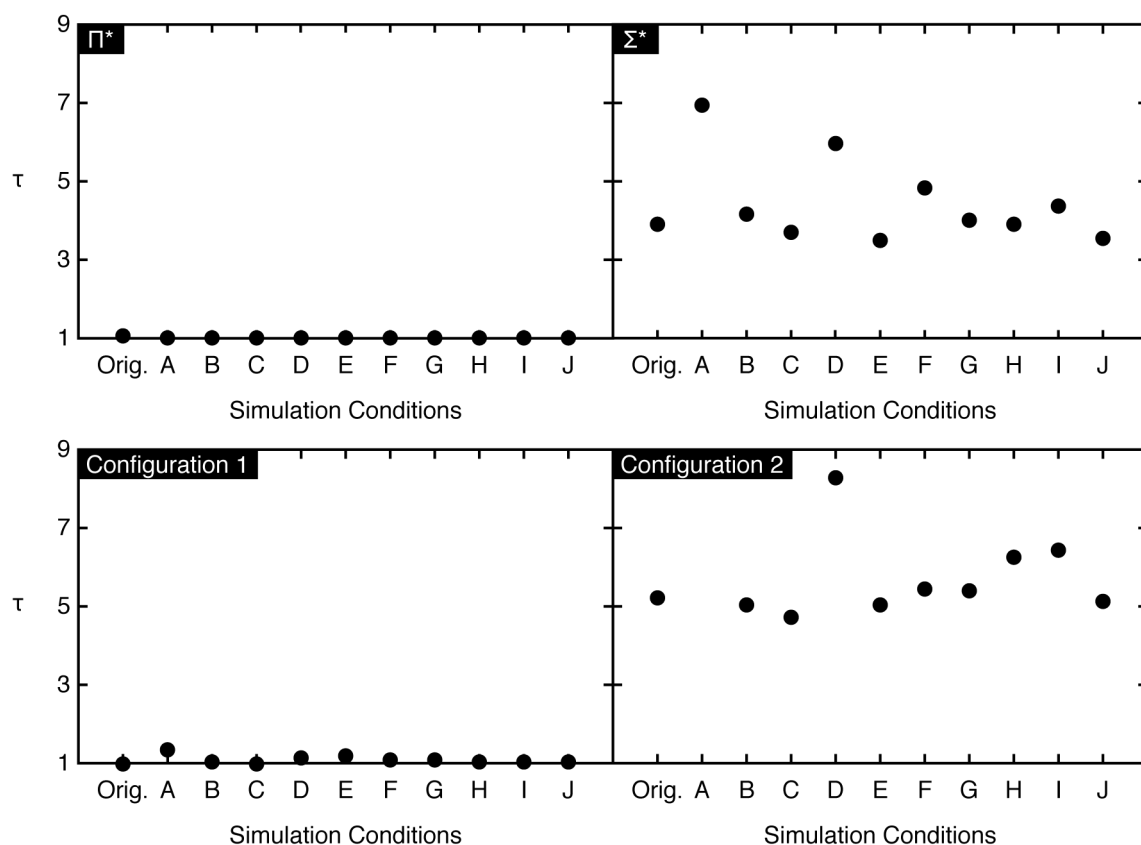


Figure 6.17: The effect of perturbing the GULP parameters on the swelling response. Ten sets of relaxation conditions (A–J of Table 6.2) were applied to the Π^* and Σ^* topologies, along with two disordered topologies, where $x = 0.5$, displaying τ values of 1.000 and 5.205 in the original study (Configuration 1 and Configuration 2 respectively). Under the relaxation conditions of A the disordered entanglement with a large swelling capacity (Configuration 2) displayed a phantom move (*i.e.* a change in topology) so was discounted from this study.

ordered topologies with $x = 0.5$ are possible in principle, that being said, the probability of such an event is small and crucially all the entanglements in this study with $0 \leq x \leq 1$ exhibit trivial $P1$ symmetry, and as such, are clearly not ordered. Second, the approach used to generate disordered entanglements is limited to a single parent unit cell with $Ia\bar{3}d$ symmetry; consequently, only a small sample of disordered entanglement topologies are accessible. A simple approach to enlarge the diversity of topologies is through the use of supercells, which would give increasingly realistic approximants of disordered entanglements. However, this approach is limited by the computational efficiency of the structural relaxation procedure. Unfortunately, the simulations in this study required significant computational time (around 1 week per configuration), and as such, the studies of the swelling behaviour of supercell models of fibre entanglements was not explored. However, preliminary investigations have shown that the swelling behaviours of disordered entanglements within a $2 \times 1 \times 1$ supercell are similar to those calculated in the main study and, as such, the fundamental behaviour is unaffected. Nevertheless, the limited sample size of disordered topologies implicitly suggests that only the lower bound of τ has been established. Indeed, there may be more complex disordered entanglements which exhibit far superior swelling responses. Moreover, only isotropic swelling has been considered in this study. Correspondingly, it is anticipated that anisotropic changes in the lattice parameters would increase the swelling response as the swelling mechanism would no longer be restricted by the cubic nature of the cell. Overall, this study implies that when engineering materials with dilatant properties, assembling specific complex topologies would be an effective design strategy for enhancing mechanical response, in contrast to the established approach of targeting simple ordered topologies.

The transformation from an open pore entanglement to the dense form bears a conceptual similarity to the ‘tension’ description for negative thermal expansion (NTE), wherein a material unconventionally contracts upon heating [428, 429]. Here, the low energy vibrations involve a flexing of the originally-linear bonding arrangements.

At higher temperatures, the amplitude of these low-energy modes increases, causing the structure to fold in on itself and reduce in volume [Fig. 6.18]. Under this regime, the existence of NTE relies simply on the existence of low-frequency phonons which enable a collective bond flexing mechanism to take place, as found in materials such as $\text{Zn}(\text{CN})_2$ [64] and ZrW_2O_8 [429]. Indeed, the link between the negative thermal expansion behaviour of $\text{Zn}(\text{CN})_2$ and the deviations from linearity of the Zn–C–N–Zn linkages—*i.e.* curvature—is observable within pair distribution function data [430]. In much the same way, this study reveals that an increase in fibre curvature is able to reduce the volume of disordered fibre packings. In this comparison, the $L_{\min}$ structure would contain bent linkages, representing the denser, high temperature form of these NTE materials, and the $L_{\max}$ configuration the low-temperature, straight-linkage, less dense form [Fig. 6.18]. Similar parallels can also be drawn to the auxetic (negative Poisson’s ratio) behaviour of amorphous foams [259, 420, 431]. The key challenge for both fields involves a shared goal: to understand how disordered topologies can exhibit these collective mechanical responses, whether it be the swelling of fibre entanglements such as keratin [383] or NTE of amorphous materials (*e.g.* silica [432] and liquid water [433]). Indeed these examples help to illustrate that, while the extreme swelling capacity of disordered entanglements may initially be counter-intuitive, the collective mechanical responses of disordered structures is not a wholly unfamiliar phenomenon.

This study has also established a methodology to introduce disorder into ordered weavings in a quantifiable manner. This approach is sufficiently general as to be applicable to other rod arrangements. At its core the generation of disordered entanglements involves the introduction of sensible changes in the local structure to affect the fibre topology. As such, this could also be used to introduce quantifiable topological changes into other rod packings *e.g.* Γ or Π^+ . Furthermore, this generalised methodology could also be adapted to generate disordered topologies of three-dimensional networks—*e.g.* *a*-Si [154]—by increasing the connectivity of a

given node above the current value of two. From these topological representations—and their known deviation from ordered systems—it would be possible to begin developing understanding of physical properties for which topology is known to be an important factor such as photonic properties [434], phase behaviour [435, 436] and porosity and hardness in disordered framework materials [155, 437, 438]. However, in cases where these network topologies were subject to a structural relaxation procedure, it would be extremely difficult to check for changes in the network topology by inspection. Moreover, the structural relaxations would require much longer running times due to the increased number of atoms within the unit cell.

A good candidate for such a study lies in the blue phases of cholesteric liquid crystals. Two ordered phases are well characterised—BP-1 and BP-2—which are Π^+ and Π^* rod packings of self-assembled double-twisted cylinders—with the structure of the third phase (BP-III, also known as blue fog) still poorly-understood [439]. BP-III is known to be disordered and has previously been theorised as a spaghetti-like entanglement of curved fibres [440]—as yet this proposed model is unconfirmed; other candidates including a quasicrystal [441, 442] and a disordered network [187, 443] are yet to be discounted. The modelling of BP-III as an entanglement has been

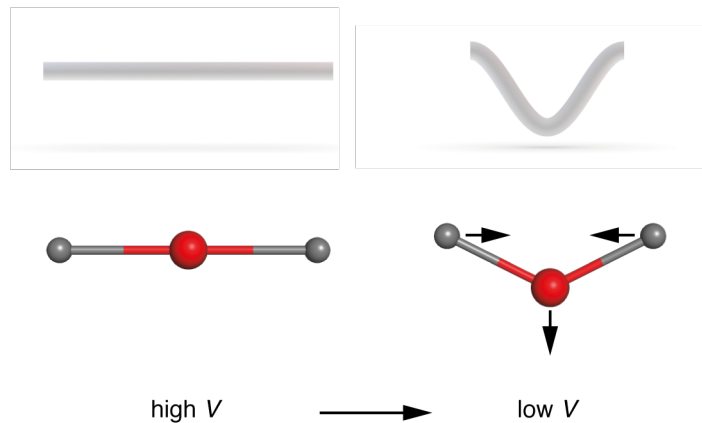


Figure 6.18: Fibre curvature and negative thermal expansion. The relationship between the variation of fibre curvature (top) and the tension mechanism of negative thermal expansion (bottom). In negative thermal expansion materials an increase of temperature acts to increase transverse displacements, reducing volume by increasing the curvature of the framework.

previously been particularly challenging but is now potentially approachable using the methodology presented in this chapter.

Chapter 7

Conclusions and future work

This thesis began by detailing the well-established links between crystalline order and the physical behaviours of a material including vibrational, electronic and optical properties. By comparison, the current understanding of disorder–property relationships is less well-developed. Firstly, disorder introduces structural complexity, which is often difficult to interpret in a systematic manner. Moreover, in some cases, approaches to understand material properties have been developed for crystalline materials *i.e.* where the methodology is reliant upon a unit cell description of the structure. As such, the work presented in this thesis has aimed to tackle three questions: (i) Can a unified approach for highly constrained disorder be developed? (ii) Do the disorder correlations in these systems produce characteristic scattering behaviour to aid the interpretation of experimental data? (iii) What effect does this highly constrained disorder have on the physical properties of a material?

In Chapter 3 the procrySTALLine state was introduced. This classification of disorder represents a generalisation of ice-rules, in which different forms of strongly-correlated disorder could be categorised. Here, the methodology to produce procrySTALLine configurations was set out—a high symmetry topological template (*e.g.* the square net) is decorated with sensible low-symmetry building units which are connected with strict local bonding constraints. The procrySTALLine phases derived from six high symmetry nets (square, hexagonal, triangular, primitive, diamond and pyrochlore) were detailed along with their simulated scattering behaviour. Here, the form of the diffuse scattering is different from one procrySTALLine phase to the next and, as such, acts as a characteristic signature of the local bonding constraints. Correspondingly, physical realisations of the procrySTALLine state have been identified either directly from the literature or via experimental characterisation techniques

including powder and single-crystal diffraction, pair distribution function measurements and microscopy . Indeed, the geometrical nature of the procrySTALLine classification aids the comparison of disordered systems in a wide variety of scientific areas. For instance, the triangular Ising antiferromagnet and the hydrogen-bonding network formed by TPTC molecules both belong to the same procrySTALLine phase, $\mathbf{H}_2$, and as such, share similar characteristics including scattering behaviour and ground state entropies.

The remaining results presented in this thesis were concerned with understanding the effect of strongly-correlated disorder on the physical behaviours of a material. Initially, the vibrational properties of disordered structures were considered, with the SCLD method being presented in Chapter 4. Here, the phonon modes for a large supercell representation of a structure at the Γ point are determined using conventional lattice dynamical approaches. The corresponding eigenvectors are then projected upon the Brillouin zone of the parent structure, where allowed $\mathbf{k}$ -points are determined by the size and shape of the supercell. In this way, the SCLD method allows the determination of the extent and nature of disorder-induced phonon broadening. As a proof-of-concept, this methodology was applied to a handful of very simple case studies, which demonstrated the expected result, that the form of the phonon broadening was sensitive to the type of disorder—*e.g.* masses or bond strengths—and its correlations.

Following the development of the SCLD approach, this methodology was then applied to systems containing procrySTALLine disorder (Chapter 5). In the initial studies contained within this chapter, two main effects were evident. On the one hand, for some procrySTALLine phases (*e.g.* $\mathbf{C}_3\mathbf{M}$) the form of the disorder-induced phonon broadening was essentially indistinguishable to that of a randomly disordered system with an equivalent average structure, despite the presence of strongly-correlated disorder. On the other hand, procrySTALLine phases containing distinct longer-range features (*e.g.* $\mathbf{C}_3\mathbf{F}$) gave phonon spectra which were fundamentally different in their

basic form from that of the average structure and its randomly disordered counterpart. A particular feature observed in this study was the opening of phononic band gaps. Subsequent studies into the electronic and photonic band structure of procrystalline systems also revealed the emergence of gapped behaviour, in turn developing a relationship between the disorder correlations and the electronic and optical properties, respectively. A similar effect was further demonstrated to occur in the presence of a dense decoration of dimers, corresponding to the $\mathbf{C}_1$ and $\mathbf{S}_1$ procrystalline states, where again phononic and photonic band gaps were observed.

The research in Chapter 6 was concerned with the swelling responses of disordered fibre entanglements. In the limit of ordered weavings, the arrangement of fibres is known to have a dramatic impact on its swelling properties. For instance, the Π^* weaving cannot swell, whereas the Σ^* topology can admit a five-fold decrease in volume from its most-porous form, so there existed a natural question as to the impact of disorder on the swelling response. In this study, a continuum of states was laid out, with bounding topologies of Π^* and Σ^* —*i.e.* with extremely different swelling ratios. The intermediate disordered topologies were then generated in a similar fashion to those of the procrystalline states, *i.e.* a high-symmetry template decorated with specific geometries of low-symmetry building units connected by linear linkers. The swelling ratios were determined through a structural relaxation methodology which revealed two effects: (i) for many of the disordered systems, the swelling response was quenched as the topology deviated from that of Σ^* ; (ii) a subset of disordered entanglements were able to exhibit a large swelling ratio, in some cases beyond that of Σ^* . In summary, while in many cases, the disorder introduced knots which prevented the system from swelling, some disordered configurations were found to admit cooperative rearrangements of the fibres.

So what future directions emerge from the work presented in this thesis? Models containing procrystalline disorder have been shown to produce changes in the vibrational, electronic and photonic band structure which adds importance to seeking

new ways to make physical realisations of specific procrySTALLine phases. Here, the design of procrySTALLine phases will rely upon the geometry of the local unit and inspiration for potential candidates of procrySTALLine phases can be drawn from the physical realisations detailed in Chapter 3. Correspondingly, features such as molecular geometry (TPTC molecules) and nanoparticle shape (domino packings) emerge as interesting avenues to explore in this regard.

Additionally, the calculation of disorder-induced phonon coupling through the SCLD method may potentially be of importance in the development of new design strategies for thermoelectric materials. It is well documented that it is extremely difficult to reduce the thermal transport of a material—*i.e.* broaden the phonons responsible for thermal conduction, which are usually the low-frequency modes [67]—while retaining/accentuating its electrical conductivity. The preliminary work using the SCLD method has shown that correlated disorder can impact the broadening of phonon branches in a highly specific manner—both in energy and region of reciprocal space. Electron-phonon coupling is also a function of wave-vector. As such, it may be possible to target disorder-phonon coupling (low thermal conductivity) in one region of reciprocal space while minimising electron-phonon coupling in a separate region to give high electronic conductivity. This set of circumstances would therefore offer a route to the highly sought after ‘phonon-glass electron-crystal’ state. Correspondingly, a comprehensive study to investigate whether correlated disorder could selectively broaden only the low-energy phonons in these regions of reciprocal space could be of interest to the thermoelectric community.

Bibliography

- [1] T. Hahn, *International Tables for Crystallography. Volume A, Space Group Symmetry* (Kluwer Academic, 2002).
- [2] R. E. Newnham, *Properties of materials* (Oxford University Press, 2005).
- [3] N. A. Benedek, C. J. Fennie, *Phys. Rev. Lett.* **106**, 107204 (2011).
- [4] J.-R. Li, R. J. Kuppler, H.-C. Zhou, *Chem. Soc. Rev.* **38**, 1477 (2009).
- [5] M. M. J. Treacy, K. B. Borisenko, *Science* **335**, 950 (2012).
- [6] D. A. Keen, A. L. Goodwin, *Nature* **521**, 303 (2015).
- [7] P. M. M. Thygesen et al., *Phys. Rev. B* **95**, 174107 (2017).
- [8] Y. Dubi, Y. Meir, Y. Avishai, *Nature* **449**, 876 (2007).
- [9] R. Comès, M. Lambert, A. Guinier, *Acta Crystallogr. A* **26**, 244 (1970).
- [10] E. S. Božin, C. D. Malliakas, P. Souvatzis, T. Proffen, N. A. Spaldin, M. G. Kanatzidis, S. J. L. Billinge, *Science* **330**, 1660 (2010).
- [11] M. Jang, Y. Horie, A. Shibukawa, J. Brake, Y. Liu, S. M. Kamali, A. Arbabi, H. Ruan, A. Faraon, C. Yang, *Nat. Photon.* **12**, 84 (2018).
- [12] P. W. Anderson, *Mater. Res. Bull.* **8**, 153 (1973).
- [13] G. Baskaran, *Curr. Trends Sci.* **73**, 279 (2009).
- [14] L. Pauling, *J. Am. Chem. Soc.* **51**, 1010 (1929).
- [15] A. F. Wells, *Structural Inorganic Chemistry* (Clarendon Press, 1984).
- [16] J. B. Goodenough, *Phys. Rev.* **98**, 391 (1955).
- [17] J. D. Dunitz, L. E. Orgel, *J. Phys. Chem. Solids* **3**, 318 (1957).
- [18] M. D. Sturge, *Solid State Phys.* **20**, 91 (1968).
- [19] J. J. Wolff, *Angew. Chem. Int. Ed.* **35**, 2195 (1996).
- [20] G. R. Desiraju, *Angew. Chem. Int. Ed.* **34**, 2311 (1995).
- [21] G. Day, *Cryst. Rev.* **17**, 3 (2010).
- [22] M. A. Neumann, F. J. J. Leusen, J. Kendrick, *Angew. Chem. Int. Ed.* **47**, 2427 (2008).
- [23] L. W. Finger, R. M. Hazen, H. K. Mao, P. M. Bell, *Appl. Phys. Lett.* **39**, 892 (1981).

- [24] W. H. Keesom, H. H. Mooy, *Nature* **125**, 889 (1930).
- [25] G. Natta, G. Nasini, *Nature* **125**, 457 (1930).
- [26] W. I. F. David, R. M. Ibberson, J. C. Matthewman, K. Prassides, T. J. S. Dennis, J. P. Hare, H. W. Kroto, R. Taylor, D. R. M. Walton, *Nature* **353**, 147 (1991).
- [27] V. S. Reddy, S. K. Natchiar, P. L. Stewart, G. R. Nemerow, *Science* **329**, 1071 (2010).
- [28] A. Bravais, *J. Ecole Polytech.* **19**, 1 (1850).
- [29] F. Bloch, *Z. Phys.* **52**, 555 (1928).
- [30] M. T. Dove, *Introduction to Lattice Dynamics* (Cambridge University Press, 1993).
- [31] F. Bloch, *Z. Phys.* **61**, 206 (1930).
- [32] J. D. Joannopoulos, R. D. Meade, J. N. Winn, *Photonic crystals: Molding the flow of light* (Princeton University Press, 1995).
- [33] G. L. Dirichlet, *J. Reine Angew. Math.* **40**, 209 (1850).
- [34] G. Voronoi, *J. Reine Angew. Math.* **134**, 198 (1908).
- [35] W. Setyawan, S. Curtarolo, *Comp. Mater. Sci.* **49**, 299 (2010).
- [36] A. P. Cracknell, B. L. Davies, S. C. Miller, W. F. Love, *Kronecker Product Tables. Vol. 1. General Introduction and Tables of Irreducible Representations of Space Groups* (IFI/Plenum, 1979).
- [37] A. Van de Walle, *Nat. Mater.* **7**, 455 (2008).
- [38] W. H. Bragg, W. L. Bragg, *Proc. Roy. Soc. Lond. A* **88**, 428 (1913).
- [39] M. T. Dove, *Structure and dynamics* (Oxford University Press, 2003).
- [40] H. G. Smith et al., *Neutron Inelastic Scattering (Vol. I)* (Vienna: Academic, 1968).
- [41] K. Shimada, *Phys. Status Solidi B* **61**, 325 (1974).
- [42] A. D. B. Woods, B. N. Brockhouse, R. H. March, A. T. Stewart, R. Bowers, *Phys. Rev.* **128**, 1112 (1962).
- [43] R. A. Cowley, A. D. B. Woods, G. Dolling, *Phys. Rev.* **150**, 487 (1966).
- [44] J. R. D. Copley, B. N. Brockhouse, *Can. J. Phys.* **51**, 657 (1973).
- [45] Y. Endoh, G. Shirane, J. Skalyo Jr., *Phys. Rev. B* **11**, 1681 (1975).
- [46] J. Skalyo Jr., Y. Endoh, G. Shirane, *Phys. Rev. B* **9**, 1797 (1974).
- [47] N. A. Lurie, G. Shirane, J. Skalyo Jr., *Phys. Rev. B* **9**, 5300 (1974).
- [48] Y. Fujii, N. A. Lurie, R. Pynn, G. Shirane, *Phys. Rev. B* **10**, 3647 (1974).
- [49] A.-T. Petit, P.-L. Dulong, *Ann. Chim. Phys.* **10**, 395 (1819).
- [50] M. J. Buckingham, M. R. Schafroth, *Proc. Phys. Soc. A* **67**, 828 (1954).
- [51] A. Einstein, *Ann. Phys. (Berlin)* **327**, 180 (1907).

- [52] P. J. W. Debye, *Ann. Phys. (Berlin)* **344**, 789 (1912).
- [53] D. R. Lide, *Handbook of Chemistry and Physics* (CRC Press, 2003).
- [54] G. Burns, *Solid State Physics* (Academic Press, 1985).
- [55] P. M. Morse, *Phys. Rev.* **34**, 87 (1929).
- [56] J. E. Jones, *Proc. R. Soc. A* **106**, 463 (1924).
- [57] E. Gruneisen, *Ann. Phys. (Berlin)* **344**, 257 (1912).
- [58] M. Baise, P. M. Maffettone, F. Trouselet, N. P. Funnell, F.-X. Coudert, A. L. Goodwin, *arXiv:1804.04906* (2018).
- [59] J. W. Zwanziger, *Phys. Rev. B* **76**, 052102 (2007).
- [60] K. D. Hammonds, A. Bosenick, M. T. Dove, V. Heine, *Am. Mineral.* **83**, 476 (1998).
- [61] M. T. Dove, *Am. Mineral.* **82**, 213 (1997).
- [62] A. K. A. Pryde, K. D. Hammonds, M. T. Dove, V. Heine, J. D. Gale, M. C. Warren, *Phase Transit.* **61**, 141 (1997).
- [63] M. G. Tucker, A. L. Goodwin, M. T. Dove, D. A. Keen, S. A. Wells, J. S. O. Evans, *Phys. Rev. Lett.* **95**, 255501 (2005).
- [64] A. L. Goodwin, C. J. Kepert, *Phys. Rev. B* **71**, 140301 (2005).
- [65] R. E. Peierls, *Ann. Phys.* **395**, 1055 (1929).
- [66] C. Kittel, *Introduction to Solid State Physics* (Wiley, 2004).
- [67] A. L. Pope, T. M. Tritt, *Thermal conductivity: Theory, properties and applications* (Kluwer Academic, 2004).
- [68] G. Tan, L.-D. Zhao, M. G. Kanatzidis, *Chem. Rev.* **116**, 12123 (2016).
- [69] J. Yang, L. Xi, W. Qiu, L. Wu, X. Shi, L. Chen, J. Yang, W. Zhang, C. Uher, D. J. Singh, *Npj Comput. Mater.* **2**, 15015 (2016).
- [70] M. Christensen, A. Abrahamsen, N. Christensen, F. Juranyi, N. Andersen, K. Lefmann, J. Andreasson, C. Bahl, B. Iversen, *Nat. Mater.* **7**, 811 (2008).
- [71] G. J. Snyder, E. S. Toberer, *Nat. Mater.* **7**, 105 (2008).
- [72] M. H. Elsheikh, D. A. Shnawah, M. F. M. Sabri, S. B. M. Said, M. H. Hassan, M. B. A. Bashir, M. Mohamad, *Renew. Sustain. Energy Rev.* **30**, 337 (2014).
- [73] O. Delaire, J. Ma, K. Marty, A. F. May, M. A. McGuire, M.-H. Du, D. J. Singh, A. Podlesnyak, G. Ehlers, M. D. Lumsden, B. C. Sales, *Nat. Mater.* **10**, 614 (2011).
- [74] L. N. Cooper, *Phys. Rev.* **104**, 1189 (1956).
- [75] J. Bardeen, L. N. Cooper, J. R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957).
- [76] A. M. Glazer, S. A. Mabud, *Acta Crystallogr. B* **34**, 1605 (1978).
- [77] G. Burns, B. A. Scott, *Phys. Rev. Lett.* **25**, 167 (1970).
- [78] G. Shirane, J. D. Axe, J. Harada, J. P. Remeika, *Phys. Rev. B* **2**, 155 (1970).

- [79] G. Dolino, *Phase Transit.* **21**, 59 (1990).
- [80] R. A. Cowley, W. J. L. Buyers, G. Dolling, *Solid State Commun.* **7**, 181 (1969).
- [81] G. Shirane, Y. Yamada, *Phys. Rev.* **177**, 858 (1969).
- [82] J. Robertson, *Prog. Solid State Chem.* **21**, 199 (1991).
- [83] E. J. W. Verwey, P. W. Haayman, *Physica* **8**, 979 (1941).
- [84] H. P. Rooksby, B. T. M. Willis, *Acta Crystallogr.* **6**, 565 (1953).
- [85] N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements* (Butterworth-Heinemann, 1997).
- [86] R. E. Peierls, *Quantum Theory of Solids* (Clarendon Press, 1955).
- [87] H. A. Jahn, E. Teller, *Proc. Roy. Soc. A* **161**, 220 (1937).
- [88] R. M. Wentzcovitch, W. W. Schulz, P. B. Allen, *Phys. Rev. Lett.* **72**, 3389 (1994).
- [89] J. B. Goodenough, *Phys. Rev.* **117**, 1442 (1960).
- [90] J. Ashkenazi, W. E. Pickett, H. Krakauer, C. S. Wang, B. M. Klein, S. R. Chubb, *Phys. Rev. Lett.* **62**, 2016 (1989).
- [91] P. W. Anderson, P. A. Lee, M. Saitoh, *Solid State Commun.* **13**, 595 (1973).
- [92] P. Weiss, *J. Phys. (Paris)* **6**, 667 (1907).
- [93] L. Néel, *Proc. Phys. Soc. A* **65**, 869 (1952).
- [94] P. Bak, M. H. Jensen, *J. Phys. C* **13**, L881 (1980).
- [95] P. F. Damasceno, M. Engel, S. C. Glotzer, *Science* **337**, 453 (2012).
- [96] M. A. Boles, M. Engel, D. V. Talapin, *Chem. Rev.* **116**, 11220 (2016).
- [97] Y. Wang, Y. Wang, X. Zheng, E. Ducrot, J. S. Yodh, M. Weck, D. J. Pine, *Nat. Commun.* **6**, 8253 (2015).
- [98] V. A. Tolmachev, E. V. Astrova, J. A. Pilyugina, T. S. Perova, R. A. Moore, J. K. Vij, *Opt. Mater.* **27**, 831 (2005).
- [99] M. Campbell, D. N. Sharp, M. T. Harrison, R. G. Denning, A. J. Turberfield, *Nature* **404**, 53 (2000).
- [100] R. Halir et al., *Laser Photon. Rev.* **9**, 25 (2015).
- [101] K. M. Ho, C. T. Chan, C. M. Soukoulis, *Phys. Rev. Lett.* **65**, 3152 (1990).
- [102] T. R. Welberry, T. Weber, *Crystallogr. Rev.* **22**, 2 (2016).
- [103] T. Egami, S. J. L. Billinge, *Underneath the Bragg Peaks* (Pergamon, 2012).
- [104] C. A. Young, A. L. Goodwin, *J. Mater. Chem.* **21**, 6464 (2011).
- [105] D. Shechtman, I. Blech, D. Gratias, J. W. Cahn, *Phys. Rev. Lett.* **53**, 1951 (1984).
- [106] T. Janssen, A. Janner, *Acta Crystallogr. B* **70**, 617 (2014).

- [107] H. Maynard-Casely, *To the ends of the earth and beyond—the search for ‘impossible’ quasicrystals* (The Conversation, 2012).
- [108] Z. V. Vardeny, A. Nahata, A. Agrawal, *Nat. Photon.* **7**, 177 (2013).
- [109] R. Penrose, *Math. Intelligencer* **2**, 32 (1979).
- [110] A. L. Mackay, *Physica A* **114**, 609 (1982).
- [111] P. Kramer, T. Kramer, *From quasicrystals to more complex systems (Ch. 4)* (Springer-Verlag, 1998).
- [112] S. Coates, J. A. Smerdon, R. McGrath, H. R. Sharma, *Nat. Commun.* **9**, 3435 (2018).
- [113] G. Ungar, Y. Liu, X. Zenx, V. Percec, W.-D. Cho, *Science* **299**, 1208 (2003).
- [114] X. Zeng, G. Ungar, V. Percec, A. E. Dulcey, J. K. Hobbs, *Nature* **428**, 157 (2004).
- [115] D. V. Talapin, E. V. Shevchenko, M. I. Bodnarchuk, X. Ye, J. Chen, C. B. Murray, *Nature* **461**, 964 (2009).
- [116] S. Lee, M. J. Bluemle, F. S. Bates, *Science* **330**, 349 (2010).
- [117] K. Hayashida, T. Dotera, A. Takano, Y. Matsushita, *Phys. Rev. Lett.* **98**, 195502 (2007).
- [118] S. Fischer, A. Exner, K. Zielske, J. Perlich, S. Deloudi, W. Steurer, P. Lindner, S. Förster, *Proc. Natl. Acad. Sci.* **108**, 1810 (2011).
- [119] L. Bindi, P. J. Steinhardt, N. Yao, P. J. Lu, *Science* **324**, 1306 (2009).
- [120] A. Haji-Akbari, M. Engel, A. S. Keys, X. Zheng, R. G. Petschek, P. Palffy-Muhoray, S. C. Glotzer, *Nature* **462**, 773 (2009).
- [121] T. Janssen, *From quasicrystals to more complex systems (Ch. 1)* (Springer-Verlag, 1998).
- [122] N. Rivier, *J. Non-Cryst. Solids* **153**, 458 (1993).
- [123] J. J. Lovelace, P. D. Simone, V. Petříček, G. E. O. Borgstahl, *Acta Crystallogr. D* **69**, 1062 (2013).
- [124] J. Hadermann, O. Pérez, N. Créon, C. Michel, M. Hervieu, *J. Mater. Chem.* **17**, 2344 (2007).
- [125] V. Heine, R. M. Lynden-Bell, J. Desmond, C. McConnell, I. R. McDonald, *Z. Phys. B Condens. Matter* **56**, 229 (1984).
- [126] A. M. Abakumov, R. Erni, A. A. Tsirlin, M. D. Rossell, D. Batuk, G. Nénert, G. Van Tendeloo, *Chem. Mater.* **25**, 2670 (2013).
- [127] R. Erni, A. M. Abakumov, M. D. Rossell, D. Batuk, A. A. Tsirlin, G. Nénert, G. Van Tendeloo, *Nat. Mater.* **13**, 216 (2014).
- [128] D. A. Rusakov, A. M. Abakumov, K. Yamaura, A. A. Belik, G. Van Tendeloo, E. Takayama-Muromachi, *Chem. Mater.* **23**, 285 (2011).
- [129] C. Benkert, *J. Phys. C* **20**, 3369 (1987).

- [130] P. Launois, F. Moussa, M. H. Lemée-Cailleau, H. Cailleau, *Phys. Rev. B* **40**, 5042 (1989).
- [131] J. L. Baudour, M. Sanquer, *Acta Crystallogr. B* **39**, 75 (1983).
- [132] V. Heine, S. L. Price, *J. Phys. C* **18**, 5259 (1985).
- [133] B. Doudin, G. Chapuis, *Acta Crystallogr. B* **46**, 180 (1990).
- [134] P. Murault, *J. Phys. C* **19**, 1689 (1986).
- [135] K. D. M. Harris, J. M. Thomas, *J. Chem. Soc., Faraday Trans.* **86**, 2985 (1990).
- [136] A. E. Smith, *Acta Crystallogr.* **5**, 224 (1952).
- [137] R. Forst, H. Jagodzinski, H. Boysen, F. Frey, *Acta Crystallogr. B* **43**, 187 (1987).
- [138] X. Wang, A. J. Jacobsen, *J. Solid State Chem.* **236**, 230 (2015).
- [139] A. L. Goodwin, B. J. Kennedy, C. J. Kepert, *J. Am. Chem. Soc.* **131**, 6334 (2009).
- [140] K. Krogmann, *Angew. Chem. Int. Ed.* **8**, 35 (1969).
- [141] R. Comès, M. Lambert, H. Launois, H. R. Zeller, *Phys. Rev. B* **8**, 571 (1973).
- [142] M. Verweft, G. Van Tendeloo, D. G. Hinks, B. Dabrowski, D. R. Richards, A. W. Mitchell, D. T. Marx, S. Pei, J. D. Jorgensen, *Phys. Rev. B* **44**, 9547 (1991).
- [143] S. Hull, *Rep. Prog. Phys.* **67**, 1233 (2004).
- [144] A. J. Stone, D. J. Wales, *Chem. Phys. Lett.* **128**, 501 (1986).
- [145] A. G. Martin, *A basketmaker's approach to structural morphology* (International Association of Spatial and Shell Structures, 2015).
- [146] M. O'Keeffe, W. J. Moore, *J. Phys. Chem.* **65**, 1438 (1961).
- [147] A. C. Pierre, D. R. Uhlmann, *J. Non-Cryst. Solids* **82**, 271 (1986).
- [148] S. Guo, C. T. Liu, *Prog. Nat. Sci.: Mater. Int.* **21**, 433 (2011).
- [149] J. H. Wendorff, *Polymer* **23**, 543 (1982).
- [150] M. Shiojiri, Y. Saito, H. Okada, H. Sasaki, *Jap. Soc. Appl. Phys.* **18**, 1931 (1979).
- [151] S. Torquato, F. H. Stillinger, *Rev. Mod. Phys.* **82**, 2633 (2010).
- [152] G. Van den Mooter, *Drug Discov. Today: Technol.* **9**, e79 (2012).
- [153] S. Baghel, H. Cathcart, N. J. O'Reilly, *J. Pharm. Sci.* **105**, 2527 (2016).
- [154] M. J. Cliffe, A. P. Bartók, R. N. Kerber, C. P. Grey, G. Csányi, A. L. Goodwin, *Phys. Rev. B* **95**, 224108 (2017).
- [155] T. D. Bennett et al., *Phys. Rev. Lett.* **104**, 115503 (2010).
- [156] C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **359**, 710 (1992).
- [157] H. Sillescu, *J. Non-Cryst. Solids* **243**, 81 (1999).

- [158] P. G. Debendetti, F. H. Stillinger, *Nature* **410**, 259 (2001).
- [159] S. F. Edwards, P. W. Anderson, *J. Phys. F: Met. Phys.* **5**, 965 (1975).
- [160] P. W. Anderson, *J. Less-Common Met.* **62**, 291 (1978).
- [161] T. D. Bennett, A. K. Cheetham, *Acc. Chem. Res.* **47**, 1555 (2014).
- [162] A. K. Cheetham, T. D. Bennett, F.-X. Coudert, A. L. Goodwin, *Dalton Trans.* **45**, 4113 (2016).
- [163] Y. Zhang, T. T. Zuo, Z. Tang, M. C. Gao, K. A. Dahmen, P. K. Liaw, Z. P. Lu, *Prog. Mater. Sci.* **61**, 1 (2014).
- [164] L. Owen, H. Y. Playford, H. J. Stone, M. G. Tucker, *Acta Mater.* **115**, 155 (2016).
- [165] L. Owen, H. Y. Playford, H. J. Stone, M. G. Tucker, *Acta Mater.* **125**, 15 (2017).
- [166] A. J. Carmichael, C. Hardacre, J. D. Holbery, M. Nieuwenhuyzen, K. R. Seddon, *Mol. Phys.* **99**, 795 (2001).
- [167] A. M. Smith, A. A. Lee, S. Perkin, *J. Phys. Chem. Lett.* **7**, 2157 (2016).
- [168] C. Tubandt, E. Lorenz, *Z. Phys. Chem.* **87**, 513 (1914).
- [169] L. W. Strock, *Z. Phys. Chem.* **25**, 441 (1934).
- [170] G. Collin, P. Boilot, J. P. Colombar, R. Comès, *Phys. Rev. B* **34**, 5838 (1986).
- [171] G. Collin, J. P. Boilot, R. Comès, *Phys. Rev. B* **34**, 5850 (1986).
- [172] C. E. Derrington, M. O’Keeffe, *Nat. Phys. Sci.* **246**, 44 (1973).
- [173] H. A. Harwig, A. G. Gerards, *J. Solid State Chem.* **26**, 265 (1978).
- [174] T. Takahashi, H. Iwahara, *Mater. Res. Bull.* **13**, 1447 (1978).
- [175] T. H. Estell, S. N. Flengas, *Chem. Rev.* **70**, 339 (1970).
- [176] A. Wakagi, J. Kuwano, *J. Mater. Chem.* **4**, 973 (1994).
- [177] H. Rickert, *Electrochemistry of Solids* (Springer-Verlag, 1982).
- [178] C. R. A. Catlow, *Solid State Ion.* **12**, 67 (1984).
- [179] F. Reinitzer, *Monatsh. Chem.* **9**, 421 (1888).
- [180] S. Chandrasekhar, G. S. Ranganath, *Rep. Prog. Phys.* **53**, 57 (1990).
- [181] L. Wang, S. Huang, L. Lam, Z. Cheng, *Liq. Cryst. Today* **26**, 85 (2017).
- [182] G. W. Gray, S. W. Kelly, *J. Mater. Chem.* **9**, 2037 (1999).
- [183] S. Chandrasekhar, *Liquid Crystals* (Cambridge University Press, 1992).
- [184] L. Onsager, *Ann. N. Y. Acad. Sci.* **51**, 627 (1949).
- [185] M. D. A. Rahman, S. M. Said, S. Balamurugan, *Sci. Technol. Adv. Mater.* **16**, 033501 (2015).
- [186] M. Schadt, W. Helfrich, *Appl. Phys. Lett.* **18**, 127 (1971).

- [187] V. A. Belyakov, E. I. Demikhov, V. E. Dmitrienko, V. K. Dolganov, *Sov. Phys. JETP* **62**, 1173 (1985).
- [188] J. Timmermans, *J. Phys. Chem. Solids* **18**, 1 (1961).
- [189] T. Komatsu, M. Tachibana, K. Kojima, *Philos. Mag. A* **81**, 659 (2001).
- [190] M. T. Dove, G. Pawley, *J. Phys. C* **16**, 5969 (1983).
- [191] J. C. W. Folmer, R. L. Withers, T. R. Welberry, J. D. Martin, *Phys. Rev. B* **77**, 144205 (2008).
- [192] L. A. K. Staveley, *Ann. Rev. Phys. Chem.* **13**, 351 (1962).
- [193] A. S. Karas, J. Dshemuchadse, G. van Anders, S. C. Glotzer, *In Preparation* (2018).
- [194] D. R. MacFarlane, M. Forsyth, *Adv. Mater.* **19**, 957 (2001).
- [195] J. Luo et al., *Energy Environ. Sci.* **8**, 1276 (2015).
- [196] J. M. Pringle, *Phys. Chem. Chem. Phys.* **15**, 1339 (2013).
- [197] M. E. Fisher, *Phys. Rev.* **124**, 1664 (1961).
- [198] P. W. Kasteleyn, *J. Math. Phys.* **4**, 287 (1963).
- [199] V. Elser, *J. Phys. A: Math. Gen.* **17**, 1509 (1984).
- [200] D. A. Huse, W. Krauth, R. Moessner, S. L. Sondhi, *Phys. Rev. Lett.* **91**, 167004 (2003).
- [201] C. L. Henley, *J. Stat. Phys.* **89**, 483 (1997).
- [202] M. C. Gimenez, A. J. Ramirez-Pastor, *Phys. Rev. E* **94**, 032129 (2016).
- [203] L. Pauling, *J. Am. Chem. Soc.* **57**, 2680 (1935).
- [204] H. Cohn, R. Kenyon, J. Propp, *J. Am. Math. Soc.* **14**, 297 (2001).
- [205] H. W. J. Blote, H. J. Hilborst, *J. Phys. A* **15**, L631 (1982).
- [206] G. H. Wannier, *Phys. Rev.* **79**, 357 (1950).
- [207] R. D. Diehl, M. F. Toney, S. C. Fain Jr., *Phys. Rev. Lett.* **48**, 177 (1982).
- [208] M. O. Blunt, J. C. Russell, M. d. C. Giménez-López, J. P. Garrahan, X. Lin, M. Schröder, N. R. Champness, P. H. Beton, *Science* **322**, 1077 (2008).
- [209] S. T. Bramwell, M. J. P. Gingras, *Science* **294**, 1495 (2001).
- [210] A. Koda, R. Kadono, K. Ohishi, S. R. Saha, W. Higemoto, Y. Matsushita, Y. Ueda, *J. Phys. Condens. Matter* **17**, L257 (2005).
- [211] V. E. Fairbank, A. L. Thompson, R. I. Cooper, A. L. Goodwin, *Phys. Rev. B* **86**, 104113 (2012).
- [212] S. Torquato, F. H. Stillinger, *Phys. Rev. E* **68**, 041113 (2003).
- [213] Y. Jiao, T. Lau, H. Hatzikirou, M. Meyer-Hermann, J. C. Corbo, S. Torquato, *Phys. Rev. E* **89**, 022721 (2014).

- [214] E. C. Oğüz, J. E. S. Socolar, P. J. Steinhardt, S. Torquato, *Phys. Rev. B* **95**, 054119 (2017).
- [215] S. Getzin et al., *Proc. Natl. Acad. Sci.* **113**, 3551 (2016).
- [216] W. Man et al., *Proc. Natl. Acad. Sci.* **110**, 145886 (2013).
- [217] L. S. Froufe-Pérez, M. Engel, P. F. Damasceno, N. Muller, J. Haberko, S. C. Glotzer, F. Scheffold, *Phys. Rev. Lett.* **117**, 053902 (2016).
- [218] M. Florescu, K. Busch, J. P. Dowling, *Phys. Rev. B* **75**, 201101 (2007).
- [219] M. Florescu, S. Torquato, P. J. Steinhardt, *Proc. Natl. Acad. Sci.* **106**, 20658 (2009).
- [220] M. Florescu, S. Torquato, P. J. Steinhardt, *Phys. Rev. B* **80**, 155112 (2009).
- [221] W. Friedrich, P. Knipping, M. Laue, *Sitzungsberichte der Kgl. Bayer. Akad. der Wiss.* pp. 303–322 (1912).
- [222] M. Laue, *Sitzungsberichte der Kgl. Bayer. Akad. Der Wiss.* pp. 363–373 (1912).
- [223] W. Friedrich, *Phys. Z.* **14**, 1079 (1913).
- [224] W. H. Bragg, W. L. Bragg, *Proc. Roy. Soc. Lond. A* **89**, 277 (1913).
- [225] V. F. Sears, *Neutron News* **3**, 26 (1992).
- [226] K. Lonsdale, H. Smith, *Proc. Roy. Soc. Lond. A* **179**, 8 (1941).
- [227] K. Lonsdale, *Proc. Phys. Soc.* **54**, 314 (1942).
- [228] L. H. Thomas, T. R. Welberry, D. J. Goossens, A. P. Heerdegen, M. J. Gutmann, S. J. Teat, P. L. Lee, C. C. Wilson, J. M. Cole, *Acta Crystallogr. B* **63**, 663 (2007).
- [229] P. J. W. Debye, *Ann. Phys.* **348**, 49 (1913).
- [230] L. Brillouin, *Ann. Phys.* **9**, 88 (1922).
- [231] W. H. Zachariasen, *Phys. Rev.* **57**, 597 (1940).
- [232] T. R. Welberry, B. D. Butler, *J. Appl. Cryst.* **27**, 205 (1994).
- [233] T. R. Welberry, *Diffuse X-ray scattering and models of disorder* (Oxford University Press, 2004).
- [234] M. Paściak, T. R. Welberry, A. P. Heerdegen, V. Laguta, T. Ostapchuk, S. Leoni, J. Hlinka, *Phase Transit.* **88**, 273 (2015).
- [235] J. A. M. Paddison, H. Jacobsen, O. A. Petrenko, M. T. Fernández Díaz, P. P. Deen, A. L. Goodwin, *Science* **350**, 179 (2015).
- [236] P. Schaub, T. Weber, W. Steurer, *J. Appl. Cryst.* **44**, 134 (2011).
- [237] A. Simonov, T. Weber, W. Steurer, *J. Appl. Cryst.* **47**, 2011 (2014).
- [238] D. Silver et al., *Nature* **529**, 484 (2016).
- [239] P. P. Boyle, *J. Financ. Econ.* **4**, 323 (1977).
- [240] O. Breivik, A. Allen, *J. Mar. Syst.* **69**, 99 (2008).

- [241] D. A. Keen, R. L. McGreevy, *Nature* **344**, 423 (1990).
- [242] R. L. McGreevy, *J. Phys. Condens. Matter* **13**, R877 (2001).
- [243] A. P. Ramirez, A. Hayashi, R. J. Cava, R. Siddharthan, B. S. Shastry, *Nature* **399**, 333 (1999).
- [244] P. A. Flinn, G. M. McManus, *Phys. Rev.* **124**, 54 (1961).
- [245] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, E. Teller, *J. Chem. Phys.* **21**, 1087 (1953).
- [246] S. Kirkpatrick, C. D. Delatt Jr., M. P. Vecchi, *Science* **220**, 671 (1983).
- [247] S. V. Semenovskaya, K. A. Khachatryan, A. G. Khachatryan, *Acta Crystallogr. A* **41**, 268 (1985).
- [248] E. Anderson et al., *LAPACK User's Guide* (Society for Industrial and Applied Mathematics, 1999).
- [249] J. D. Gale, *J. Chem. Soc., Faraday Trans.* **93**, 629 (1997).
- [250] P. P. Ewald, *Ann. Phys.* **64**, 253 (1921).
- [251] S. G. Johnson, J. D. Joannopoulos, *Opt. Express* **8**, 173 (2001).
- [252] A. R. Overy, A. B. Cairns, M. J. Cliffe, A. Simonov, M. G. Tucker, A. L. Goodwin, *Nat. Commun.* **7**, 10445 (2016).
- [253] G. Algara-Siller, O. Lehtinen, F. C. Wang, R. R. Nair, U. Kaiser, H. A. Wu, A. K. Geim, I. V. Grigorieva, *Nature* **519**, 443 (2015).
- [254] M. Yang, J. Oró-Solé, J. A. Rodgers, A. B. Jorge, A. Fuertes, J. P. Attfield, *Nat. Chem.* **3**, 47 (2011).
- [255] P. J. Camp, A. Fuertes, J. P. Attfield, *J. Am. Chem. Soc.* **134**, 6762 (2012).
- [256] M. S. Senn, J. R. Wright, J. P. Attfield, *Nature* **481**, 173 (2012).
- [257] R. Comès, M. Lambert, A. Guinier, *Solid State Commun.* **6**, 715 (1968).
- [258] D. A. Keen, A. L. Goodwin, M. G. Tucker, M. T. Dove, J. S. O. Evans, W. A. Crichton, M. Brunelli, *Phys. Rev. Lett.* **98**, 225501 (2007).
- [259] R. Lakes, *Science* **235**, 1038 (1987).
- [260] D. R. Reid, N. Pashine, J. M. Wozniak, H. M. Jaeger, A. J. Liu, S. R. Nagel, J. J. de Pablo, *Proc. Natl. Acad. Sci.* **115**, E1384 (2018).
- [261] M. S. Senn, D. A. Keen, T. C. A. Lucas, J. A. Hriljac, A. L. Goodwin, *Phys. Rev. Lett.* **116**, 207602 (2016).
- [262] J. M. Ziman, *Models of Disorder* (Cambridge University Press, 1979).
- [263] L. S. Froufe-Pérez, M. Engel, J. J. Sáenz, F. Scheffold, *Proc. Natl. Acad. Sci.* **114**, 9570 (2017).
- [264] O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **423**, 705 (2003).

- [265] N. P. Funnell, M. T. Dove, A. L. Goodwin, S. Parsons, M. G. Tucker, *J. Phys. Condens. Matter* **25**, 454204 (2013).
- [266] G. Harburn, C. A. Taylor, T. R. Welberry, *Atlas of Optical Transforms* (Cornell University Press, 1975).
- [267] C. L. Henley, *Annu. Rev. Cond. Matter Phys.* **1**, 179 (2010).
- [268] M. J. Whitaker, C. Greaves, *J. Solid State Chem.* **215**, 171 (2014).
- [269] G. E. Bacon, R. S. Pease, *Proc. Roy. Soc. A* **220**, 397 (1953).
- [270] G. E. Bacon, R. S. Pease, *Proc. Roy. Soc. A* **230**, 359 (1955).
- [271] J. Kondev, *Phys. Rev. Lett.* **78**, 4320 (1997).
- [272] R. Moessner, S. L. Sondhi, E. Fradkin, *Phys. Rev. B* **65**, 024504 (2001).
- [273] R. Moessner, S. L. Sondhi, P. Chandra, *Phys. Rev. B* **64**, 144416 (2001).
- [274] E. Günther, R. Hagenmayer, M. Jansen, *Z. Anorg. Allg. Chem.* **626**, 1519 (2000).
- [275] E. Tostatti, P. Fazekas, *J. Phys. Coll.* **37**, 165 (1976).
- [276] L. Gross, F. Mohn, N. Moll, P. Liljeroth, G. Meyer, *Science* **235**, 1110 (2009).
- [277] A. M. Sweetman, S. P. Jarvis, H. Sang, I. Lekkas, Y. Wang, J. Wang, N. R. Champness, L. Kantorovich, P. Moriarty, *Nat. Commun.* **5**, 3931 (2014).
- [278] A. Stannard, J. C. Russell, M. O. Blunt, C. Salesiotis, M. d. C. Giménez-López, N. Taleb, M. Schroder, N. R. Champness, P. H. Beton, *Nat. Chem.* **4**, 112 (2012).
- [279] M. G. Francesconi, C. Greaves, *Supercond. Sci. Technol.* **10**, A29 (1997).
- [280] F. J. Berry, F. C. Coomer, C. Hancock, O. Helgason, E. A. Moore, P. R. Slater, A. J. Wright, M. F. Thomas, *J. Solid State Chem.* **184**, 1361 (2011).
- [281] A. A. Coelho, P. A. Chater, A. Kern, *J. Appl. Cryst.* **48**, 869 (2015).
- [282] A. L. Goodwin, M. T. Dove, A. M. Chippindale, S. J. Hibble, A. H. Pohl, A. C. Hannon, *Phys. Rev. B* **80**, 054101 (2009).
- [283] S. J. Hibble, A. M. Chippindale, E. J. Bilbé, E. Marelli, P. J. F. Harris, A. C. Hannon, *Inorg. Chem.* **50**, 104 (2011).
- [284] E. H. Wolpert, A. R. Overy, P. M. M. Thygesen, A. Simonov, M. S. Senn, A. L. Goodwin, *Phys. Rev. B* **97**, 134106 (2018).
- [285] R. Comès, M. Lambert, A. Guinier, *Solid State Commun.* **6**, 715 (1968).
- [286] M. Lambert, R. Comès, *Solid State Commun.* **7**, 305 (1969).
- [287] A. R. Overy, A. Simonov, P. A. Chater, M. G. Tucker, A. L. Goodwin, *Phys. Status Solidi B* **254**, 1600586 (2017).
- [288] P. B. Pereira, I. Sergueev, S. Gorsse, J. Dadda, E. Müller, R. P. Hermann, *Phys. Status Solidi B* **250**, 1300 (2013).
- [289] C. W. Li, J. Hong, A. F. May, D. Bansal, S. Chi, T. Hong, G. Ehlers, O. Delaire, *Nat. Phys.* **11**, 1063 (2015).

- [290] F. Körmann, Y. Ikeda, B. Grabowski, M. H. F. Sluiter, *Npj Comput. Mater.* **3**, 36 (2017).
- [291] F. J. DiSalvo, *Science* **285**, 703 (1999).
- [292] R. Franz, G. Wiedemann, *Ann. Phys. (Berlin)* **165**, 497 (1853).
- [293] H. Wang, Y. Pei, A. D. LaLonde, G. J. Snyder, *Proc. Natl. Acad. Sci.* **109**, 9705 (2011).
- [294] A. L. Pope, T. M. Tritt, M. A. Chernikov, M. Feuerbacher, *Appl. Phys. Lett.* **75**, 1854 (1999).
- [295] M. Asaad, J. Buckman, R. I. Smith, J. W. G. Bos, *RSC Adv.* **6**, 56511 (2016).
- [296] R. A. Downie, D. A. MacLaren, R. I. Smith, J. W. G. Bos, *Chem. Commun.* **49**, 4184 (2013).
- [297] C. Fu, S. Bai, Y. Liu, Y. Tang, L. Chen, X. Zhao, T. Zhu, *Nat. Commun.* **6**, 9144 (2015).
- [298] H. Xie, H. Wang, C. Fu, Y. Liu, G. J. Snyder, X. Zhao, T. Zhu, *Sci. Rep.* **4**, 6888 (2014).
- [299] W. G. Zeier, J. Schmitt, G. Hautier, U. Aydemir, Z. M. Gibbs, C. Felser, G. J. Snyder, *Nat. Rev. Mater.* **1**, 16032 (2016).
- [300] M. Lax, *Phys. Rev.* **95**, 1391 (1954).
- [301] A. A. Maradudin, *Rep. Prog. Phys.* **28**, 331 (1965).
- [302] G. Schafer, *J. Phys. Chem. Solids* **12**, 233 (1960).
- [303] D. W. Taylor, *Phys. Rev.* **156**, 1017 (1967).
- [304] P. Soven, *Phys. Rev.* **156**, 809 (1969).
- [305] P. G. Klemens, *Proc. Phys. Soc. Sec. A* **68**, 1113 (1955).
- [306] P. G. Klemens, *Proc. Phys. Soc. Sec. A* **70**, 833 (1957).
- [307] J. Callaway, *Phys. Rev.* **113**, 1046 (1959).
- [308] D. C. Mattis, J. Bardeen, *Phys. Rev.* **111**, 412 (1958).
- [309] W. A. Kamitakahara, B. N. Brockhouse, *Phys. Rev. B* **10**, 1200 (1974).
- [310] A. Alam, R. K. Chouhan, A. Mookerjee, *Phys. Rev. B* **83**, 054201 (2011).
- [311] J. M. Larkin, A. J. H. McGaughey, *J. Appl. Phys.* **114**, 023507 (2013).
- [312] Y. M. Beltukov, V. I. Kozub, D. A. Parshin, *Phys. Rev. B* **87**, 134203 (2013).
- [313] W. Löwenstein, *Am. Miner.* **39**, 92 (1954).
- [314] K. Prasai, P. Biswas, D. A. Drabold, *Semicond. Sci. Technol.* **31**, 073002 (2016).
- [315] H. Uwe, K. B. Lyons, H. L. Carter, P. A. Fleury, *Phys. Rev. B* **33**, 6436 (1986).
- [316] K. Inoue, A. Hasegawa, K. Watanabe, H. Yamaguchi, H. Uwe, T. Sakudo, *Phys. Rev. B* **38**, 6352 (1988).

- [317] H. Fukazawa, S. Mae, *Phys. Ice Core Rec.* pp. 25–42 (2000).
- [318] K. Dornberger-Schiff, *Acta Crystallogr.* **9**, 593 (1956).
- [319] J. M. Cowley, *Phys. Rev.* **77**, 669 (1950).
- [320] C. Broennimann et al., *J. Synchrotron Rad.* **13**, 120 (2006).
- [321] P. Pangaud et al., *Nucl. Instrum. Methods Phys. Res. A* **11**, 159 (2008).
- [322] E. N. Gimenez, R. Ballabriga, M. Campbell, I. Horswell, X. Llopart, J. Marchal, K. J. S. Sawhney, N. Tartoni, D. Turecek, *IEEE Trans. Nucl. Sci.* **58**, 323 (2011).
- [323] T. R. Welberry, D. J. Goossens, *IUCrJ* **3**, 309 (2016).
- [324] C. A. Young, E. Dixon, M. G. Tucker, D. A. Keen, M. A. Hayward, A. L. Goodwin, *Z. Kristallogr.* **227**, 280 (2012).
- [325] H. J. Silverstein et al., *Phys. Rev. B* **89**, 054433 (2014).
- [326] P. M. M. Thygesen et al., *Phys. Rev. Lett.* **118**, 067201 (2017).
- [327] A. Walsh, J. L. F. Da Silva, S.-H. Wei, *Chem. Mater.* **21**, 5119 (2009).
- [328] D. A. Keen, *J. Appl. Cryst.* **34**, 172 (2001).
- [329] I. Farnan, P. J. Grandinetti, J. H. Baltisberger, J. F. Stebbins, U. Werner, M. A. Eastman, A. Pines, *Nature* **358**, 31 (1992).
- [330] R. E. Youngman, S. T. Haubrich, J. W. Zwanziger, M. T. Janicke, B. F. Chmelka, *Science* **269**, 1416 (1995).
- [331] J. F. Stebbins, Z. Xu, *Nature* **390**, 60 (1997).
- [332] C. R. A. Catlow, L. M. Moroney, A. V. Chadwick, C. Greaves, *EXAFS Studies of Disorder in Crystalline Solids in EXAFS and Near Edge Structure* (Springer, 1983).
- [333] F. Farges, G. Brown Jr., J. J. Rehr, *Phys. Rev. B* **56**, 1809 (1997).
- [334] K. M. Poduska, L. Regev, E. Boaretto, L. Addadi, S. Weiner, L. Kronik, S. Curtarolo, *Adv. Mater.* **23**, 550 (2011).
- [335] D. Michel, M. Perez Y Jorba, R. Collongues, *J. Raman Spectrosc.* **5**, 163 (1976).
- [336] E. A. V. Ebsworth, D. W. H. Rankin, S. Cradock, *Structural Methods in Inorganic Chemistry* (Wiley-Blackwell, 1986).
- [337] J. M. Eiler, *Quat. Sci. Rev.* **30**, 3575 (2011).
- [338] R. A. Eagle, E. A. Schauble, A. K. Tripathi, T. Tütken, R. C. Hulber, J. M. Eiler, *Proc. Natl. Acad. Sci.* **107**, 10377 (2010).
- [339] O. Gereben, L. Pusztai, *Phys. Rev. B* **50**, 14136 (1994).
- [340] M. J. Cliffe, M. T. Dove, D. A. Drabold, A. L. Goodwin, *Phys. Rev. Lett.* **104**, 125501 (2010).
- [341] J. Dědeček, D. Kaucký, B. Wichterlová, O. Gonsiorová, *Phys. Chem. Chem. Phys.* **4**, 5406 (2002).

- [342] P. S. Neuhoﬀ, S. Kroeker, L.-S. Du, T. Fridriksson, J. F. Stebbins, *Am. Mineral.* **87**, 1307 (2002).
- [343] R. L. Withers, F. J. Brink, Y. Liu, L. Norén, *Polyhedron* **26**, 290 (2007).
- [344] M. Yang, J. A. Rodgers, L. C. Middler, J. Oró-Solé, A. B. Jorge, A. Fuertes, J. P. Attfield, *Inorg. Chem.* **48**, 11498 (2009).
- [345] R. J. Bell, P. Dean, *Disc. Faraday Soc.* **50**, 55 (1970).
- [346] P. Dean, *Rev. Mod. Phys.* **44**, 127 (1972).
- [347] H. Böttger, *Phys. Status Solidi B* **62**, 9 (1974).
- [348] S. Katano, M. Iizumi, Y. Noda, *J. Phys. F* **18**, 2195 (1988).
- [349] M. D. McClusky, *J. Appl. Phys.* **87**, 3593 (2000).
- [350] R. T. Howie, I. B. Magdău, A. F. Goncharov, G. J. Ackland, E. Gregoryanz, *Phys. Rev. Lett.* **113**, 175501 (2014).
- [351] W. R. Mondal, N. S. Vidhyadhiraja, T. Berlijn, J. Moreno, M. Jarrell, *Phys. Rev. B* **96**, 014203 (2017).
- [352] M. Zhao, W. Pan, C. Wan, Z. Qu, Z. Li, J. Yang, *J. Eur. Ceram. Soc.* **37**, 1 (2017).
- [353] P. B. Allen, T. Berlijn, D. A. Casavant, J. M. Soler, *Phys. Rev. B* **87**, 085322 (2013).
- [354] T. B. Boykin, A. Ajoy, H. Ilatikhameneh, M. Povolotskyi, G. Klimeck, *Phys. Rev. B* **90**, 205214 (2014).
- [355] H. Huang, *J. Phys. Condens. Matter* **27**, 305402 (2015).
- [356] F. Zheng, P. Zhang, *Comp. Mater. Sci.* **125**, 218 (2016).
- [357] Y. Ikeda, A. Carreras, A. Seko, A. Togo, I. Tanaka, *Phys. Rev. B* **95**, 024305 (2017).
- [358] Y. Xu, A. Chen, P.-E. Chen, Q. Xu, Y. Jiao, *Phys. Rev. E* **96**, 043301 (2017).
- [359] D. V. Louzguine-Luzgin, A. Inoue, *Annu. Rev. Mater. Res.* **38**, 403 (2008).
- [360] H. Wolff, R. Dronskowski, *J. Comput. Chem.* **29**, 2260 (2008).
- [361] M. Yang, J. Oró-Solé, A. Kusmartseva, A. Fuertes, J. P. Attfield, *J. Am. Chem. Soc.* **132**, 4822 (2010).
- [362] F. Yonezawa, K. Morigaki, *Suppl. Prog. Theor. Phys.* **53**, 1 (1973).
- [363] R. J. Elliott, J. A. Krumhansl, P. L. Leath, *Rev. Mod. Phys.* **46**, 465 (1974).
- [364] X. Gonze et al., *Comp. Phys. Commun.* **180**, 2582 (2009).
- [365] H. Fröhlich, *Proc. Roy. Soc. A* **233**, 296 (1954).
- [366] N. Rivier, *Adv. Phys.* **36**, 95 (1987).
- [367] S. R. Sellers, M. Weining, S. Sahba, M. Florescu, *Nat. Commun.* **8**, 14439 (2017).
- [368] M. E. Zoorob, M. D. B. Charlton, G. J. Parker, J. J. Baumberg, M. C. Nett, *Nature* **404**, 740 (2000).

- [369] S. Kinoshita, S. Yoshioka, J. Miyazaki, *Rep. Prog. Phys.* **71**, 076401 (2008).
- [370] D. S. Wiersma, *Nat. Photon.* **7**, 188 (2013).
- [371] S. Vignolini, P. J. Rudall, A. V. Rowland, A. Reed, E. Moyroud, R. B. Faden, J. J. Baumberg, B. J. Glover, U. Stiener, *Proc. Natl. Acad. Sci.* **109**, 15712 (2012).
- [372] M. Burrelli, L. Cortese, L. Pattelli, M. Kolle, P. Vukusic, D. S. Wiersma, U. Steiner, S. Vignolini, *Sci. Rep.* **4**, 6075 (2014).
- [373] N. F. Mott, R. E. Peierls, *Proc. Phys. Soc.* **49**, 72 (1937).
- [374] N. F. Mott, *Proc. Phys. Soc. A* **62**, 416 (1949).
- [375] L. Kong, G. R. Ziegler, *Biomacromolecules* **13**, 2247 (2012).
- [376] R. H. Baughman, *J. Chem. Phys.* **58**, 2976 (1973).
- [377] R. E. Teixeira, A. K. Dambal, D. H. Richter, E. S. G. Shaqfeh, S. Chu, *Macromolecules* **40**, 2461 (2007).
- [378] E. L. Hesketh, Y. Meshcheriakova, K. C. Dent, P. Saxena, R. F. Thompson, J. J. Cockburn, G. P. Lomonosoff, N. A. Ranson, *Nat. Commun.* **6**, 10113 (2015).
- [379] L. J. Hall, V. R. Coluci, D. S. Galvão, M. E. Kozlov, M. Zhang, S. O. Dantas, R. H. Baughman, *Science* **320**, 504 (2008).
- [380] R. Hu et al., *Nano Lett.* **10**, 838 (2010).
- [381] I. Brody, *J. Ultrastruct. Res.* **4**, 264 (1960).
- [382] D. L. Stokes, D. J. DeRosier, *Biophys. J.* **59**, 456 (1991).
- [383] L. Norlén, A. Al-Amoudi, *J. Invest. Dermatol.* **123**, 715 (2004).
- [384] P. T. Spicer, L. K. Hayden, M. L. Lynch, A. Ofori-Boateng, J. L. Burns, *Langmuir* **17**, 5748 (2001).
- [385] G. Mol, K. Harris, C. Bastiaansen, D. Broer, *Adv. Funct. Mater.* **15**, 1155 (2005).
- [386] S. Mühlbauer, B. Binz, F. Jonietz, C. Pfeleiderer, A. Rosch, R. Georgii, P. Böni, *Science* **323**, 915 (2009).
- [387] N. L. Rosi, J. Kim, M. Eddaoudi, B. Chen, M. O’Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **127**, 1504 (2005).
- [388] A. A. Abrikosov, *J. Phys. Chem. Solids* **2**, 199 (1957).
- [389] P. Saludjian, F. Reiss-Husson, *Proc. Natl. Acad. Sci.* **77**, 6991 (1980).
- [390] A. R. Overy, R. Pandya, P. M. Maffettone, P. A. Chater, A. Simonov, A. L. Goodwin, *arXiv:1802.07629* (2018).
- [391] M. O’Keeffe, S. Andersson, *Acta Crystallogr. A* **33**, 914 (1977).
- [392] M. O’Keeffe, *Acta Crystallogr. A* **48**, 879 (1992).
- [393] M. Duneau, M. Audier, *Acta Crystallogr. A* **55**, 746 (1999).
- [394] M. Audier, M. Duneau, *Acta Crystallogr. A* **56**, 49 (2000).

- [395] J. G. Parkhouse, A. Kelly, *Proc. Roy. Soc. Lond. A* **454**, 1889 (1998).
- [396] M. O’Keeffe, J. Plevvert, Y. Teshima, Y. Watanabe, T. Ogama, *Acta Crystallogr. A* **57**, 110 (2001).
- [397] Y. Teshima, T. Matsumoto, *Glass Phys. Chem.* **38**, 41 (2012).
- [398] M. D. Kelzenberg, S. W. Boettcher, J. A. Petykiewicz, D. B. Turner-Evans, M. C. Putnam, E. L. Warren, J. M. Spurgeon, R. M. Briggs, N. S. Lewis, H. A. Atwater, *Nat. Mater.* **9**, 239 (2010).
- [399] M. E. Evans, S. T. Hyde, *J. R. Soc. Interface* **8**, 1274 (2011).
- [400] P. Niggli, *Z. Kristallogr.* **64**, 357 (1926).
- [401] D. McGrouther, R. J. Lamb, M. Krajnak, S. McFadzean, S. McVitie, R. L. Stamps, A. O. Leonov, A. N. Bogdanov, Y. Togawa, *New J. Phys.* **18**, 095004 (2016).
- [402] S. Yoo, A. G. Kreutzer, N. L. Truex, J. S. Nowick, *Chem. Sci.* **7**, 6946 (2016).
- [403] D. Brown, B. D. Cutforth, C. G. Davies, R. J. Gillespie, P. R. Ireland, J. E. Vekris, *Can. J. Chem.* **52**, 791 (1974).
- [404] F. Tuinstra, *Physica* **34**, 113 (1967).
- [405] W. Bragg, R. E. Gibbs, *Proc. Roy. Soc. A* **109**, 405 (1925).
- [406] K. Aurivillius, *Acta. Chem. Scand.* **14**, 2196 (1960).
- [407] V. Robins, S. J. Ramsden, S. T. Hyde, *Eur. Phys. J. B* **48**, 107 (2005).
- [408] V. Robins, S. J. Ramsden, S. T. Hyde, *Eur. Phys. J. B* **39**, 365 (2004).
- [409] V. Robins, S. J. Ramsden, S. T. Hyde, *Physica A* **339**, 173 (2004).
- [410] H. Nyman, C. E. Carroll, B. G. Hyde, *Z. Kristallogr.* **196**, 39 (1991).
- [411] H. Hartmann, F. Ebert, O. Bretschneider, *Z. Anorg. Allg. Chem* **198**, 116 (1931).
- [412] C. B. Shoemaker, D. P. Shoemaker, T. E. Hopkins, S. Yindepit, *Acta Crystallogr. B* **34**, 3573 (1978).
- [413] G. E. Pringle, *Acta Crystallogr. B* **28**, 2326 (1972).
- [414] H. G. von Schnering, R. Nesper, *Angew. Chem. Int. Ed.* **26**, 1059 (1987).
- [415] M. E. Evans, R. Roth, *Phys. Rev. Lett.* **112**, 038102 (2014).
- [416] M. E. Evans, V. Robins, S. T. Hyde, *Acta Crystallogr. A* **69**, 262 (2013).
- [417] P. Pieranski, *Ideal knots, series on knots and everything (Vol. 19)* (Singapore World Scientific, 1998).
- [418] E. Segerman, P. G. Stern, *Nature* **210**, 1258 (1966).
- [419] D. Rodney, B. Gadot, O. R. Martinez, S. R. du Roscoat, L. Orgeas, *Nat. Mater.* **15**, 72 (2016).
- [420] A. Alderson, J. Rasburn, K. E. Evans, *Phys. Status Solidi A* **244**, 817 (2007).
- [421] G. He, Q. Tan, G. Jiang, Q. Li, *Smart Mater. Struct.* **23**, 095011 (2014).

- [422] H. L. De Almeida Jr., L. Monteiro, R. M. e Silva, N. M. Rocha, H. Scheffer, *An. Bras. Dermatol.* **88**, 966 (2013).
- [423] O. V. Kim, R. I. Litvinov, J. Chen, D. Z. Chen, J. W. Weisel, M. S. Alber, *Matrix Biol.* **60–61**, 141 (2017).
- [424] A. Sierra-Fernandez, L. S. Gomez-Villalba, M. E. Rabanal, R. Fort, L. Csòka, *RSC Adv.* **6**, 51583 (2016).
- [425] J. P. F. Santos, A. Bruna da Silva, U. Sundararaj, R. E. S. Brestas, *Polym. Eng. Sci.* **55**, 1263 (2015).
- [426] http://www.intermediates.basf.com/chemicals/web/en/function/conversions:/publish/images/products-and-industries/spandex/spandex_fibre_350.jpg (Last checked March 2018).
- [427] D. E. Moore, D. A. Lockner, H. Tanaka, K. Iwata, *Int. Geol. Rev.* **46**, 385 (2010).
- [428] T. H. K. Barron, K. J. Rogers, *J. Mol. Simul.* **4**, 27 (1989).
- [429] T. A. Mary, J. S. O. Evans, T. Vogt, A. W. Sleight, *Science* **272**, 90 (1996).
- [430] K. W. Chapman, P. J. Chupas, C. J. Kepert, *J. Am. Chem. Soc.* **127**, 15630 (2005).
- [431] G. N. Greaves, A. L. Greer, R. S. Lakes, T. Rouxel, *Nat. Mater.* **10**, 823 (2011).
- [432] M. T. Dove, M. J. Harris, A. C. Hannon, J. M. Parker, I. P. Swainson, M. Gambhir, *Phys. Rev. Lett.* **78**, 1070 (1997).
- [433] P. G. Debendetti, *J. Phys. Condens. Matter* **15**, R1669 (2003).
- [434] L. Lu, J. D. Joannopoulos, M. Solijačić, *Nat. Photon.* **8**, 821 (2014).
- [435] S. Meiboom, M. Sammon, W. F. Brinkman, *Phys. Rev. A* **27**, 438 (1983).
- [436] E. Dubois-Violette, B. Pansu, *Mol. Cryst. Liq. Cryst.* **165**, 151 (1988).
- [437] T. D. Bennett, S. Cao, J.-C. Tan, D. A. Keen, E. G. Bithell, P. J. Beldon, T. Friscic, A. K. Cheetham, *J. Am. Chem. Soc.* **133**, 14546 (2011).
- [438] T. D. Bennett, D. A. Keen, J.-C. Tan, E. R. Barney, A. L. Goodwin, A. K. Cheetham, *Angew. Chem. Int. Ed.* **50**, 3067 (2011).
- [439] O. Henrich, K. Stratford, M. E. Cates, D. Marenduzzo, *Phys. Rev. Lett.* **106**, 107801 (2011).
- [440] R. M. Hornreich, M. Kugler, S. Shtrikman, *Phys. Rev. Lett.* **48**, 1404 (1982).
- [441] R. M. Hornreich, S. Shtrikman, *Phys. Rev. Lett.* **56**, 1723 (1986).
- [442] D. S. Rokhsar, J. P. Sethna, *Phys. Rev. Lett.* **56**, 1727 (1986).
- [443] P. J. Collings, *Phys. Rev. A* **30**, 1990 (1984).
- [444] T. Loiseau, C. Serre, C. Huguenard, G. Fink, F. Taulelle, M. Henry, T. Bataille, G. Férey, *Chem. Eur. J.* **10**, 1373 (2004).
- [445] M. Schmidt, W. Ratcliff, P. G. Radaelli, K. Refson, N. M. Harrison, S. W. Cheong, *Phys. Rev. Lett.* **92**, 056402 (2004).
- [446] A. Rohatgi, <http://arohatgi.info/WebPlotDigitizer> (Last checked Jul. 2015).
- [447] A. A. Coelho, TOPAS-Academic, version 4.1.

Appendix A

Summary of procrySTALLINE states

A.1 Single crystal diffraction

Single crystal diffraction patterns of procrySTALLINE states were generated from atomistic configurations using the SingleCrystal software. Nb and O atoms were placed at each node position and linker site for which $e_{ij} = +1$ respectively. The linker sites in which $e_{ij} = -1$ were left vacant. The subsequent diffuse scattering observed in the simulated single crystal diffraction patterns is therefore solely due to contributions from the partially occupied linker sites.

A.2 Procrystalline notation, point symmetry and entropy

Each of the node geometries shown in Figure 3.4 forms an independent subset of the procrystalline state. The notation with which each individual subset can be clearly identified is summarised in Table A.2.1. Each descriptor makes use of the relevant distinguishing features for each state and is of the form $\mathbf{A}_n(\mathbf{B}_\mathbf{C})$ where,

- A** describes the underlying the parent lattice,
- n gives the number of linkers distinguished for each node,
- B** denotes the stereochemistry of the distinguished linkers, where necessary, and
- C** identifies racemic or chiral forms of node, when applicable.

A corresponding summary of the point symmetry and Pauling number, p , for each procrystalline phase is summarised in Table A.2.2.

Table A.2.1: Notation used for identification of procrySTALLine configurations.

Lattice	Notation	Stereochemistry	Notation	Stereochemistry	Notation
Square	S	Cis	C	Facial	F
Hexagonal	H	Trans	T	Meridional	M
Triangular	T	Ortho	O	Acute Cis	C
Primitive Cubic	C	Meta	M	Obtuse Cis – Racemate	O_R
Diamond	D	Para	P	Obtuse Cis – Enantiopure	O_x
Pyrochlore	P	Vicinal	V	Acute Facial	A
		Unsymmetrical – Racemate	U_R	Obtuse Facial	F
		Unsymmetrical – Enantiopure	U_x	Meridional – Racemate	M_R
		Symmetrical	S	Meridional – Enantiopure	M_x

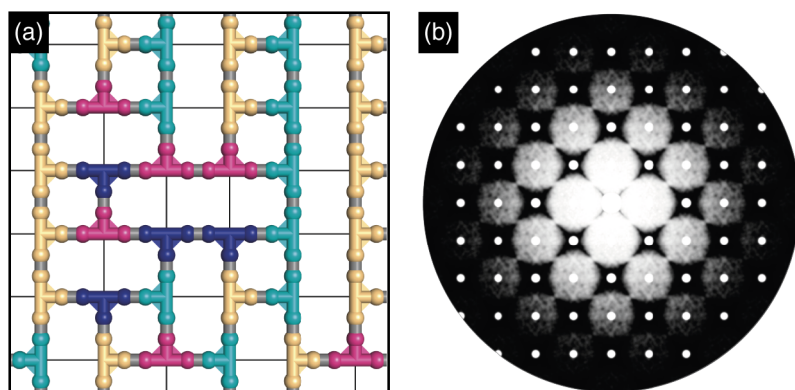
Table A.2.2: A summary of procrySTALLine phases including node symmetry and Pauling number, p . For the chiral phases the absence of a point-symmetry element to interconvert enantiomeric nodes reduces the Pauling number by a factor of two.

Phase	Parent Symmetry	Node Symmetry	Pauling number (p)
S₃	D _{4h}	C _{2v}	1.00
S₂C	D _{4h}	C _{2v}	1.00
S₂T	D _{4h}	D _{2h}	0.50
H₂	D _{3h}	C _{2v}	1.06
T₅	D _{6h}	C _{2v}	0.75
T₄O	D _{6h}	C _{2v}	0.75
T₄M	D _{6h}	C _{2v}	0.75
T₄P	D _{6h}	D _{2h}	0.38
T₃V	D _{6h}	C _{2v}	0.75
T₃U_R	D _{6h}	C _s	1.50
T₃U_X	D _{6h}	C _s [*]	0.75
T₃S	D _{6h}	D _{3h}	0.25
C₅	O _h	C _{4v}	0.75
C₄C	O _h	C _{2v}	1.50
C₄T	O _h	D _{4h}	0.38
C₃F	O _h	C _{3v}	1.00
C₃M	O _h	C _{2v}	1.50
D₃	T _d	C _{3v}	1.00
D₂	T _d	C _{2v}	1.50
P₅	D _{3d}	C _s	0.75
P₄C	D _{3d}	C _s	0.75
P₄O_R	D _{3d}	C ₂	0.75
P₄O_X	D _{3d}	C ₂ [*]	0.38
P₄T	D _{3d}	C _{2h}	0.38
P₃A	D _{3d}	C _{3v}	0.25
P₃F	D _{3d}	C _s	0.75
P₃M_R	D _{3d}	C ₁	1.50
P₃M_X	D _{3d}	C ₁ [*]	0.75

A.3 Known realisations and diffraction behaviour of procrySTALLine phases

In this section, the single crystal diffraction patterns and known realisations for the procrySTALLine phases—including those for the pyrochlore net—are summarised. Real space representations of each phase are also shown alongside their associated Pauling number, p , and point group symmetry. The details of the generation of the procrySTALLine phases for the calculation of the single crystal diffraction pattern are presented in Table A.3.3.

S_1/S_3



Procrystalline symmetry:

Pauling number (p)	1.00
Point group of parent node	D_{4h}
Point group of node	C_{2v}

Figure A.3.1: (a) Configuration and (b) corresponding $(hk)^*$ diffraction pattern for the S_3 procrystalline system.

Known examples for S_1/S_3 :

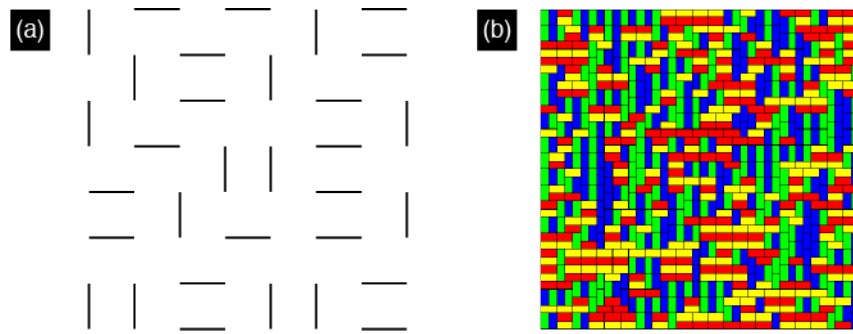
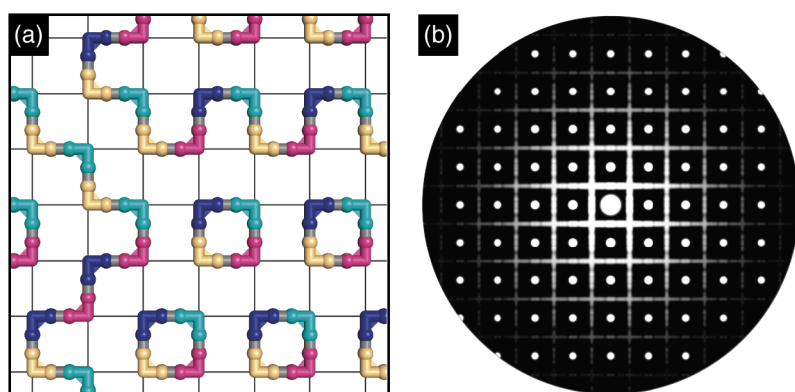


Figure A.3.2: (a) Anderson's resonating valence bond (RVB) description of electronic states in cuprate superconductors [13]. (b) A tiling of dominos – a 1×2 rectangle – on a square [204].

S_2C



Procrystalline symmetry:

Pauling number (p)	1.00
Point group of parent node	D_{4h}
Point group of node	C_{2v}

Figure A.3.3: (a) Configuration and (b) corresponding $(hk)^*$ diffraction pattern for the S_2C procrystalline system.

Known examples for S_2C :

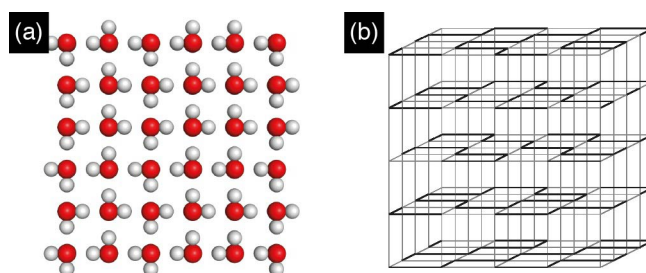
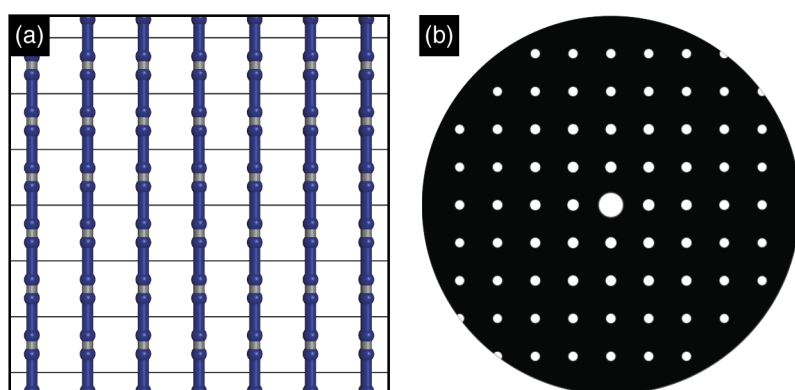


Figure A.3.4: (a) A square ice configuration with each molecule accepting two hydrogen bonds and donating two hydrogen bonds. Reprinted by permission from Springer Nature: Springer Nature, *Nature*, The crystallography of correlated disorder, D. A. Keen and A. L. Goodwin, copyright 2015 [6]. (b) Anion order observed in perovskite oxynitrides – SrNbO₂N – with cis oriented oxygens and nitrogen atoms around square planar niobium nodes. Reprinted by permission from Springer Nature: Springer Nature, *Nat. Chem.*, Anion order in perovskite oxynitrides, M. Yang, J. Oró-Solé, J. A. Rodgers, A. B. Jorge, A. Fuertes and J. P. Attfield, copyright 2011 [254].

S_2T

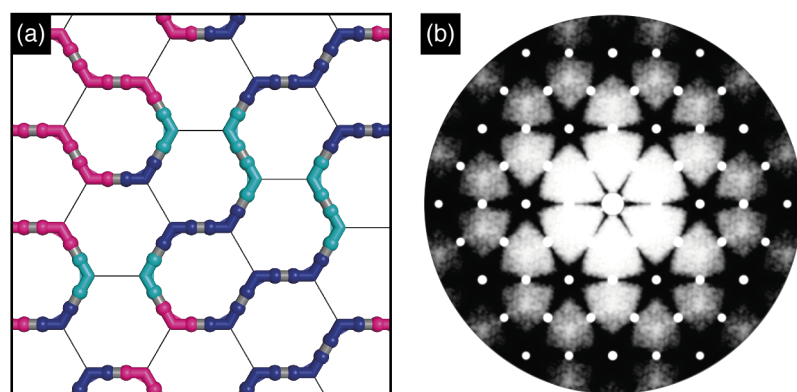


Procrystalline symmetry:

Pauling number (p)	0.50
Point group of parent node	D_{4h}
Point group of node	D_{2h}

Figure A.3.5: (a) Configuration and (b) corresponding $(hk)^*$ diffraction pattern for the S_2T procrystalline system. The lattice ordered and has rectangular symmetry. In the absence of lattice relaxation, this symmetry lowering is evident only in the distribution of Bragg intensities (not discernible here).

H_1/H_2



Procrystalline symmetry:

Pauling number (p)	1.06
Point group of parent node	D_{3h}
Point group of node	C_{2v}

Figure A.3.6: (a) Configuration and (b) corresponding $(hk)^*$ diffraction pattern for the H_2 procrystalline system.

Known examples for H_1/H_2 :

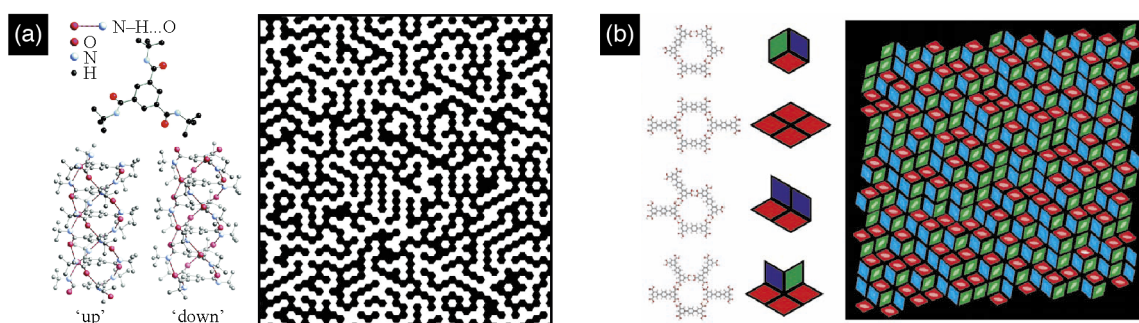
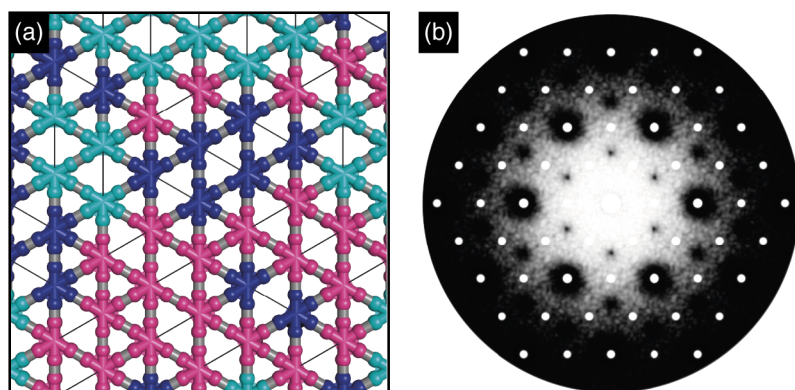


Figure A.3.7: (a) A representation of columnar polarisation states in solid-phase tris-*tert*-butyl-1,3,5-benzene tricarboxamide, giving a physical realisation of the Ising triangular anti-ferromagnet [237]. Reproduced with permission of the International Union of Crystallography. (b) A hydrogen-bonded network of *p*-terphenyl-3,4,3',5'-tetracarboxylic acid molecules on pyrolytic graphite – mapping onto rhombus tiling. From M. O. Blunt, J. C. Russell, M. d. C. Giménez-López, J. P. Garrahan, X. Lin, M. Schröder, N. R. Champness and P. H. Beton, *Science*, **322**, 1077–1081, 2008 [208]. Reprinted with permission from AAAS.

T_1/T_5



Procrystalline symmetry:

Pauling number (p)	0.75
Point group of parent node	D_{6h}
Point group of node	C_{2v}

Figure A.3.8: (a) Configuration and (b) corresponding $(hk)^*$ diffraction pattern for the T_5 procrystalline system.

Known examples for T_1/T_5 :

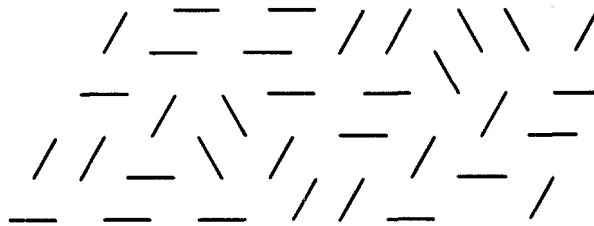
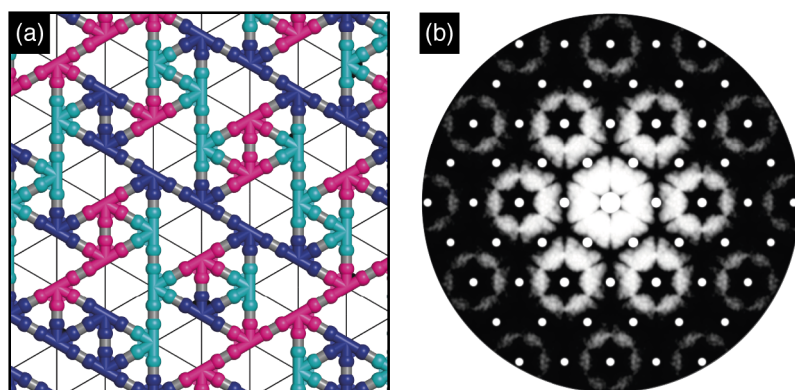


Figure A.3.9: Anderson's resonating valence bond (RVB) description of singlet formation for a d^1 triangular lattice; his specific example was TaS_2 . Reprinted from *Mater. Res. Bull.*, **8**, P. W. Anderson, Resonating valence bonds: A new kind of insulator?, 153–160, copyright 1973, with permission from Elsevier [12].

$\text{T}_2\text{O}/\text{T}_4\text{O}$

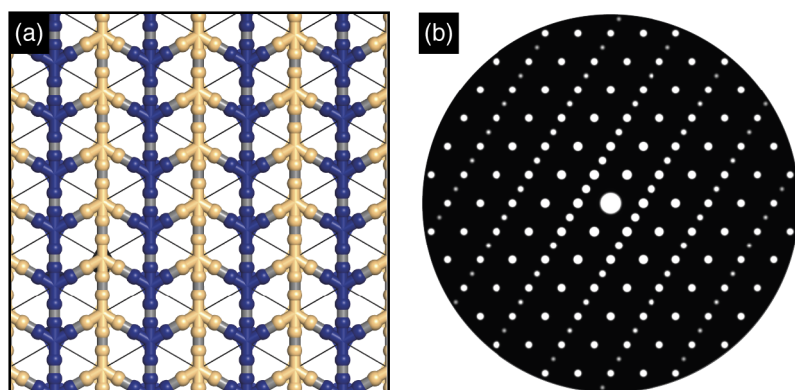


Procrystalline symmetry:

Pauling number (p)	0.75
Point group of parent node	D_{6h}
Point group of node	C_{2v}

Figure A.3.10: (a) Configuration and (b) corresponding $(hk)^*$ diffraction pattern for the T_4O procrystalline system.

T_2M/T_4M

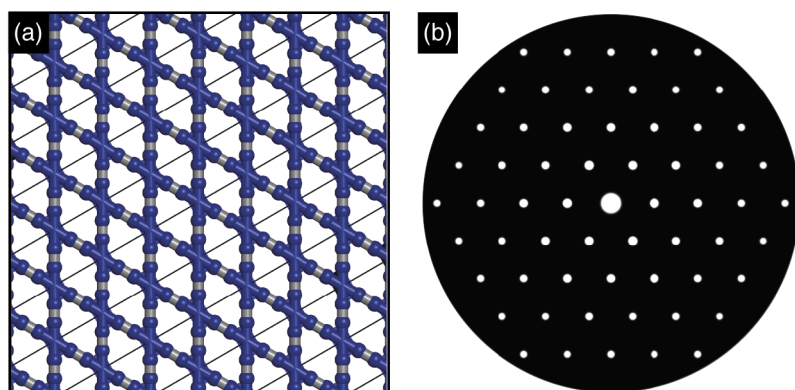


Procrystalline symmetry:

Pauling number (p)	0.75
Point group of parent node	D_{6h}
Point group of node	C_{2v}

Figure A.3.11: (a) Configuration and (b) corresponding $(hk)^*$ diffraction pattern for the T_4M procrystalline system. This lattice is ordered, with rectangular symmetry.

T_2P/T_4P



Procrystalline symmetry:

Pauling number (p)	0.38
Point group of parent node	D_{6h}
Point group of node	D_{2h}

Figure A.3.12: (a) Configuration and (b) corresponding $(hk)^*$ diffraction pattern for the T_4P procrystalline system. This lattice is ordered, with rectangular symmetry.

Known example for T_2P/T_4P :

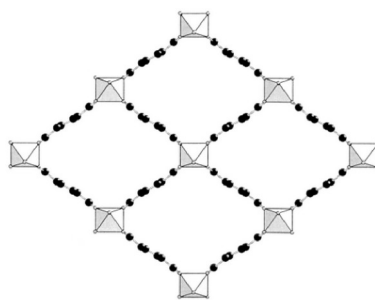
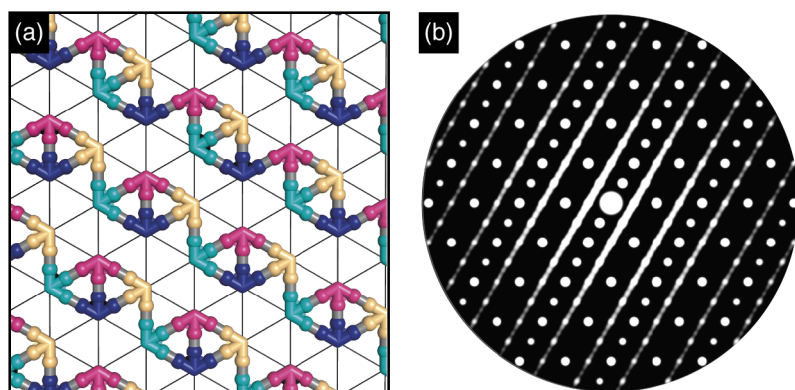


Figure A.3.13: MIL-53 – A Metal-Organic Framework (MOF) with the same topology as the T_4P procristalline phase [444].

T_3V

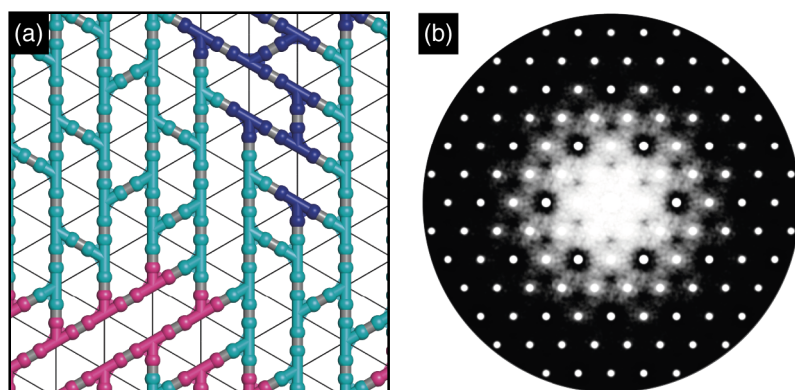


Procrystalline symmetry:

Pauling number (p)	0.75
Point group of parent node	D_{6h}
Point group of node	C_{2v}

Figure A.3.14: (a) Configuration and (b) corresponding $(hk)^*$ diffraction pattern for the T_3V procrystalline system. Though not long-range ordered, this lattice has rectangular symmetry at the macroscopic scale.

$\mathbf{T}_3\mathbf{U}_R$

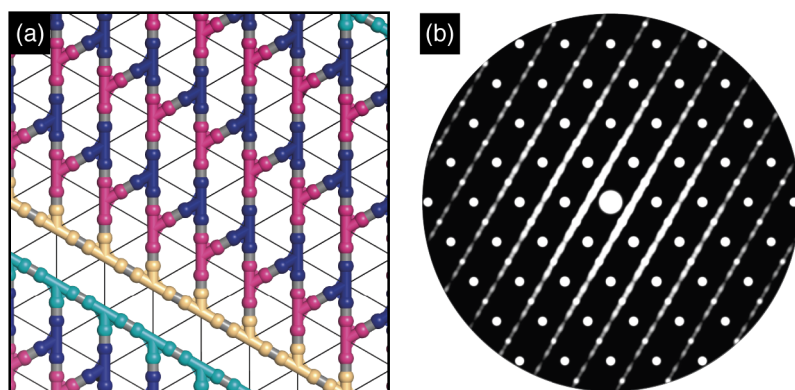


Procrystalline symmetry:

Pauling number (p)	1.50
Point group of parent node	D_{6h}
Point group of node	C_s

Figure A.3.15: (a) Configuration and (b) corresponding $(hk)^*$ diffraction pattern for the $\mathbf{T}_3\mathbf{U}_R$ procrystalline system.

T_3U_X



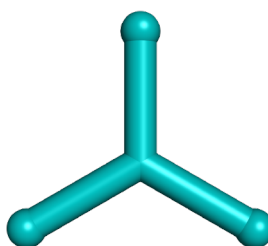
Procrystalline symmetry:

Pauling number (p)	0.75
Two dimensional point group of parent node	D_6
Two dimensional point group of node	C_1

Figure A.3.16: (a) Configuration and (b) corresponding $(hk)^*$ diffraction pattern for the T_3U_X procrySTALLine system. Though not long-range ordered, this lattice has rectangular symmetry at the macroscopic scale.

$\mathbf{T}_3\mathbf{S}$

A configuration of $\mathbf{T}_3\mathbf{S}$ is not realisable.

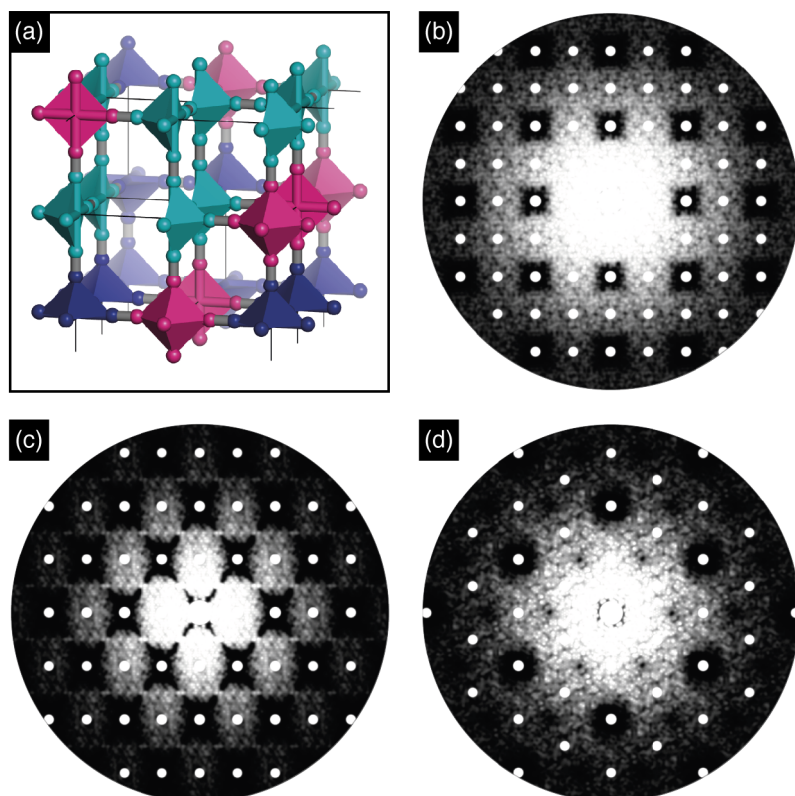


Procrystalline symmetry:

Pauling number (p)	0.25
Point group of parent node	D_{6h}
Point group of node	D_{3h}

Figure A.3.17: A description of the $\mathbf{T}_3\mathbf{S}$ state, which can not form a configuration on the triangular lattice.

C_1/C_5

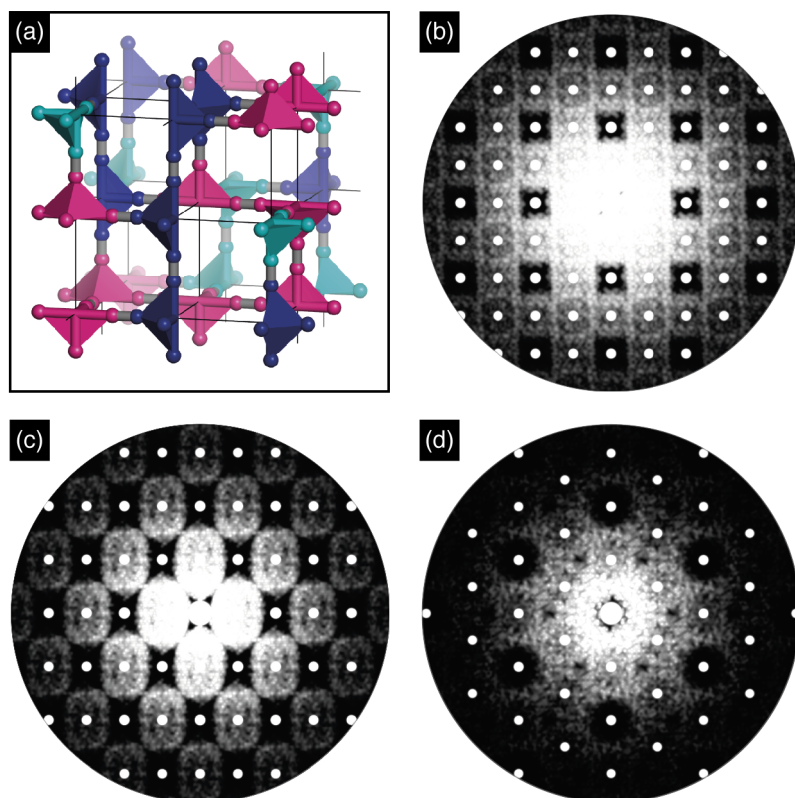


Procrystalline symmetry:

Pauling number (p)	0.75
Point group of parent node	O_h
Point group of node	C_{4v}

Figure A.3.18: (a) Configuration and corresponding diffraction patterns in the (b) $(100)^*$ (c) $(110)^*$ and (d) $(111)^*$ planes for the C_5 procrySTALLine system.

C_2C/C_4C

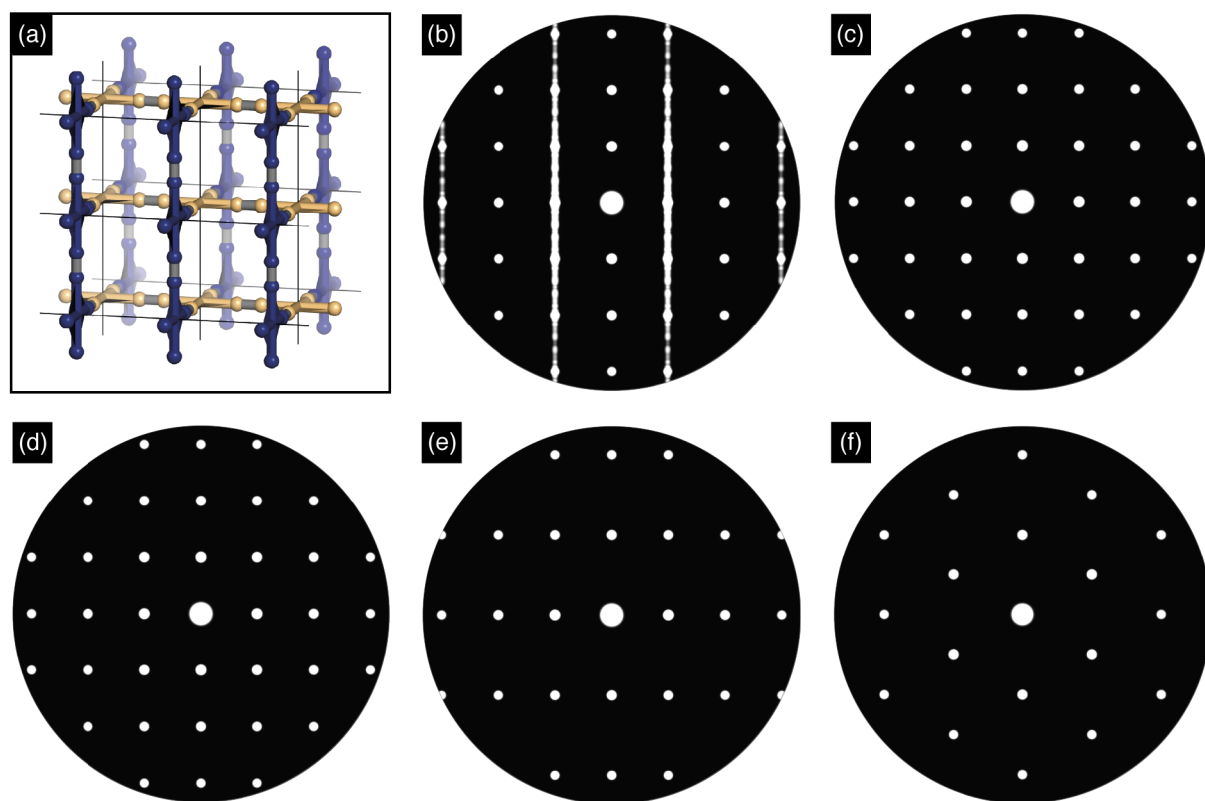


Procrystalline symmetry:

Pauling number (p)	1.50
Point group of parent node	O_h
Point group of node	C_{2v}

Figure A.3.19: (a) Configuration and corresponding diffraction patterns in the (b) $(100)^*$ (c) $(110)^*$ and (d) $(111)^*$ planes for the C_4C procrystalline system.

C_2T/C_4T



Procrystalline symmetry:

Pauling number (p)	0.38
Point group of parent node	O_h
Point group of node	D_{4h}

Figure A.3.20: (a) Configuration and corresponding diffraction patterns in the (b) $(100)^*$ (c) $(010)^*$ (d) $(001)^*$ (e) $(110)^*$ and (f) $(111)^*$ planes for the C_4T procrystalline system. Though not long-range ordered, this lattice has tetragonal symmetry at the macroscopic scale.

Known example for C_2T/C_4T :

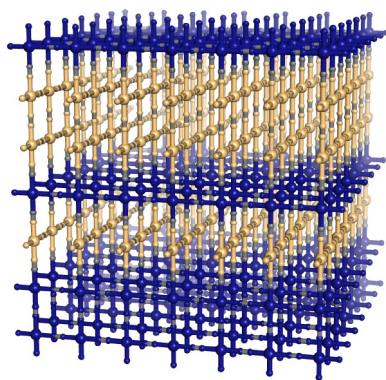
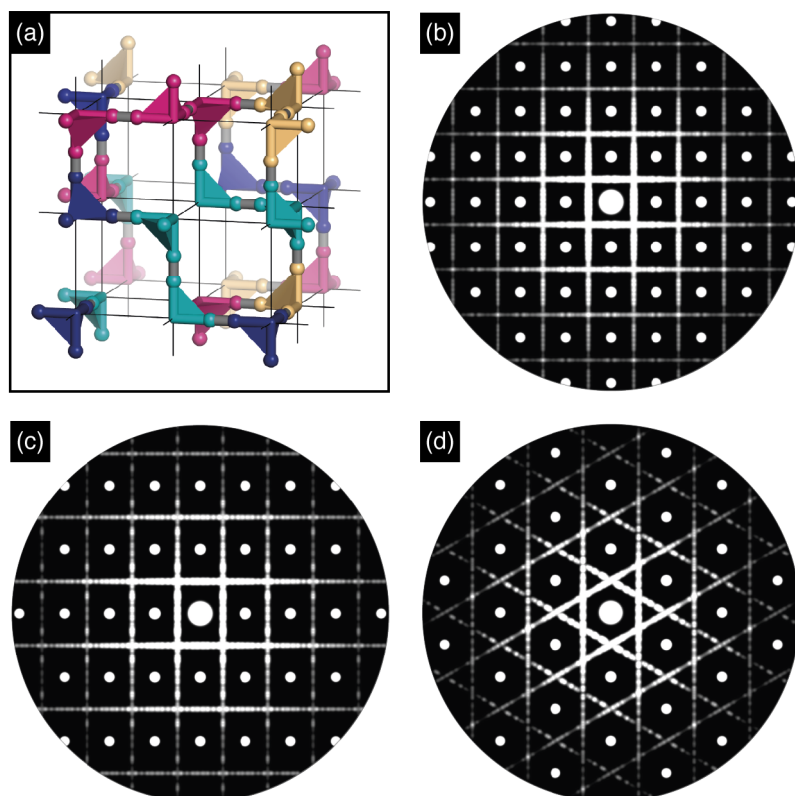


Figure A.3.21: The procrystalline model of $\text{Pd}(\text{CN})_2/\text{Pt}(\text{CN})_2$.



Procrystalline symmetry:

Pauling number (p)	1.00
Point group of parent node	O_h
Point group of node	C_{3v}

Figure A.3.22: (a) Configuration and corresponding diffraction patterns in the (b) $(100)^*$ (c) $(110)^*$ and (d) $(111)^*$ planes for the $\mathbf{C}_3\mathbf{F}$ procrystalline system.

Known example for C_3F :

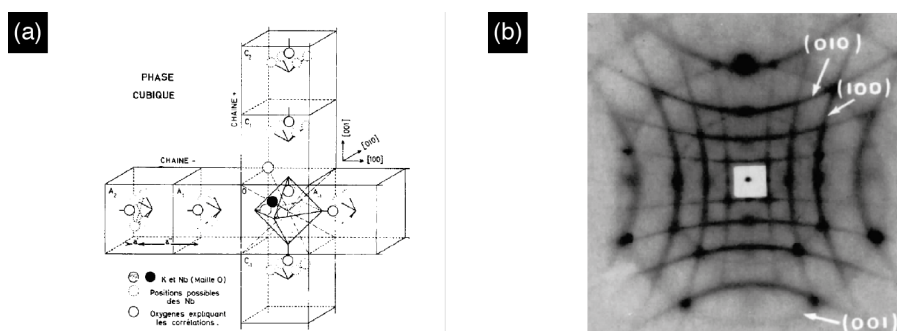
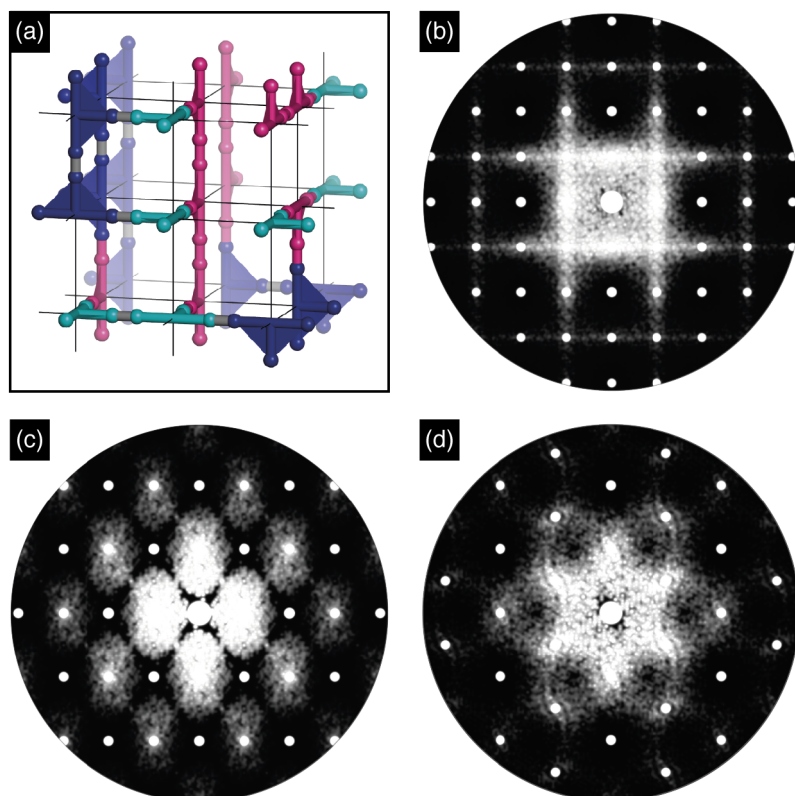


Figure A.3.23: (a) The structure of KNbO₃; isostructural to BaTiO₃. The procrystalline phase is realised through correlated displacements of the Nb atoms towards a face of the octahedral coordination environment – the $\langle 111 \rangle$ directions – such that no pair of neighbouring Nb atoms move toward each other in any of the $\langle 100 \rangle$ directions, as described in the main text. (b) The single crystal diffraction pattern of the cubic phase of KNbO₃ in the (100)* plane [285]. Reproduced with permission of the International Union of Crystallography.

C_3M

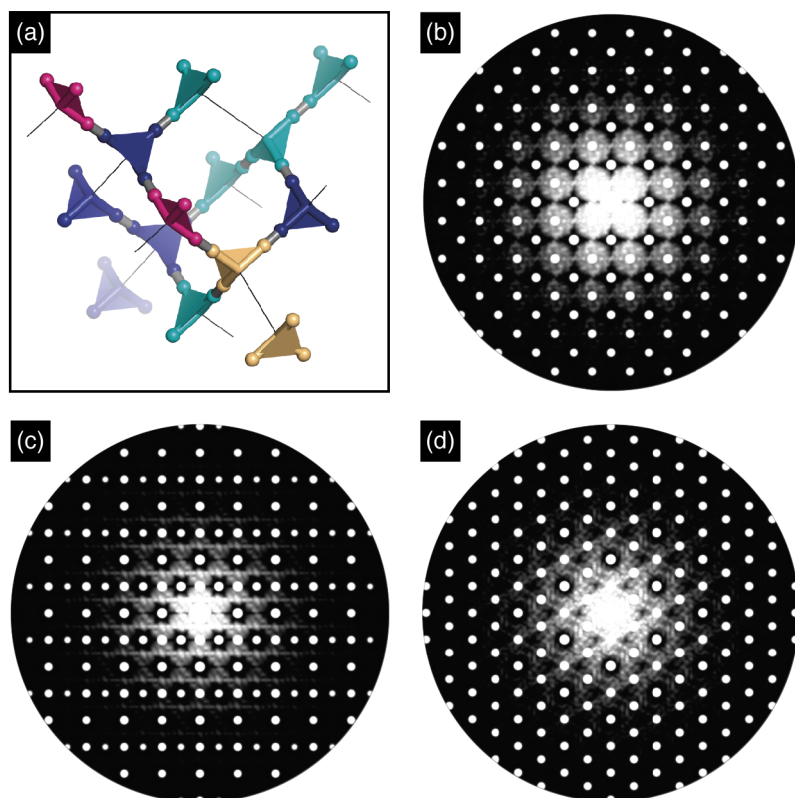


Procrystalline symmetry:

Pauling number (p)	1.50
Point group of parent node	O_h
Point group of node	C_{2v}

Figure A.3.24: (a) Configuration and corresponding diffraction patterns in the (b) $(100)^*$ (c) $(110)^*$ and (d) $(111)^*$ planes for the C_3M procrySTALLine system.

D_1/D_3

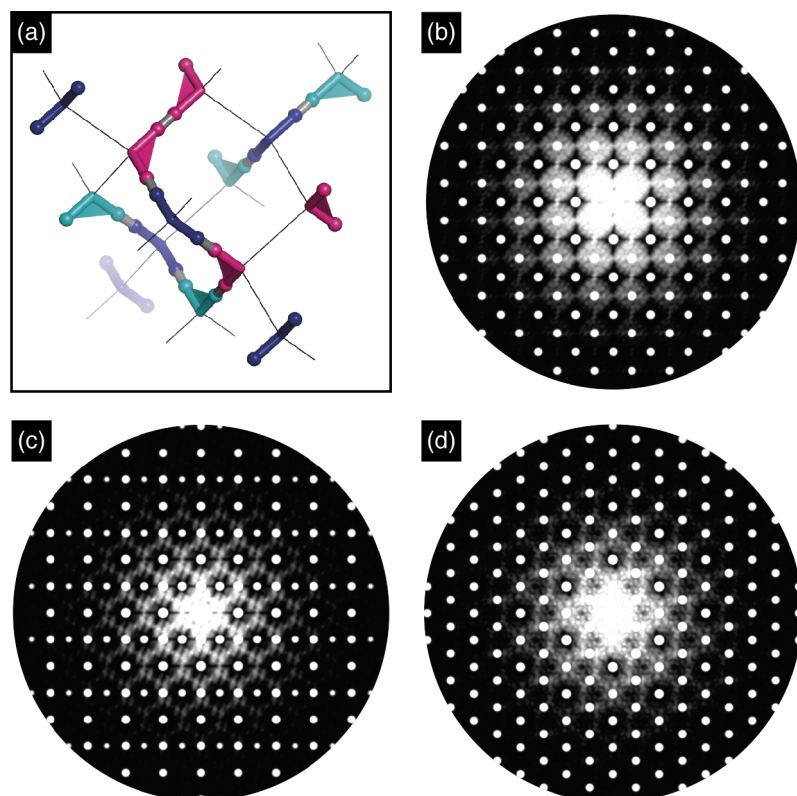


Procrystalline symmetry:

Pauling number (p)	1.00
Point group of parent node	T_d
Point group of node	C_{3v}

Figure A.3.25: (a) Configuration and corresponding diffraction patterns in the (b) $(100)^*$ (c) $(110)^*$ and (d) $(111)^*$ planes for two interpenetrating nets of the D_3 procrystalline system.

D_2



Procrystalline symmetry:

Pauling number (p)	1.50
Point group of parent node	T_d
Point group of node	C_{2v}

Figure A.3.26: (a) Configuration and corresponding diffraction patterns in the (b) $(100)^*$ (c) $(110)^*$ and (d) $(111)^*$ planes for two interpenetrating nets of the D_2 procrystalline system.

Known examples for D_2 :

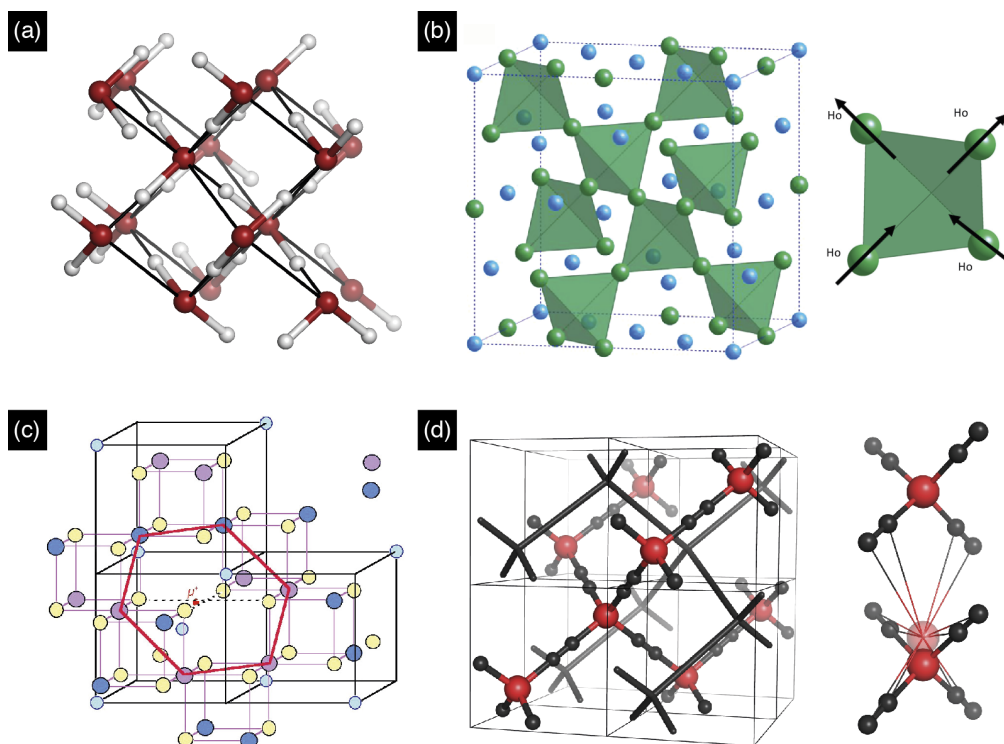
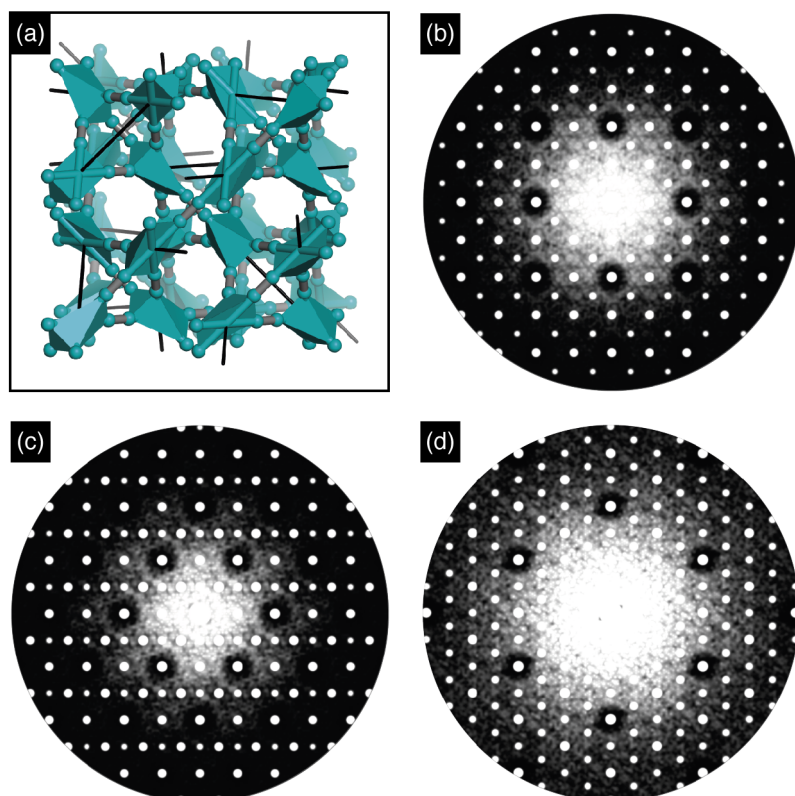


Figure A.3.27: (a) A configuration of ice whereby each oxygen atom accepts two hydrogen bonds and donates two hydrogen bonds. (b) Magnetic ordering in the pyrochlore spin ice $\text{Ho}_2\text{CrSbO}_7$ [268]. Note that in this case it is not only the spin arrangement, but also the distribution of Cr and Sb atoms that is described by the $\mathbf{D}_2$ lattice. (c) A configuration of LiV_2O_4 in which each vanadium tetrahedron contains two V^{3+} ions and two V^{4+} ions [210]. (d) Correlated off-centering of cadmium in $\text{Cd}(\text{CN})_2$, driven by $\mathbf{D}_2$ -type orientational disorder of cyanide ions. Reprinted figure with permission from V. E. Fairbank, A. L. Thompson, R. I. Cooper and A. L. Goodwin, *Phys. Rev. B*, **86**, 104113, 2012 [211]. Copyright 2012 by the American Physical Society.

P_1/P_5



Procrystalline symmetry:

Pauling number (p)	0.75
Point group of parent node	D_{3d}
Point group of node	C_s

Figure A.3.28: (a) Configuration and corresponding diffraction patterns in the (b) $(100)^*$ (c) $(110)^*$ and (d) $(111)^*$ planes for two interpenetrating nets of the P_5 procrystalline system.

Known example for $\mathbf{P}_1/\mathbf{P}_5$:

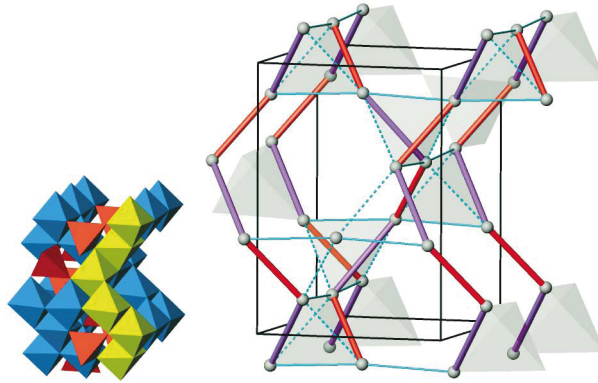
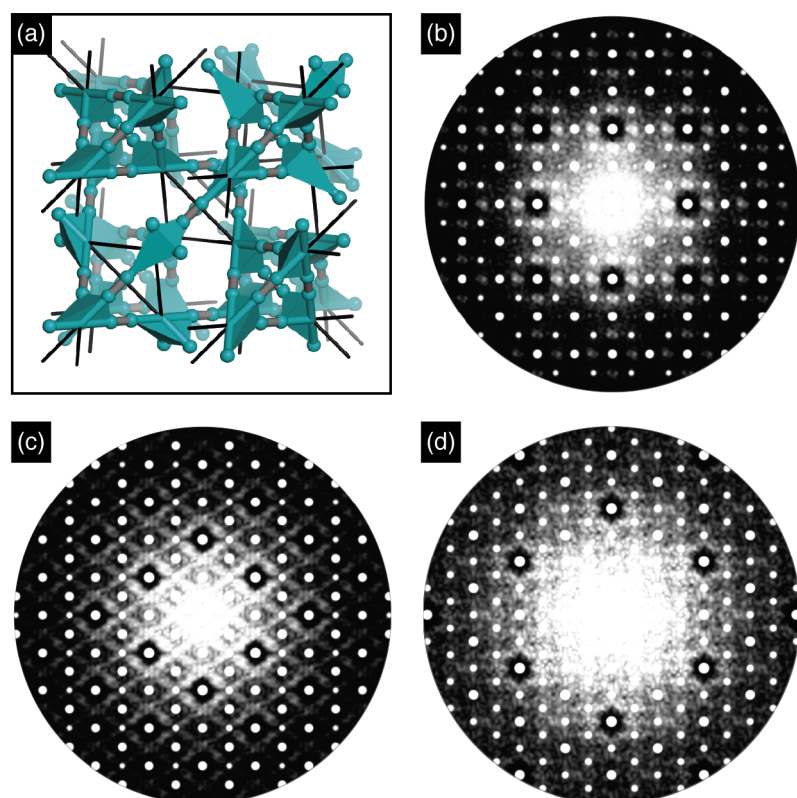


Figure A.3.29: Ti–Ti bond formation in the insulating phase of MgTi_2O_4 adopts an ordered configuration contained within the ensemble of configurations defined by $\mathbf{P}_5$. An RVB description of the metallic state at $T > 260\text{ K}$ corresponds to the procristalline model. Reprinted figure with permission from M. Schmidt, W. Ratcliff, P. G. Radaelli, K. Refson, N. M. Harrison and S. W. Cheong, *Phys. Rev. Lett.*, **92**, 056402, 2004 [445]. Copyright 2004 by the American Physical Society.

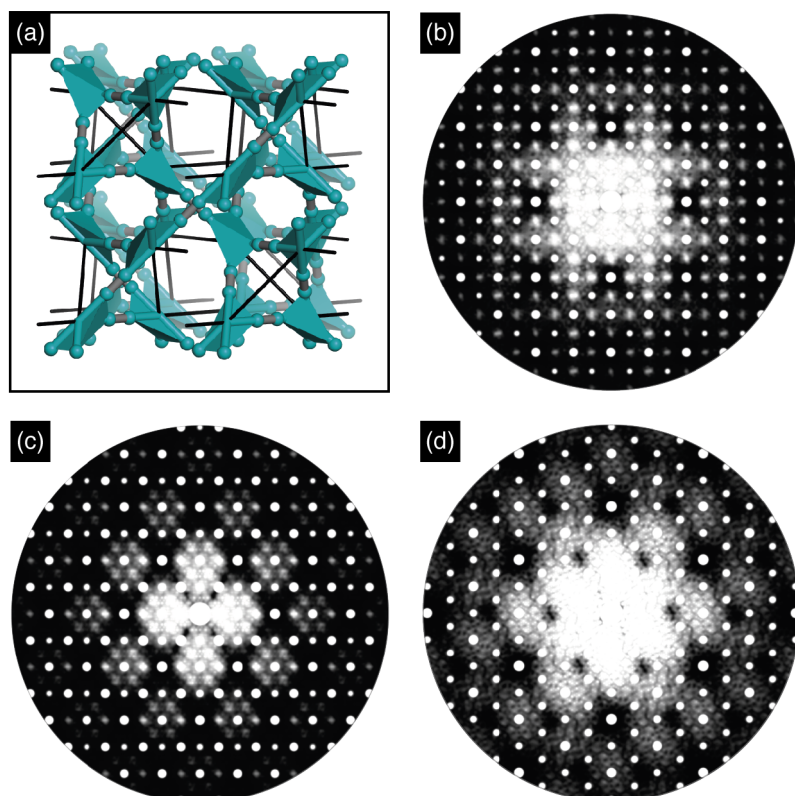
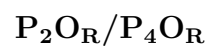
P_2C/P_4C



Procrystalline symmetry:

Pauling number (p)	0.75
Point group of parent node	D_{3d}
Point group of node	C_s

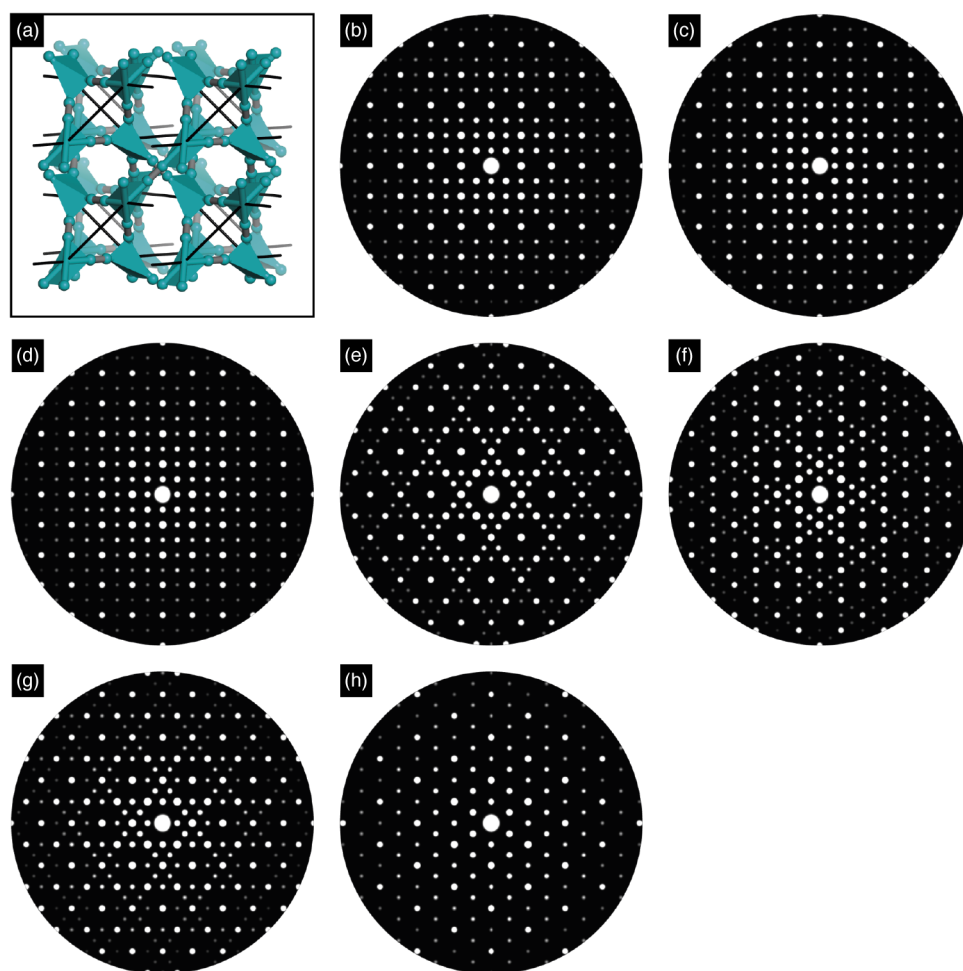
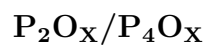
Figure A.3.30: (a) Configuration and corresponding diffraction patterns in the (b) $(100)^*$ (c) $(110)^*$ and (d) $(111)^*$ planes for two interpenetrating nets of the P_4C procrystalline system.



Procrystalline symmetry:

Pauling number (p)	0.75
Point group of parent node	D_{3d}
Point group of node	C_2

Figure A.3.31: (a) Configuration and corresponding diffraction patterns in the (b) $(100)^*$ (c) $(110)^*$ and (d) $(111)^*$ planes for two interpenetrating nets of the $\text{P}_4\text{O}_\text{R}$ procrystalline system.

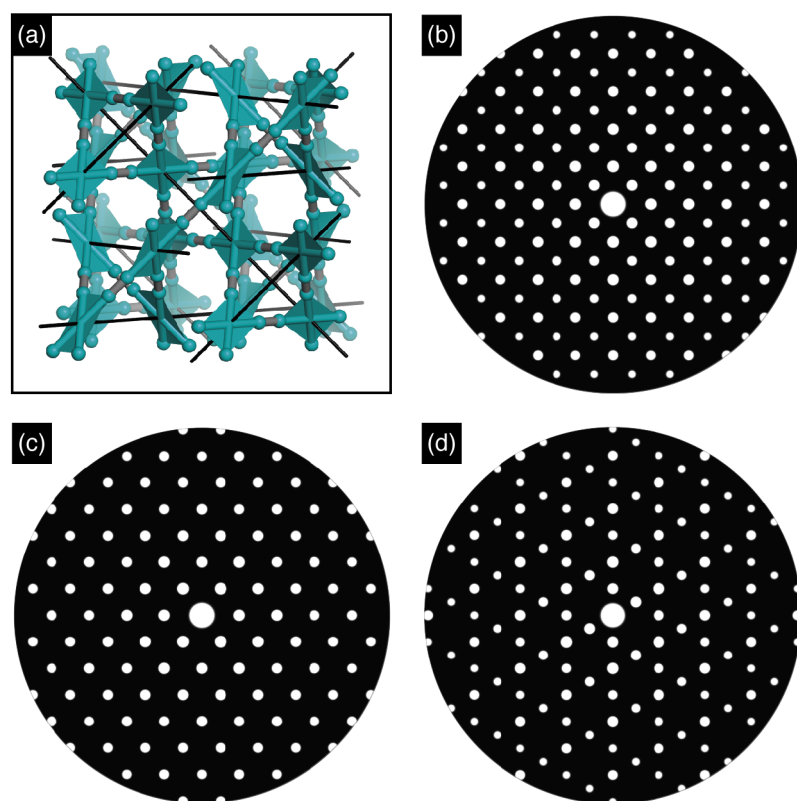


Procrystalline symmetry:

Pauling number (p)	0.38
Point group of parent node	D_{3d}
Point group of node	C_2

Figure A.3.32: (a) Configuration and corresponding diffraction patterns in the (b) $(100)^*$ (c) $(010)^*$ (d) $(001)^*$ (e) $(110)^*$ (f) $(101)^*$ (g) $(011)^*$ and (h) $(111)^*$ planes for two interpenetrating nets of the P_4O_x procrystalline system. This lattice is ordered, with tetragonal symmetry.

P_2T/P_4T

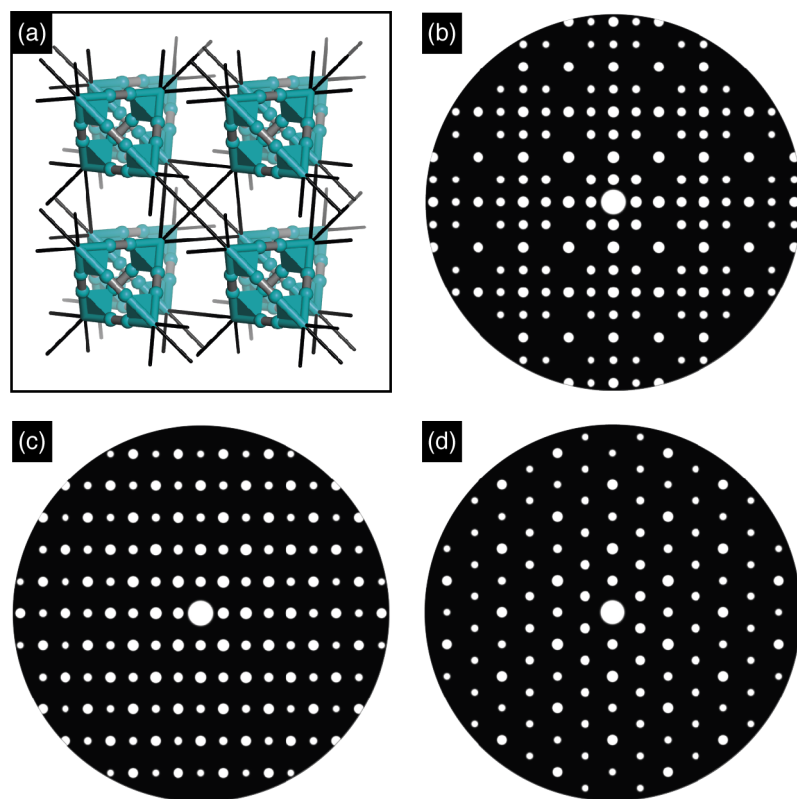


Procrystalline symmetry:

Pauling number (p)	0.38
Point group of parent node	D_{3d}
Point group of node	C_{2h}

Figure A.3.33: (a) Configuration and corresponding diffraction patterns in the (b) $(100)^*$ (c) $(110)^*$ and (d) $(111)^*$ planes for two interpenetrating nets of the P_4T procrystalline system. This configuration is ordered, with cubic symmetry

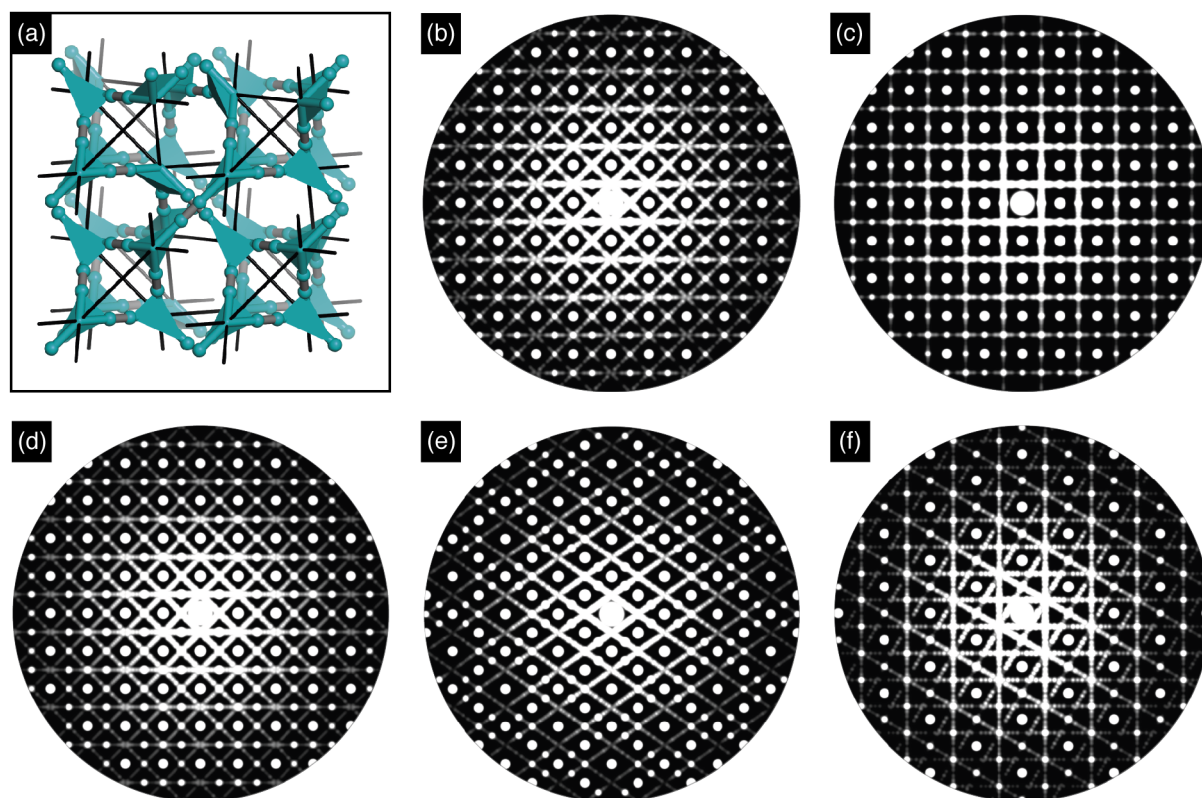
P_3A



Procrystalline symmetry:

Pauling number (p)	0.25
Point group of parent node	D_{3d}
Point group of node	C_{3v}

Figure A.3.34: (a) Configuration and corresponding diffraction patterns in the (b) $(100)^*$ (c) $(110)^*$ and (d) $(111)^*$ planes for two interpenetrating nets of the P_3A procrystalline system. This lattice is ordered, with cubic symmetry.

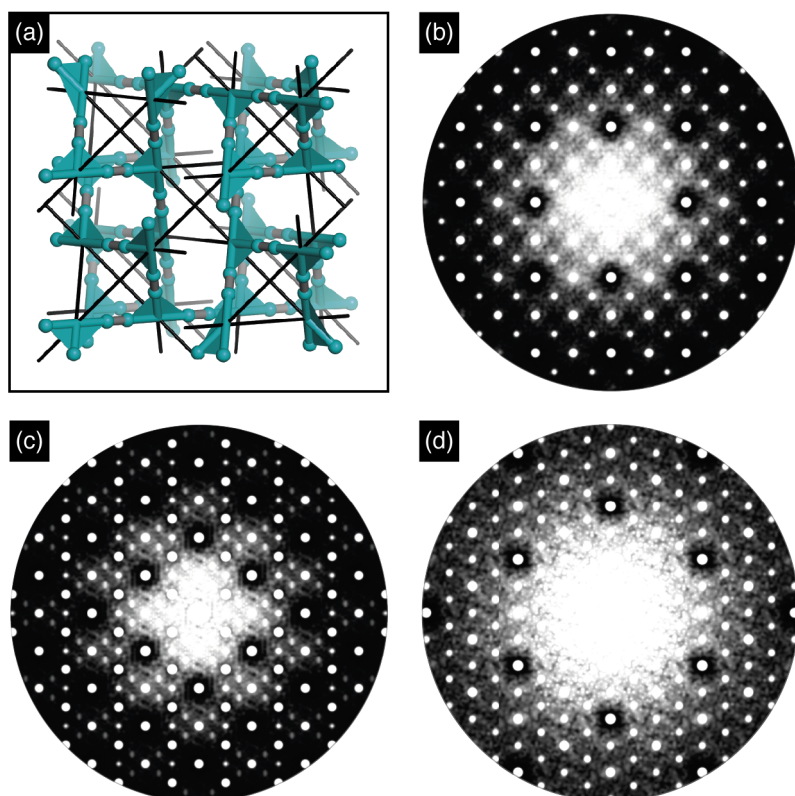


Procrystalline symmetry:

Pauling number (p)	0.75
Point group of parent node	D_{3d}
Point group of node	C_s

Figure A.3.35: (a) Configuration and corresponding diffraction patterns in the (b) $(100)^*$ (c) $(010)^*$ (d) $(001)^*$ (e) $(110)^*$ and (f) $(111)^*$ planes for two interpenetrating nets of the P_3F procrystalline system. Though not long-range ordered, this lattice has tetragonal symmetry at the macroscopic scale.

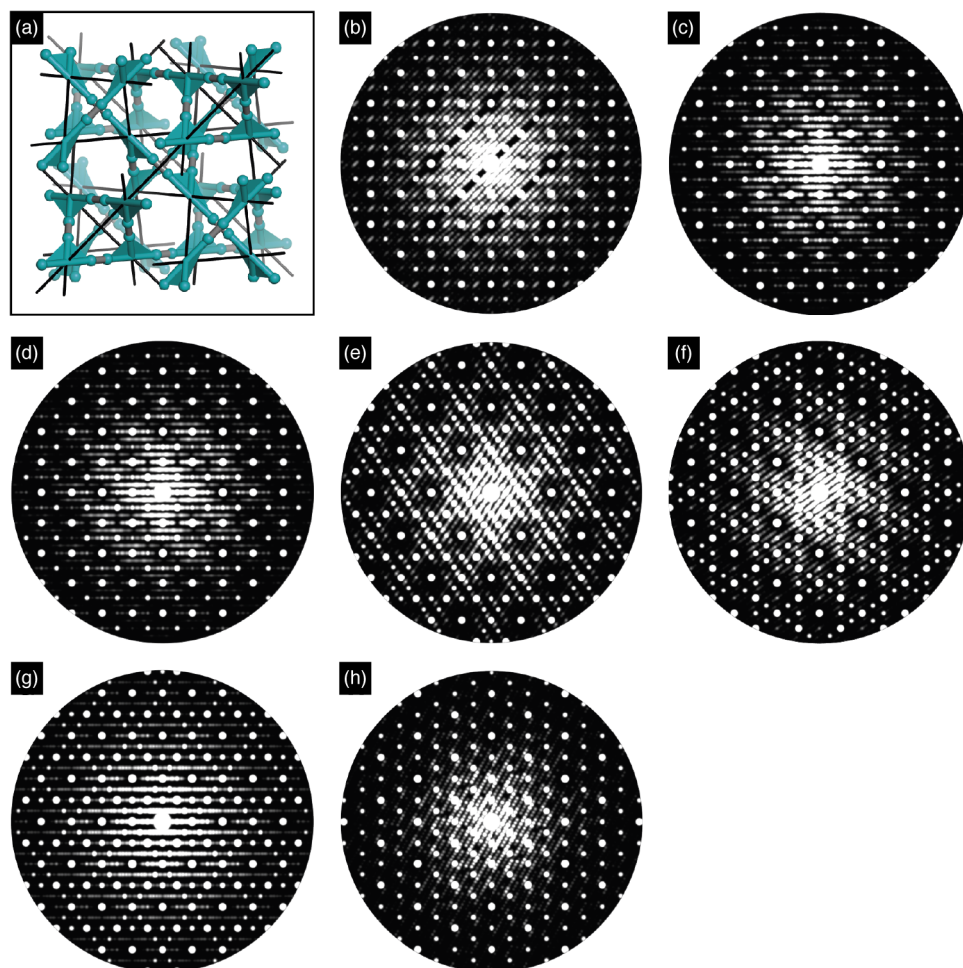
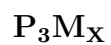
P_3M_R



Procrystalline symmetry:

Pauling number (p)	1.50
Point group of parent node	D_{3d}
Point group of node	C_1

Figure A.3.36: (a) Configuration and corresponding diffraction patterns in the (b) $(100)^*$ (c) $(110)^*$ and (d) $(111)^*$ planes for two interpenetrating nets of the P_3M_R procrystalline system.



Procrystalline symmetry:

Pauling number (p)	0.75
Point group of parent node	D_{3d}
Point group of node	C_1

Figure A.3.37: (a) Configuration and corresponding diffraction patterns in the (b) $(100)^*$ (c) $(010)^*$ (d) $(001)^*$ (e) $(110)^*$ (f) $(101)^*$ (g) $(011)^*$ and (h) $(111)^*$ planes for two interpenetrating nets of the $\text{P}_3\text{M}_\text{X}$ procrystalline system. Though not long-range ordered, this lattice has tetragonal symmetry at the macroscopic scale.

Table A.3.3: Details of supercell configurations used for Monte Carlo generation of procrystalline configurations. *When convergence of a procrystalline phase was not possible in a 40×40 supercell a 42×42 supercell was used. [†]A doubly interpenetrating network.

Lattice	Plane/space group	Lattice points/unit cell	Supercell dimensions	Total number of lattice points
Square	$p4m$	1	40×40	1600
Hexagonal	$p3m1$	2	40×40	3200
Triangular	$p6m$	1	$40 \times 40^*$	1600
Cubic	$Pm\bar{3}m$	1	$20 \times 20 \times 20$	8000
Diamondoid [†]	$Pn\bar{3}m$	2	$10 \times 10 \times 10$	2000
Pyrochlore [†]	$Pn\bar{3}m$	4	$10 \times 10 \times 10$	4000

Appendix B

Supporting information for procrystalline refinements

B.1 BaFeO₂F

The weighted pattern fit statistics, R_{wp} , for the refinements of each of the sixteen models employed in the study of Section 3.3.5 are summarised in Table B.1.1. The associated average R_{wp} and standard deviation σ are also included.

Table B.1.1: Details of the fitting of each of the disorder models in the study of the oxyfluoride material BaFeO₂F.

	C₄C	C₄T	C₄C+T	RND
R_{wp} (Model 1)	13.577	15.830	13.706	13.858
R_{wp} (Model 2)	13.533	15.779	13.543	13.763
R_{wp} (Model 3)	13.506	15.631	13.610	13.947
R_{wp} (Model 4)	13.644	15.864	13.642	13.852
$\langle R_{\text{wp}} \rangle$	13.565	15.776	13.625	13.855
σ	0.0521	0.0890	0.0586	0.0652

B.2 Pd(CN)₂ and Pt(CN)₂

The powder diffraction data as a function of 2θ was extracted from Figure 2 of Ref. [283] using Plot Digitizer [446]. The data were interpolated and rebinned before fitting using TOPAS [447]. As the average structure of the **C₄T** procrystalline model is unstable with respect to ferroelastic distortion, the *Cmmm* space group was used in the subsequent Rietveld analysis. Full structural details of the Rietveld refinements are given in Tables B.2.2 and B.2.3, with the fit to data shown in Figure B.2.1. As the data were extracted from

Ref [283], these refinements were restricted to refine peak shape profiles and lattice parameters while making use of fixed atomic coordinates. As such, the fits are not of the quality expected but do serve to confirm the more physically sensible $\mathbf{C}_4\mathbf{T}$ structure.

Table B.2.2: Crystallographic information determined by powder X-ray diffraction for the crystalline approximant of $\text{Pd}(\text{CN})_2$.

Space Group	$Cmmm$				
$a / \text{\AA}$	6.26(3)				
$b / \text{\AA}$	7.29(3)				
$c / \text{\AA}$	5.008(18)				
$V / \text{\AA}^3$	228.7(17)				
Z	2				
R_{wp}	0.828				
Atom	occ.	x	y	z	$B_{\text{iso}} (\text{\AA}^2)$
Pd	1.0	0	0	0	2
C	0.5	0	0	0.4	2
N	0.5	0	0	0.4	2
C	0.25	0.2	0.2	0	2
N	0.25	0.2	0.2	0	2

Table B.2.3: Crystallographic information determined by powder X-ray diffraction for the crystalline approximant of $\text{Pt}(\text{CN})_2$.

Space Group	$Cmmm$				
$a / \text{\AA}$	6.652(16)				
$b / \text{\AA}$	7.429(9)				
$c / \text{\AA}$	5.088(4)				
$V / \text{\AA}^3$	251.4(7)				
Z	2				
R_{wp}	3.325				
Atom	occ.	x	y	z	$B_{\text{iso}} (\text{\AA}^2)$
Pt	1.0	0	0	0	2
C	0.5	0	0	0.4	2
N	0.5	0	0	0.4	2
C	0.25	0.2	0.2	0	2
N	0.25	0.2	0.2	0	2

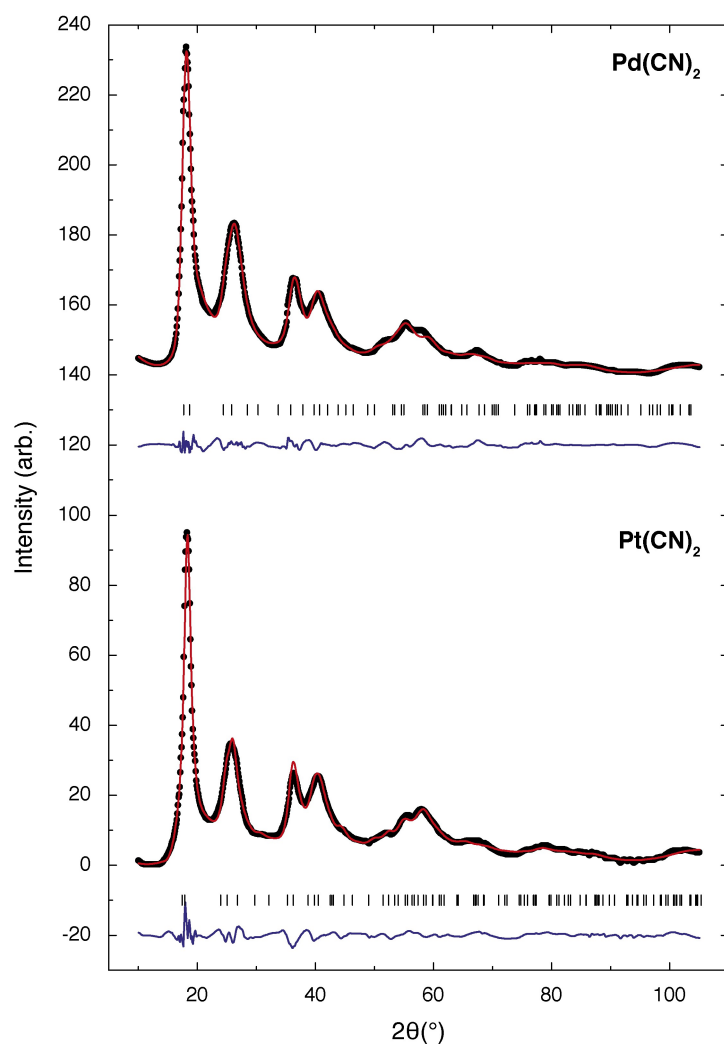


Figure B.2.1: Rietveld fits (red lines) to X-ray powder diffraction data from Ref. [283] (black points) for Pd(CN)_2 (top) and Pt(CN)_2 (bottom). Difference curve (data–fit) shown in blue; tick marks correspond to expected peak positions.

Appendix C

Simulation details for electronic density of states calculations

In each simulation, the cell parameters were initially relaxed with the atomic positions remaining fixed, using an $85 \text{ \AA}^{-1}$ spacing for the k-point mesh, and a 24 Ha cutoff. The subsequent calculation of the electronic density of states was established using a $20 \times 20 \times 20$ k-point grid. A sample input file for the DFT calculations within ABINIT is included within the CD Appendix.

Appendix D

The nomenclature of rod packings

A conversion chart of the multiple naming conventions applied to the rod packings is included in Table D.0.1. Here, the symmetry of the packing, associated generalised rod coordinates, and the packing density, ρ , are also included.

Table D.0.1: A summary of the common rod packings.

Greek letter label	Minimal surface label	Other common names	Packing symmetry	Rod position	Packing density
—	P_{114}	Honeycomb	$P6/mmm$	$(0, 0, u)$	0.907
—	P_{123}	Simple square	$P4/mmm$	$(0, 0, u)$	0.785
—	D_{123}	Two-layer, PtO	$P4_2/mmc$	$(0, u, 0)$	0.785
—	—	Four-layer	$I4_1/amd$	$(0, u, 0)$	0.785
—	—	Three-layer, High Quartz	$P6_222$	$(u, 0, 0)$	0.785
Π^+	G_{124}	β -Mn	$I4_132$	$(\frac{1}{4}, 0, u)$	0.295
Π^*	D_{124}	β -W	$Pm\bar{3}n$	$(u, 0, \frac{1}{2})$	0.589
Σ^+	G_{129}	SrSi ₂	$I4_132$	$(\frac{1}{3} + u, \frac{2}{3} + u, u)$	0.075
Σ^*	—	d -SrSi ₂	$Ia\bar{3}d$	$(\frac{1}{8}, u, -u + \frac{1}{4})$	0.151
Γ	$G_{123}(2)$	β -Mn	$Ia\bar{3}d$	(u, u, u)	0.680
Ω^+	P_{129}	—	$I432$	$(\frac{1}{3} + u, \frac{2}{3} + u, u)$	0.302

Appendix E

Publications

Publications arising from the work in this DPhil are listed below. Those which are incorporated within this thesis are marked with an asterisk. In addition, articles relating to work completed during the same time period, but not included within this thesis, are listed.

- *Design of crystal-like aperiodic solids with selective disorder-phonon coupling
A. R. Overy, A. B. Cairns, M. J. Cliffe, A. Simonov, M. G. Tucker
and A. L. Goodwin
Nat. Commun., **7**, 10445 (2016).
- *Phonon broadening from supercell lattice dynamics: Random and correlated disorder
A. R. Overy, A. Simonov, P. A. Chater, M. G. Tucker and A. L. Goodwin
Phys. Status Solidi B, **254**, 1600586 (2017).
- Uniaxial negative thermal expansion and metallophilicity in $\text{Cu}_3[\text{Co}(\text{CN})_6]$
A. F. Sapnik, X. Liu, H. L. B. Boström, C. S. Coates, **A. R. Overy**,
E. M. Reynolds, A. Tkatchenko and A. L. Goodwin
J. Solid State Chem., **258**, 298 (2018).
- Hybrid local-order mechanism for inversion symmetry breaking
E. H. Wolpert, **A. R. Overy**, P. M. M. Thygesen, A. Simonov, M. S. Senn
and A. L. Goodwin
Phys. Rev. B, **97**, 134106 (2018).
Reprinted article with permission from E. H. Wolpert, A. R. Overy, P. M. M. Thygesen, A. Simonov, M. S. Senn and A. L. Goodwin, *Phys. Rev. B*, **97**, 134106, 2018. Copyright 2018 by the American Physical Society.
- *Extreme cooperative swelling in topologically disordered fibre entanglements
A. R. Overy, R. Pandya, P. M. Maffettone, P. A. Chater, A. Simonov
and A. L. Goodwin
arXiv:1802.07629 (2018). Accepted and awaiting publication in *Phys. Commun.*

ARTICLE

Received 2 Sep 2015 | Accepted 11 Dec 2015 | Published 4 Feb 2016

DOI: 10.1038/ncomms10445

OPEN

Design of crystal-like aperiodic solids with selective disorder-phonon coupling

Alistair R. Overy^{1,2}, Andrew B. Cairns^{1,3}, Matthew J. Cliffe^{1,4}, Arkadiy Simonov¹, Matthew G. Tucker^{2,5}
& Andrew L. Goodwin¹

Functional materials design normally focuses on structurally ordered systems because disorder is considered detrimental to many functional properties. Here we challenge this paradigm by showing that particular types of strongly correlated disorder can give rise to useful characteristics that are inaccessible to ordered states. A judicious combination of low-symmetry building unit and high-symmetry topological template leads to aperiodic ‘procrystalline’ solids that harbour this type of disorder. We identify key classes of procrystalline states together with their characteristic diffraction behaviour, and establish mappings onto known and target materials. The strongly correlated disorder found in these systems is associated with specific sets of modulation periodicities distributed throughout the Brillouin zone. Lattice dynamical calculations reveal selective disorder-driven phonon broadening that resembles the poorly understood ‘waterfall’ effect observed in relaxor ferroelectrics. This property of procrystalline solids suggests a mechanism by which strongly correlated topological disorder might allow independently optimized thermal and electronic transport behaviour, such as required for high-performance thermoelectrics.

¹Department of Chemistry, University of Oxford, Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, UK. ²Diamond Light Source, Chilton, Oxfordshire, OX11 0DE, UK. ³European Synchrotron Radiation Facility, 71 avenue des Martyrs, 38043 Grenoble, France. ⁴Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK. ⁵ISIS Facility, Rutherford Appleton Laboratory, Harwell Oxford, Didcot, Oxfordshire OX11 0QX, UK. Correspondence and requests for materials should be addressed to A.L.G. (email: andrew.goodwin@chem.ox.ac.uk).

The relationship between building block geometry and bulk material structure is one of the cornerstones of structural science. By way of example, the solid phases of elemental Xe (ref. 1), C_{60} (ref. 2) and human adenovirus³ are all structurally related, not by virtue of any particular chemical similarity but because each of these phases reflects the same solution to the problem of packing weakly interacting spherical objects in three-dimensional (3D) space. The reticular approach to understanding zeolite and metal–organic framework topologies is related from a conceptual viewpoint, because it links the geometries of molecule-like components (coordination polyhedra, molecular linkers) to the 3D architectures formed by their assemblies^{4,5}. The importance of structure in determining the physical properties of solids is what then gives sense to the approach of developing new types of functional materials through informed design of constituent building blocks. It is precisely this type of ‘ground-up’ approach that has recently been exploited in the rational design of, for example, solid oxide fuel-cell cathodes and room-temperature multiferroic candidates^{6,7}.

To a large extent, the rich structural information accessible using crystallographic techniques has focussed effort on the design of crystalline materials. There are also obvious functional advantages to the long-range periodicity characteristic of crystals, because it governs useful correlated properties—including the lattice dynamics, electronic states, and charge, orbital and magnetic order. Moreover, crystal symmetry is central to mechanical properties such as piezoelectricity and ferroelasticity, and is clearly pivotal in determining phase transition behaviour. While certain building block geometries allow—or can even force^{8,9}—non-crystalline assemblies, the link to function is usually much less clear in these cases. Indeed the received wisdom is that disorder is something to be avoided, despite increasingly strong empirical evidence that links disordered states to advanced functionalities¹⁰. So the development of disorder—property relationships, and the eventual control over these properties through suitable building block design have emerged as key challenges in the field.

Here we develop an approach of intentionally designing functional disordered materials by focussing on systems in which structural disorder is extremely strongly correlated. The type of disorder we consider is similar to that found in ice, and our paper begins by developing a generalization of ice-like states to arbitrary materials geometries. We proceed to establish a link between the geometry of structural building blocks and the propensity for specific types of strongly correlated disorder in the resulting material assembly. This is the design element of our approach. Having made this connection, we suggest a number of physical realizations of these correlated disordered states. Our paper concludes by demonstrating how the correlated disorder deliberately engineered within one representative affects its lattice dynamics in a highly specific manner. This is the functional element of our approach because the effect we observe suggests, for example, a fundamentally new way of optimizing thermoelectric response.

Results

Generalization of ice rules. Our starting point is the simple toy model of square ice, in which water molecules are arranged on a square lattice and oriented so as to satisfy sensible hydrogen-bonding rules (Fig. 1a). As there is no unique way of satisfying these rules the system is disordered, even if the molecule orientations are far from random. As in the real-world examples of cubic ice (I_c) and its nano-confined variants¹¹, this system is characterized by a degenerate manifold of structural ground states¹². An idea we will come to develop is that this propensity

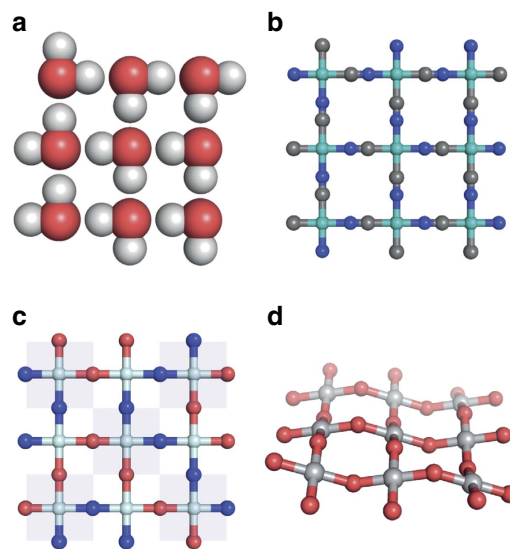


Figure 1 | Correlated disorder in square ice analogues. (a) A configurational fragment of square ice. The water molecules are arranged on a square lattice and are oriented so as to satisfy local hydrogen-bonding rules: each molecule accepts two hydrogen bonds and donates two hydrogen bonds. There is no unique solution to satisfying these local constraints, and so the square ice state is configurationally disordered. (b) A square-planar transition-metal cyanide configuration that maps onto the ice-like state in **a**. Here each metal cation (coloured green) is coordinated by two nitrogen atoms (blue) and two carbon atoms (grey) such that each N atom is opposite to a C atom. (c) Transition metal oxynitrides adopt a related structure¹⁴, in which square-grid layers consist of metal cations coordinated by two nitrogen atoms (blue) and two oxygen atoms (red). The topological equivalence to the square ice configuration can be seen by alternately considering O–M–O and N–M–N orientations for neighbouring metal centres (shaded regions)²⁶. (d) Displacive modulation of a square MO_2 lattice by in-plane $[MO_4]$ rotations gives configurations that again map onto the square ice state. The correspondence relates displacements above and below the plane with, respectively, O and N atoms of the oxynitride configuration shown in **c**.

for disorder is encoded in the combination of the symmetry of the water molecule (that is, the structural building block) and the lattice on which the water molecules are arranged (here enforced by the directionality of the chemical interactions between building blocks). Any system that shares these geometric features will be characterized by the same configurational degeneracy. So, for example, replacing O–H...O linkages by the M–C–N–M motif found in transition-metal cyanides gives a mapping that—in 3D—relates head-to-tail cyanide disorder in $Cd(CN)_2$ to water molecule orientations in cubic ice (Fig. 1b)¹³. The question of O/N ordering within square grid layers of transition-metal oxynitrides presents a related problem, which maps onto the square ice model following geometry inversion from one site to the next (Fig. 1c)¹⁴. These examples involve compositional or orientational modulations of the square lattice, but the same ideas are well-known to translate to a variety of modulation types, many of which are key to material function: for example; displacive, electronic, charge density, spin density, orbital and spin orientation (Fig. 1d). For ice-like disorder on the diamond lattice, these mappings are well-established in the literature: hence the ‘Coulomb phases’¹⁵ of charge¹⁶, orbital¹⁷ and spin¹⁸ ices.

In seeking to generalise ice-like states, we take our lead from the reticular chemistry approach for generating network

structures^{19,20}. The key idea here is that lattice topologies can be considered in terms of the assembly of nodes and linkers (Fig. 2a): the geometry of the node determines the possible topologies of the corresponding lattice. In this context, the various square-ice systems of Fig. 1 can be considered perturbations of the square lattice in which two adjacent linkers are distinguished among the four that meet at each square node. If we identify three linkers rather than two, then we generate a distinct family of disordered configurations that—from a reticular chemistry perspective—might be considered to arise from the linking of T-shaped building blocks (Fig. 2b). As for the square ices, there are many possible realizations of this same state: one mapping is to Anderson’s resonance valence bond (RVB) description of singlet pair formation in cuprate superconductors²¹; another is to so-called ‘domino’ tilings of the plane²².

There are in total just six cases to be considered for perturbations of the square lattice. Two of these are trivial (distinguishing either four or zero linkers); two are related to one another (distinguishing one linker being the same as distinguishing three); and the two cases that remain distinguish different pairings of the four linkers, as shown in Fig. 2c,d. We have

already met the first of these cases in the guise of square ice (Fig. 1c); the second case—in which the linkers distinguished are opposite one another—is ordered and results in symmetry breaking of the underlying square lattice. So there is a nontrivial relationship between perturbations of the node symmetry and the resulting configurational degeneracy.

Ice-like configurations are not confined to perturbations of the square lattice. Equivalent states for the hexagonal, triangular, diamond, cubic and pyrochlore nets are enumerated in Fig. 2e–s and Supplementary Figs 1–37. The extent of disorder can be deduced from the corresponding diffraction patterns, which contain structured diffuse scattering in cases where there is strong correlated disorder (Fig. 2; ref. 10). What emerges is that a substantive fraction of these systems admit large configurational entropies, with a complex relationship between node geometry and extent of correlated disorder. So as to provide insight into this relationship, we generalise Pauling’s approximation for the configurational entropy of ice^{12,14}:

$$S_{\text{config}} \simeq R \ln \left(\frac{n}{2^{d/2}} \right). \quad (1)$$

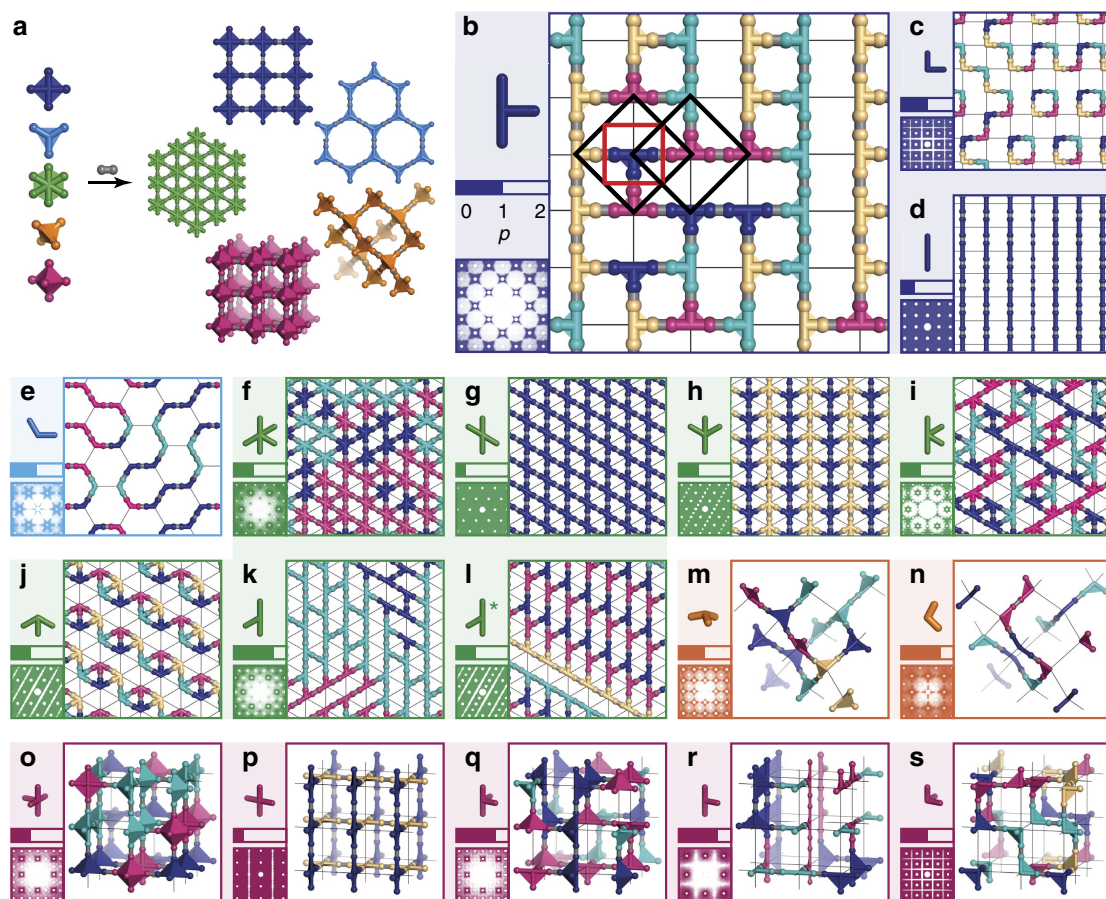


Figure 2 | Reticular design approach to generating procrySTALLINE networks. (a) High-symmetry building blocks connect to form familiar two- and three-dimensional networks: square (indigo), hexagonal (blue), triangular (green), diamondoid (orange) and cubic (red). (b–s) Distinguishing different possible subsets of linkers for these high-symmetry lattices gives a variety of ordered and disordered states, which are grouped here according to the parent lattice. For each panel, the perturbed node geometry is shown in the top-left corner, followed immediately below by a representation of the Pauling number p , a qualitative indicator of the propensity for disorder. A representative network configuration is shown as the main image, with nodes coloured according to their orientation. One suitable projection of the corresponding X-ray diffraction pattern is given in the bottom-left corner (see Supplementary Figs 1–37 for further details). For the configuration shown in **b** two overlapping neighbourhoods are outlined in black. The Dirichlet–Voronoi cell of the neighbourhood lattice is shown in red; the neighbourhood itself is generated by augmenting this cell to include connected latticed points (see Supplementary Figs 38 and 39 and Supplementary Note 1 for further details). The asterisk in **l** indicates that a single enantiomer of the node geometry is used (cf. **k**); this node is chiral when constrained to lie in two dimensions. Further discussion, including extension to the pyrochlore lattice, is given in Supplementary Tables 2 and 3 and Supplementary Note 2.

Here d represents the underlying node connectivity and n corresponds to the number of symmetry-equivalent node perturbations of a given type. The value of n can often be determined by inspection, but it is given more rigorously by the ratio of the orders of the point groups of the parent and perturbed node geometries; for example, $n = |D_{4h}|/|C_{2v}| = 4$ for square ice. We call $p = n/2^{d/2}$ the Pauling number, with the significance that maximising p maximises the propensity for disorder. In this way one expects low-symmetry perturbations of high-symmetry lattices to lead to states of the greatest configurational entropy, a qualitative relationship that is borne out in practice (Fig. 2). From a materials design perspective, what we are saying is that building block geometry and the arrangement of the interactions between building blocks can together encode for specific types of correlated structural disorder.

The procristalline state. Common to many of the configurations of Fig. 2 is the absence of translational periodicity characteristic of the crystalline state. For a given configuration, every node experiences the same local environment—and hence it is not meaningful to think of these structures as defective in the vernacular sense. Yet there is no unit cell and space group symmetry that properly describes the topological connectivity. We proceed to argue that these systems should not be considered as crystals, but form a separate class of aperiodic solid with its own characteristics. We will use the term ‘procristalline’ to describe this state and to emphasise that conventional crystals might be seen as a special case of the definitions that follow.

The procristalline state is a dense, overlapping packing of identical fundamental structural units (we use the term ‘neighbourhoods’), which are positioned periodically but orientationally permuted as permitted by the point symmetry of the neighbourhood geometry. For magnetic systems, these permutations may involve time reversal operations as realized in, for example, the Ising spin ices²³. In simple cases the neighbourhood corresponds to the Dirichlet–Voronoi cell of the underlying lattice augmented to include neighbouring, correlated lattice points (Fig. 2b; Supplementary Note 1 and Supplementary Figs 38 and 39). Whereas crystals correspond to the special case in which the neighbourhood orientations are themselves periodic, the more general procristalline state allows for discrete orientational disorder (cf. the continuous orientational degrees of freedom in, for example, plastic crystals and superionics). Any such disorder will always be correlated since neighbourhoods overlap.

Because their underlying neighbourhood lattice is periodic, all procristalline states admit a Bragg diffraction pattern and have a well-defined reciprocal lattice. This diffraction pattern can be analysed using conventional crystallographic approaches but doing so yields a structural model in which neighbourhoods are averaged over their different possible orientations and all information regarding orientational correlation is lost; for example, the states represented in Fig. 2r,s share identical Bragg diffraction patterns in spite of their distinct local symmetries. Like crystals, procristalline phases are characterized by macroscopic point symmetry that can be as high as that of the neighbourhood lattice. Yet, unlike crystals, they can support a complete absence of any point or translational symmetry at the microscopic level. It is the existence of a periodic 3D reciprocal lattice that distinguishes procristalline from incommensurate and quasicrystalline phases, and which also guarantees a well-defined Brillouin zone and Bloch-wave-like description of phonon and electronic states.

Physical realizations of procristallinity. The structures of a number of well- and lesser-known materials can be thought of in precisely these terms. This is true by construction for any phase

with ice-like disorder; in addition to the various systems described above, the family of ferroelectric phases related to KH_2PO_4 is an obvious additional example²⁴. Similarly well-established are the statistical mechanical models of RVB²⁵ and loop²⁶ states, which correspond to procristalline lattices with, respectively, one and two linkers distinguished for each node. Hence, physical realizations of either class also fall under our definition (for example, TaS_2 (ref. 27) and SrTaO_2N (ref. 28)). A less obvious example is the assembly of *p*-terphenyl-3,5,3',5'-tetracarboxylic acid molecules on pyrolytic graphite to form a hydrogen-bonded network related to the procristalline lattice illustrated in Fig. 2e (Fig. 3a,b)²⁹. This arrangement maps onto the so-called ‘rhombus’ or ‘lozenge’ tiling, which in turn corresponds at once to both the Ising triangular antiferromagnet and the RVB description of π -bonding in graphene^{30–32}. These equivalences are straightforwardly seen in reciprocal space: Fourier transform of the scanning tunnelling microscopy image of Fig. 3b reveals the same distribution of diffuse scattering and ‘pinch point’ features expected from our simple geometric model (Fig. 3c,d). A further example is the pattern of correlated Nb off-centre displacements found in the high-temperature cubic phase of KNbO_3 (ref. 33). Here the mapping is to the procristalline lattice illustrated in Fig. 2s, as reflected (again) in the diffuse scattering distribution observed in single-crystal diffraction measurements (Fig. 3e–g).

We expect the link between characteristic diffuse scattering patterns and particular procristalline states to aid in diagnosing and understanding a range of problems of correlated disorder^{10,34}. For powder diffraction measurements, often the only signature of this diffuse scattering is the presence of *hkl*-dependent anisotropic peak shape broadening. This is the case, for example, in the scattering patterns of $\text{Pd}(\text{CN})_2$ and $\text{Pt}(\text{CN})_2$; a procristalline structural model based on connected square-planar $[\text{M}(\text{C/N})_4]$ units provides the first convincing description of their diffraction behaviour (Fig. 3h,i)³⁵. In other cases, procristalline states (if not necessarily recognized as such) have been inferred from the combination of a disordered average structure and clear signatures of local distortions that can persist only if suitably correlated. Examples include Jahn Teller distortions in the high-temperature orbital-disordered phase of LaMnO_3 (refs 36,37) and the high-pressure amorphous phase of ZrW_2O_8 (ref. 38). So there is good evidence that a variety of procristalline phases do exist, even if their structures are difficult to interpret using established crystallographic approaches.

Disorder–phonon coupling. But what of the link between correlated structural disorder and function? In principle, the existence of a well-defined Brillouin zone allows coupling between the structural modulations that characterize the procristalline state and other physical properties that depend on periodicity—for example, the lattice dynamics and electronic band structure³⁹. We tested for coupling of this type using as our example a two-dimensional oxynitride lattice (Fig. 1c). The idea was to set up a simple harmonic lattice dynamical model in which we assigned different equilibrium values and stiffnesses to M–O and M–N bond lengths, and/or to O–M–O, N–M–O and N–M–N bond angles, and then to determine the extent to which correlated compositional order might affect the phonon spectrum. Conventional lattice dynamical calculations are designed for periodic (crystalline) structures, and so we made use of a supercell lattice dynamical approach in order to treat compositional disorder explicitly. We first benchmarked our calculations by determining the ‘mean-field’ phonon dispersion expected for an average of the different force constant values; we found perfect agreement between our supercell lattice dynamical calculations

and those obtained using a conventional implementation of the general utility lattice programme (GULP)⁴⁰ (Fig. 4a, Supplementary Fig. 40 and Supplementary Methods 1). For random distributions of equal numbers of O and N atoms, the basic phonon structure was similar to the mean-field case, with a slight broadening of phonon frequencies throughout the Brillouin Zone (Fig. 4b). This result is in agreement with *ab initio* molecular dynamics studies of the related problem of the lattice dynamics of configurational glasses⁴¹. By contrast, for the procrySTALLINE arrangement there was a dramatic dispersion in energy of the acoustic branches that we observed most noticeably for wave-vectors near the zone corner (Fig. 4c,d). The qualitative similarity to the ‘waterfall’ phonons observed in thermoelectrics and relaxor ferroelectrics is striking, and suggests a plausible origin for the phenomenon in those systems^{42,43}.

So this is our key result: strongly correlated structural disorder allows selective control over physical properties that depend on periodicity. The implication for systems where thermal and electronic conductivities are mediated by, respectively, phonons and electronic states localised in different regions of the Brillouin zone is that disorder–phonon coupling offers a means of selectively reducing thermal conductivity (inversely proportional to phonon bandwidth) without affecting charge transport behaviour. This is an attractive design strategy for developing next-generation thermoelectrics, and one that contrasts with the

use of ‘rattlers’ which are indiscriminate in their **k**-space coupling⁴⁴.

Discussion

Our reticular chemistry methodology suggests a number of synthetic routes for realising new classes of functional procrySTALLINE solids. Metal-organic frameworks are an obvious platform, given they offer the requisite control over building unit geometry and their energetics tend to be dominated by local interactions^{45,46}. While there is reduced scope for coupling between structural disorder and electronic behaviour in these systems, porosity percolation will certainly be affected by disorder and may in turn govern sorption, mechanical and ion storage properties^{47,48}. In more conventional inorganics, local symmetry lowering can be achieved by covalency effects (as in mixed-anion perovskites) or by first- or second-order Jahn Teller distortion (as in the chalcogenide thermoelectrics and perovskite ferroelectrics). Moreover, because our analysis is essentially geometric in nature, there is clear scope to extend these concepts to magnetic or electronic states, or indeed to the macroscopic scale. The recent demonstration that disordered metamaterials can show strong structural coupling to light scattering processes is an example relevant to the generation of modern photonics⁴⁹. Thinking beyond the ground-state properties of procrySTALLS, we anticipate the existence of novel collective and hidden degrees of freedom that promise a rich physics of their own; for example, topological excitations⁵⁰ and/or ‘hidden order’ transitions between distinct local symmetries⁵¹.

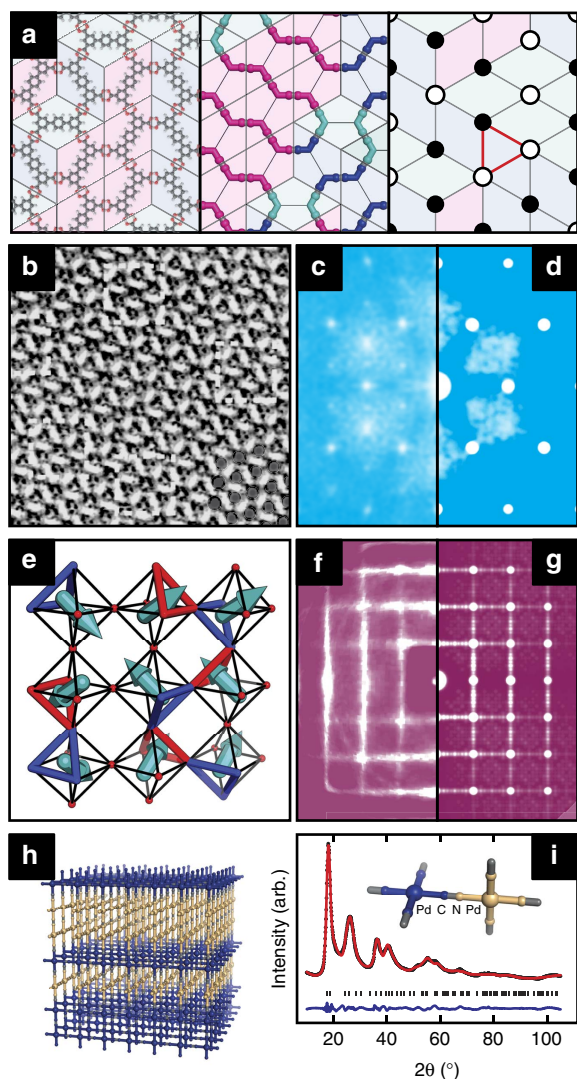


Figure 3 | Representative physical realizations of procrySTALLINE states.

(a) Molecules of *p*-terphenyl-3,5,3',5'-tetracarboxylic acid (TPTC) self assemble on pyrolytic graphite to form a hexagonal procrySTALLINE network related to that represented in Fig. 2e (ref. 29). One possible arrangement is shown here (left), together with our topological abstraction (centre); molecule orientations in the former map onto the ‘missing’ linkers of the latter. Shown in background is the configurationally-equivalent rhombus tiling, which further relates to the triangular Ising antiferromagnet (right): opposite vertices of each rhombus are decorated with pairs of ‘spin-up’ (white circles) and ‘spin-down’ (black circles) states such that each triplet of neighbouring spins (red triangle) contains at least one state of each kind. (b) A scanning tunnelling microscopy image of the corresponding experimental state. Adapted from ref. 29. Reprinted with permission from AAAS. (c) The Fourier transform of the image in **b** showing regions of structured diffuse scattering. (d) The strikingly similar scattering pattern calculated for the hexagonal procrySTALLINE network of Fig. 2e. (e) In the high-temperature cubic phase of KNbO_3 , Nb^{5+} ions displace towards one face of their octahedral coordination environment such that neighbouring Nb centres displace in the same sense relative to the vector joining the pair. Octahedral faces alternately near to (red) and away from (blue) the displaced Nb centres gives a procrySTALLINE net related to that shown in Fig. 2s. (f) Structured diffuse scattering observed in single-crystal X-ray diffraction measurements of KNbO_3 . Adapted from ref. 33. Reprinted with permission of the International Union of Crystallography. (g) Diffuse scattering calculated for the cubic procrySTALLINE network of Fig. 2s. (h) A procrySTALLINE model for the structure of $\text{Pd}(\text{CN})_2$ and $\text{Pt}(\text{CN})_2$ based on the state represented in Fig. 2p: the two possible orientations of square-planar $\text{M}(\text{C}/\text{N})_4$ nodes are shown in indigo and gold. (i) Comparison of the Rietveld fit for this structural model of $\text{Pd}(\text{CN})_2$ (red lines) and the experimental X-ray powder diffraction data of ref. 35 (black points, $\lambda = 1.54 \text{ \AA}$); tick marks indicate the positions of parent Bragg reflections and the difference (data-fit) is shown in blue (see Supplementary Fig. 42, Supplementary Tables 4 and 5, Supplementary Note 3 and Supplementary Method 2 for further discussion).

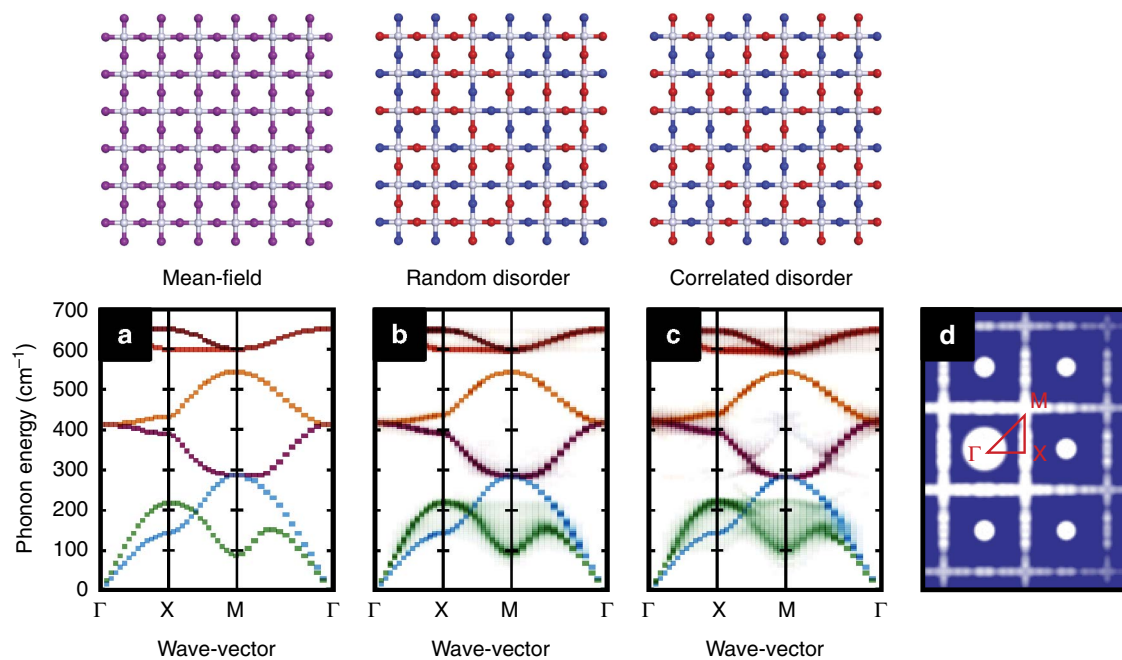


Figure 4 | Selective disorder-phonon coupling in a procrystalline network. (a) Mean-field phonon dispersion curves for a two-dimensional oxynitride lattice, determined using the SCLD approach described in the text. (b) The phonon dispersion determined using SCLD for configurations in which equal numbers of O and N atoms are distributed randomly across the O/N sites of the same oxynitride lattice. There is a slight broadening of phonon frequencies relative to (a). (c) A third set of phonon dispersion curves, again determined using SCLD but for configurations in which O and N atoms have been distributed according to the correlated disorder (procrystalline) model of Fig. 2c. There is now substantive 'waterfall'-like phonon broadening around the M point. (d) The calculated single crystal scattering pattern for the procrystalline model of Fig. 2c, demonstrating that this particular state is characterized by modulations that—like the phonon broadening—are localised around the M point of the BZ. BZ, Brillouin zone; SCLD, supercell lattice dynamics.

Methods

Procrystal lattice generation. Representative procrystalline configurations were generated using a suite of custom Monte Carlo codes. For each given lattice type, a supercell of the corresponding crystallographic cell was generated and periodic boundary conditions were applied [Supplementary Table 1]. Linkers were randomly assigned one of two initial states $e = \pm 1$. A fictitious configurational energy of typical form:

$$E = \sum_{i \in \text{nodes}} \left| \left(\sum_{j \in \text{linkers}} e_{ij} \right) - \bar{e} \right|^2 \quad (2)$$

was calculated, where e_{ij} represents the state of the j^{th} linker of the i^{th} node and the expectation value $\bar{e}$ is a function of the particular node geometry of interest. By way of example, $\bar{e} = 0$ for ice-like states on the diamond lattice, since a local '2-in-2-out' configuration is described by two linkers with $e = +1$ and two with $e = -1$. The form of equation (2) is more complex for some combinations of lattice and node geometry, but the relationship that $E = 0$ if and only if every node adopts the same local geometry was maintained throughout our study. Monte Carlo minimisation proceeded via the usual Metropolis algorithm⁵², with moves $e_{ij} \rightarrow -e_{ij}$. Because we are interested in defect-free procrystalline states, and because the absolute value of the energy term in equation (2) is not physically meaningful, we terminated our Monte Carlo minimisation not at equilibrium but only when $E = 0$. We note that in physical realizations of procrystalline states higher-order correlations may bias towards specific subsets of the $E = 0$ configurational space explored in this first-order Monte Carlo approach. All relevant code is available by request.

Diffuse scattering calculations. Physical realizations of the various procrystalline networks generated as described above were produced by placing Nb atoms at every node position and O atoms at those linker sites for which $e_{ij} = +1$. Linker sites for which $e_{ij} = -1$ were left vacant. Powder and single crystal X-ray diffraction patterns were generated from individual atomic configurations using the programs CrystalDiffraction and SingleCrystal, respectively. Note that the diffuse scattering evident in our diffraction patterns contains contributions only from the linker sites, and its intensity is proportional to the difference in scattering power for $e_{ij} = \pm 1$ occupancies. Consequently, all simple substitutional realizations of a given procrystalline state share the same diffuse scattering pattern, up to a constant factor.

Lattice dynamical calculations. Phonon calculations made use of the GULP program⁴⁰. Supercells of a fictitious two-dimensional NbON square lattice containing $30 \times 30 \times 1$ unit cells (space group symmetry Pm ; relative atom coordinates $\text{Nb}(\frac{1}{2}, \frac{1}{2}, 0)$, $\text{O}/\text{N1}(\frac{1}{2}, 0, 0)$, $\text{O}/\text{N2}(0, \frac{1}{2}, 0)$) were constructed in three ways. First, a 'mean-field' configuration was generated in which all O/N sites were treated as hybrid atoms. Second, random assignment of O/N sites to equal numbers of O and N atoms gave a 'random disorder' configuration. And, third, a suitable procrystalline configuration of the type illustrated in Fig. 1c was used to assign O and N atoms such that each Nb centre was coordinated by exactly two O and two N atoms in a *cis* arrangement; we refer to this as the 'correlated disorder' configuration. In all cases the same set of simple harmonic potentials was used to calculate the lattice enthalpy

$$E_{\text{latt}} = \frac{1}{2} k_1 \sum_{ij} (r_{ij} - r_e)^2 + \frac{1}{2} k_2 \sum_{ijk} (\theta_{ijk} - \theta_e)^2 + k_3 \sum_{ijk} (1 + \cos \theta_{ijk})^2. \quad (3)$$

Here $k_1 = 10 \text{ eV } \text{\AA}^{-2}$ is the stiffness of the Nb–O/N bond, $k_2 = 2 \text{ eV rad}^{-2}$ is the stiffness of the O/N–Nb–O/N angle, and $k_3 = 0.1 \text{ eV}$ is the stiffness of the Nb–O/N–Nb angle. This potential model was chosen because it gave a phonon spectrum with physically sensible mode frequencies, good separation between branches, and realistic low-energy mode features (e.g., low-energy tilts at the zone corner). Ultimately, we found that the difference between the phonon dispersion for random and correlated disorder configurations was sensitive to variation in any or all of the k_i , r_e , θ_e and atomic masses for O and N atoms. For the phonon dispersion curves illustrated in Fig. 4 we used the very simplest case in which only the value of θ_e was distinguished: specifically, we used values of 75° , 90° and 105° for N–Nb–N, N–Nb–O and O–Nb–O angles in each of the random and correlated disorder configurations and a common value of $\theta_e = 90^\circ$ for the mean-field configuration. In all cases, the same equilibrium bond length $r_e = 1 \text{ \AA}$ was used, corresponding to half the Nb...Nb separation in the configurations. Likewise all O and N atoms were assigned the same effective mass of 15 a.m.u.

Atomic coordinates were relaxed and phonon calculations performed at the Γ point ($\mathbf{k}_{\text{supercell}} = (0, 0, 0)$) of the supercell which corresponds to the $\mathbf{k}$ -vector grid of $\frac{1}{30}$ in the reduced mean-field unit cell. The normal modes were calculated as eigenvalues of the dynamical matrix. Despite nominal Pm symmetry, not all of the phonons with atomic displacements along z could be fully separated from in-plane displacements (most probably due to numerical errors). Thus the eigenvalues were calculated using the 'scipy' python library from the two-dimensional component of dynamical matrix which calculated by the GULP. The contribution of each

eigenvector $\mathbf{e}_i$ to all possible $\mathbf{k}$ -points was calculated by projecting the eigenvectors at each wave-vector $\mathbf{k}$ in the following way:

$$e_i|\mathbf{k} = \sum_{j\alpha} \left| \sum_{\ell} e_i(j\ell, \alpha) \exp[i\mathbf{k} \cdot \mathbf{r}(\ell)] \right|^2, \quad (4)$$

where j indexes the atoms in each unit cell ℓ of the supercell, and $\alpha \in \{x, y\}$. For the mean-field case the projection gave phonon dispersion curves indistinguishable from those obtained using a conventional single-cell GULP calculation (Supplementary Fig. 40 and Supplementary Methods 2). In the case of the random and correlated disorder configurations, the phonon dispersion curves shown in Fig. 4 represent an average over the results obtained for five independent configurations. All relevant code is available by request.

Optical Fourier transform. The scanning tunnelling microscopy image shown in Fig. 3b was Fourier transformed using the Java applet ‘Diffraction and Fourier transform’⁵³. The input data were converted to grayscale, inverted, and optimized for brightness and contrast; the output data were corrected for sample orientation and symmetrised (plane symmetry $p6mm$). The actual image used and its raw transform are shown in Supplementary Fig. 41.

References

- Natta, G. & Nasini, A. G. The crystal structure of xenon. *Nature* **125**, 457 (1930).
- David, W. I. F. *et al.* Crystal structure and bonding of ordered C_{60} . *Nature* **353**, 147–149 (1991).
- Reddy, V. S., Natchiar, K., Stewart, P. L. & Nemerow, G. R. Crystal structure of human adenovirus at 3.5 Å resolution. *Science* **329**, 1071–1075 (2010).
- Meier, W. M. *Molecular Sieves* 10–27 (Soc. of Chem. and Ind., 1968).
- Eddaoudi, M. *et al.* Modular chemistry: secondary building units as a basis for the design of highly porous and robust metal–organic carboxylate frameworks. *Acc. Chem. Res.* **34**, 319–330 (2001).
- Dyer, M. S. *et al.* Computationally assisted identification of functional inorganic materials. *Science* **340**, 847–852 (2013).
- Pitcher, M. J. *et al.* Tilt engineering of spontaneous polarization and magnetization above 300 K in a bulk layered perovskite. *Science* **347**, 420–424 (2015).
- Steinhardt, P. J. & Jeong, H.-C. A simpler approach to Penrose tiling with implications for quasicrystal formation. *Nature* **382**, 431–433 (1996).
- Damasceno, P. F., Engel, M. & Glotzer, S. C. Predictive self-assembly of polyhedra into complex structures. *Science* **337**, 453–457 (2012).
- Keen, D. A. & Goodwin, A. L. The crystallography of correlated disorder. *Nature* **521**, 303–309 (2015).
- Algara-Siller, G. *et al.* Square ice in graphene nanocapillaries. *Nature* **519**, 443–445 (2015).
- Pauling, L. The structure and entropy of ice and of other crystals with some randomness of atomic arrangement. *J. Am. Chem. Soc.* **57**, 2680–2684 (1935).
- Fairbank, V. E., Thompson, A. L., Cooper, R. I. & Goodwin, A. L. Charge-ice dynamics in the negative thermal expansion material $\text{Cd}(\text{CN})_2$. *Phys. Rev. B* **86**, 104113 (2012).
- Camp, P. J., Fuentès, A. & Attfield, J. P. Sub-extensive entropies and open order in perovskite oxynitrides. *J. Am. Chem. Soc.* **134**, 6762–6766 (2012).
- Henley, C. L. The ‘Coulomb phase’ in frustrated systems. *Ann. Rev. Cond. Matt. Phys.* **1**, 179–210 (2010).
- Shoemaker, D. P. *et al.* Atomic displacements in the charge ice pyrochlore $\text{Bi}_2\text{Ti}_2\text{O}_6\text{O}'$ studied by neutron total scattering. *Phys. Rev. B* **81**, 144113 (2010).
- Chern, G.-W. & Wu, C. Orbital ice: an exact Coulomb phase on the diamond lattice. *Phys. Rev. E* **84**, 061127 (2011).
- Bramwell, S. T. & Gingras, M. J. P. Spin ice state in frustrated magnetic pyrochlore materials. *Science* **294**, 1495–1501 (2001).
- Wells, A. F. *Structural Inorganic Chemistry* (Clarendon Press, 1984) 5th edn.
- Yaghi, O. M. *et al.* Reticular synthesis and the design of new materials. *Nature* **423**, 705–714 (2003).
- Anderson, P. W. The resonating valence bond state in La_2CuO_4 . *Science* **235**, 1196–1198 (1987).
- Kasteleyn, P. W. The statistics of dimers on a lattice. I. The number of dimer arrangements on a quadratic lattice. *Physica* **27**, 1209–1225 (1961).
- Bramwell, S. T. & Harris, M. J. Frustration in Ising-type spin models on the pyrochlore lattice. *J. Phys. Cond. Matt.* **10**, L215–L220 (1998).
- Slater, J. C. Theory of the transition in KH_2PO_4 . *J. Chem. Phys.* **9**, 16–33 (1941).
- Anderson, P. W. Resonating valence bonds: a new kind of insulator? *Mater. Res. Bull.* **8**, 153–160 (1973).
- Kondey, J. Liouville field theory of fluctuating loops. *Phys. Rev. Lett.* **78**, 4320–4323 (1997).
- Tosatti, E. & Fazekas, P. On the nature of the low-temperature phase of 1T-TaS_2 . *J. Phys. Coll.* **37**, 165–168 (1976).
- Günther, E., Hagenmayer, R. & Jansen, M. Strukturuntersuchungen an den Oxidnitriden SrTaO_2N , CaTaO_2N und LaTaO_2N mittels Neutronen- und Röntgenbeugung. *Z. Anorg. Allg. Chem.* **626**, 1519–1525 (2000).
- Blunt, M. O. *et al.* Random tiling and topological defects in a two-dimensional molecular network. *Science* **322**, 1077–1081 (2008).
- Wannier, G. H. Antiferromagnetism. The triangular Ising net. *Phys. Rev.* **79**, 357–364 (1950).
- Fisher, M. E. Statistical mechanics of dimers on a plane lattice. *Phys. Rev.* **124**, 1664–1672 (1961).
- Kasteleyn, P. W. Dimer statistics and phase transitions. *J. Math. Phys.* **4**, 287–293 (1963).
- Comès, R., Lambert, M. & Guinier, A. Désordre linéaire dans les cristaux (cas du silicium, du quartz, et des pérovskites ferroélectriques). *Acta Cryst. A* **26**, 244–254 (1970).
- Welberry, T. R. & Weber, T. One hundred years of diffuse scattering. *Cryst. Rev.* **22**, 2–78 (2016).
- Hibble, S. J. *et al.* Structures of $\text{Pd}(\text{CN})_2$ and $\text{Pt}(\text{CN})_2$: intrinsically nanocrystalline materials? *Inorg. Chem.* **50**, 104–113 (2011).
- Božin, E. S. *et al.* Local structural aspects of the orthorhombic to pseudo-cubic phase transformation in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$. *Physica B* **385–386**, 110–112 (2006).
- Ahmed, M. R. & Gehring, G. A. Volume collapse in LaMnO_3 studied using an anisotropic Potts model. *Phys. Rev. B* **79**, 174106 (2009).
- Keen, D. A. *et al.* Structural description of pressure-induced amorphization in ZrW_2O_8 . *Phys. Rev. Lett.* **98**, 225501 (2007).
- Valla, T. *et al.* Anisotropic electron–phonon coupling and dynamical nesting on the graphene sheets in superconducting CaC_6 using angle-resolved photoemission spectroscopy. *Phys. Rev. Lett.* **102**, 107007 (2009).
- Gale, J. D. GULP: a computer program for the symmetry-adapted simulation of solids. *J. Chem. Soc., Faraday Trans.* **93**, 629–637 (1997).
- Fang, H., Dove, M. T., Rimmer, L. H. N. & Misquitta, A. J. Simulation study of pressure and temperature dependence of the negative thermal expansion in $\text{Zn}(\text{CN})_2$. *Phys. Rev. B* **88**, 104306 (2013).
- Gehring, P. M., Park, S.-E. & Shirane, G. Soft phonon anomalies in the relaxor ferroelectric $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.92}\text{Ti}_{0.08}\text{O}_3$. *Phys. Rev. Lett.* **84**, 5216–5219 (2000).
- Delaire, O. *et al.* Giant anharmonic phonon scattering in PbTe . *Nat. Mater.* **10**, 614–619 (2011).
- Christensen, M. *et al.* Avoided crossing of rattler modes in thermoelectric materials. *Nat. Mater.* **7**, 811–815 (2008).
- Cairns, A. B. & Goodwin, A. L. Structural disorder in molecular framework materials. *Chem. Soc. Rev.* **42**, 4881–4893 (2013).
- Cliffe, M. J. *et al.* Correlated defect nanoregions in a metal–organic framework. *Nat. Commun.* **5**, 4176 (2014).
- Wessells, C. D., Huggins, R. A. & Cui, Y. Copper hexacyanoferrate battery electrodes with long cycle life and high power. *Nat. Commun.* **2**, 550 (2011).
- Cliffe, M. J., Hill, J. A., Murray, C. A., Coudert, F.-X. & Goodwin, A. L. Defect-dependent colossal negative thermal expansion in $\text{UiO-66}(\text{Hf})$ metal–organic framework. *Phys. Chem. Chem. Phys.* **17**, 11586–11592 (2015).
- Riboli, F. *et al.* Engineering of light confinement in strongly scattering disordered media. *Nat. Mater.* **13**, 720–725 (2014).
- Bak, P. Phenomenological theory of icosahedral incommensurate (‘quasiperiodic’) order in Mn–Al alloys. *Phys. Rev. Lett.* **54**, 1517–1519 (1985).
- Toudic, B. *et al.* Hidden degrees of freedom in aperiodic materials. *Science* **319**, 69–71 (2008).
- Metropolis, N., Rosenbluth, A. W., Rosenbluth, M. N., Teller, A. H. & Teller, E. Equation of state calculations by fast computing machines. *J. Chem. Phys.* **21**, 1087–1092 (1953).
- Schoeni, N. & Chapuis, G. Fourier Transform, <http://escher.epfl.ch.fft/> (2006).

Acknowledgements

A.R.O., A.B.C., M.J.C., A.S. and A.L.G. gratefully acknowledge financial support from the EPSRC (Grant EP/G004528/2), the ERC (Grant 279705), from the Diamond Light Source to A.R.O., and from the Leverhulme Trust and Swiss National Science Foundation to A.S. This project has received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 641887 (Project Acronym: DEFNET-ETN). We are grateful to U. Waghmare (Bangalore), D.A. Keen (ISIS), W.J.K. Fletcher (Oxford) and J.A.M. Paddison (Georgia Tech.) for relevant discussions.

Author contributions

All authors contributed to the development of the conceptual basis for describing the procristalline state. A.R.O. carried out the Monte Carlo simulations and single-crystal diffuse scattering calculations. A.R.O. and A.S. performed the lattice dynamical

calculations. A.B.C. carried out the powder diffraction refinements. A.R.O., M.G.T. and A.L.G. conceived the study. A.L.G. wrote the paper with input from all authors.

Additional information

Supplementary Information accompanies this paper at <http://www.nature.com/naturecommunications>

Competing financial interests: The authors declare no competing financial interests.

Reprints and permission information is available online at <http://npg.nature.com/reprintsandpermissions/>

How to cite this article: Overy, A. R. *et al.* Design of crystal-like aperiodic solids with selective disorder–phonon coupling. *Nat. Commun.* 7:10445 doi: 10.1038/ncomms10445 (2016).



This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>

Phonon broadening from supercell lattice dynamics: Random and correlated disorder

Editor's Choice**Alistair R. Overy^{1,2}, Arkadiy Simonov¹, Philip A. Chater², Matthew G. Tucker³, and Andrew L. Goodwin^{*1}**¹ Department of Chemistry, University of Oxford, Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, UK² Diamond Light Source, Chilton, Oxfordshire, OX11 0DE, UK³ Oak Ridge National Laboratory, 1 Bethel Valley Road, Oak Ridge, Tennessee, USA

Received 30 August 2016, revised 12 October 2016, accepted 15 October 2016

Published online 11 November 2016

Keywords disorder, lattice dynamics, thermoelectrics* Corresponding author: e-mail andrew.goodwin@chem.ox.ac.uk, Phone: +44-(0)1865-272137, Fax: +44-(0)1865-272690

We demonstrate how supercell implementations of conventional lattice dynamical calculations can be used to determine the extent and nature of disorder-induced broadening in the phonon dispersion spectrum of disordered crystalline materials. The approach taken relies on band unfolding, and is first benchmarked against virtual crystal approximation phonon calculations. The different effects of mass and interaction disorder on the phonon broadening are then presented, focussing on the example of a simple cubic binary alloy. For the mass disorder example, the

effect of introducing correlated disorder is also explored by varying the fraction of homoatomic and heteroatomic neighbors. Systematic progression in the degree of phonon broadening, on the one hand, and the form of the phonon dispersion curves from primitive to face-centered cubic type, on the other hand, is observed as homoatomic neighbors are disfavored. The implications for rationalizing selection rule violations in disordered materials and for using inelastic neutron scattering measurements as a means of characterizing disorder are discussed.

© 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

1 Introduction Phonon broadening plays a key role in thermal transport behavior and so is of central significance in the design of functional materials whose performance depends on thermal conductivity [1, 2]. In the topical field of thermoelectrics, for example, low thermal conductivity is desirable as it helps maintain a thermal gradient during current flow [3–5]. Indeed, the key figure of merit for thermoelectrics (zT) is inversely proportional to thermal conductivity. Because broadening reduces phonon lifetimes—and hence the lattice contribution to thermal conductivity—there is significant interest in understanding and controlling microscopic mechanisms by which it might be controlled [6, 7].

There are two principal effects responsible for phonon broadening. First, anharmonic phonon–phonon coupling increases phonon scattering rates and so, in turn, reduces phonon lifetimes; the involvement of heavy atoms can further amplify the contribution at low energies, where the effect on thermal conductivity is usually greatest. Anharmonic broadening is often strong in systems with incipient ferro-

electric instabilities and/or with significant electron–phonon coupling [6]. This is the mechanism generally thought relevant to thermoelectrics such as PbTe [6], and is often accompanied by a dramatic signature in the phonon dispersion where a subset of phonons disperse in energy rather than wave-vector (so-called “waterfall” phonons [8]). A second origin of phonon broadening is that of static disorder. We use the term “static” to describe structural perturbations that are long-lived with respect to phonon lifetimes: a clear example is compositional disorder, but we also include long-lived electronic-driven distortions such as Jahn–Teller (JT) instabilities, charge localization, and polaron formation (where appropriate). The exploitation of disorder to moderate thermal conductivity is a common strategy in thermoelectric design; a topical example is the family of alloys based on the Heusler and half-Heusler structure types [9–12]. The notoriously poor thermal conductivity of quasicrystal phases might also be understood (in general terms) in this same context [13, 14].

Static disorder need not be random, and may instead be associated with a (perhaps very) specific set of periodicities—this is the case of so-called “strongly correlated” disorder [15, 16] found in phases such as water ice [17] and BaTiO₃ [18, 19]. Since phonons also represent a correlated perturbation of the atomic positions in a crystal and are associated with well-defined periodicities via the corresponding wave-vector $\mathbf{k}$, there is the potential for selective coupling between disorder and phonons. In other words, strongly correlated disorder allows in principle for targeted phonon broadening where only particular phonon branches—determined by the type of disorder—exhibit increased widths while others are unaffected by the presence of static disorder. We have suggested elsewhere [16] that this phenomenon may provide a mechanism of manipulating separately electronic and thermal conductivities as required by the “phonon–glass–electron–crystal” paradigm of thermoelectric design [3]. In general, however, the extent and nature of disorder–phonon coupling for various types of correlated disorder remains relatively poorly understood, not least because of the axiomatic role of structural periodicity in conventional lattice dynamical theory [20].

In this context, there is a clear need for straightforward lattice dynamical calculations capable of quantifying the

effect of arbitrary types of static disorder on the phonon dispersion spectrum. A common and computationally inexpensive method for treating disorder within established harmonic lattice dynamical theory is via the so-called “virtual crystal approximation” (VCA), a mean-field-like approach [21]. The VCA determines the average effect of disorder on phonon dispersion and treats phonon broadening as a perturbation within the context of Klemens–Callaway theory [22–24]. This theory holds well for low-frequency phonon modes and low levels of disorder, but breaks down in other scenarios [25, 26]. At the other extreme of computational difficulty is the use of density functional theory (DFT) calculations to calculate excitation energies for explicit atomistic realizations of disordered states [27]. Such calculations are currently limited to systems of order $\sim 10^2$ atoms, which is too small for generation of phonon dispersion curves suitable for comparison to experimental data.

A compromise between these two extremes, accessible for systems where interactions may be effectively parameterized, is to carry out lattice dynamical calculations using disordered supercell configurations representing atomistic realizations of the particular state of interest. These calculations can be performed either in the (quasi-)harmonic limit or so as to account for anharmonic interactions using molecular dynamics (MD) simulations [28]. In either case, off-the-shelf lattice dynamical tools can be used, such as the general utility lattice dynamical program (GULP) [29]. This approach has been used to explore the effects of, for example, random substitution and force-constant disorder on phonon widths and eigenmode localization in canonical alloys and related systems [28, 30].

In this paper, we extend this approach to the calculation of full phonon dispersion relations for hypothetical disordered states on the primitive cubic lattice. In particular, we consider the case of non-random disorder and illustrate the gradual and continuous progression in phonon dispersion for a simple system as the strength of correlations is gradually increased. Our emphasis is on the ease of implementation of the supercell lattice dynamical (SCLD) approach detailed in Ref. [16], with a view to rapid exploration of the relationship between correlated disorder and phonon broadening for a variety of lattice types. Our paper is arranged as follows. We begin by summarizing the methodology of Refs. [28, 30], our particular implementation with the GULP software, and the details of a benchmarking exercise within the VCA. In section 3, we report the disorder-broadened phonon dispersion curves for a variety of systems based on the simple cubic lattice. We distinguish the effects of substitutional and force-constant disorder, and demonstrate the effect of including substitutional correlations in a random alloy on its corresponding phonon dispersion. We conclude with a discussion regarding the implications for rationalizing selection rule violations in disordered materials and for using inelastic neutron scattering measurements as a means of characterizing disorder.

2 Methodology Conventional harmonic lattice dynamical calculations (e.g., as implemented in the GULP



Alistair Overy is a graduate student at the University of Oxford, co-supervised by Andrew Goodwin, Matt Tucker (SNS) and Phil Chater (DLS). His first degree (MChem) is also from Oxford, for which he worked with Jonathan Burton on the total synthesis of oxazolomycin. His research now

focuses on strongly correlated disorder in aperiodic crystals, with a particular interest in the characterization of disorder and the interplay between structure and dynamics. In 2016, Alistair was elected to a Graduate Scholarship at Jesus College, Oxford.



Arkadiy Simonov is a Swiss National Science Foundation Postdoctoral Fellow, currently affiliated with Andrew Goodwin's group at the University of Oxford. Arkadiy studied Physics at Moscow State University and obtained his PhD in Crystallography from ETH Zürich. His PhD research, supervised by Thomas Weber and Walter Steurer,

was awarded the inaugural Crystallographic Thesis Prize of the Swiss Academy of Sciences. Arkadiy's expertise and interests lie chiefly in the interpretation of diffuse scattering from disordered crystals.

software [29]) make use of the dynamical matrix $\mathbf{D}(\mathbf{k})$ defined at wave-vector $\mathbf{k}$ in terms of the elements

$$D_{\alpha j, \beta j'}(\mathbf{k}) = \frac{1}{(m_j m_{j'})^{1/2}} \sum_{\ell'} \left[\Phi_{\alpha\beta} \begin{pmatrix} j & j' \\ 0 & \ell' \end{pmatrix} \times \exp\{i\mathbf{k} \cdot [\mathbf{r}(j'\ell') - \mathbf{r}(j0)]\} \right]. \quad (1)$$

Here, $\begin{pmatrix} j \\ \ell \end{pmatrix}$ denotes the atom j in unit cell ℓ with position $\mathbf{r}(j\ell)$, $\alpha, \beta \in \{x, y, z\}$, and Φ is the force-constant matrix

$$\Phi_{\alpha\beta} \begin{pmatrix} j & j' \\ 0 & \ell' \end{pmatrix} = \frac{\partial^2 W}{\partial u_{j0}^\alpha \partial u_{j'\ell'}^\beta} \quad (2)$$

that relates variations in the lattice energy W to displacements u . A well-known result of lattice dynamical theory [20] is that the $3ZN$ eigenvalues of $\mathbf{D}(\mathbf{k})$ are the squared normal mode frequencies $\omega^2(\mathbf{k}, \nu)$ (here Z is the number of atoms in the unit cell and ν labels the mode) and the corresponding eigenvectors $\mathbf{e}(\mathbf{k}, \nu)$ describe the associated atomic displacement patterns. By evaluating $\mathbf{D}(\mathbf{k})$ for a suitably dense set of wave-vectors $\mathbf{k}$ the phonon dispersion curves can be assembled.

The SCLD approach at the heart of our study differs in that a supercell containing N conventional unit cells is used. We replace the original atom labels j by the atom-cell labels jl to track the position of the corresponding unit cell l within the SCLD supercell. Each atom jl within the supercell may now be assigned arbitrary mass $m(jl)$; likewise the force constants $\Phi_{\alpha\beta} \begin{pmatrix} jl & j'l' \\ 0 & \ell' \end{pmatrix}$ can vary throughout the configuration—that is, for different choices of l, l' —even for constant j, j', ℓ' . The incorporation of disorder in m or Φ usually means that the supercell configuration must first be relaxed to minimize W and to determine the equilibrium atomic coordinates. Whether or not relaxation is required, the corresponding dynamical matrix now contains a total of $3ZN \times 3ZN$ entries.

Diagonalization of $\mathbf{D}(\mathbf{k} = \mathbf{0})$ yields the $3ZN$ frequencies $\omega(\nu)$ and eigenvectors $\mathbf{e}(\nu)$ (each with $3ZN$ components $e_{jl}^\alpha(\nu)$, indexed by atom-cell jl and cartesian direction α) associated with usable normal modes of the supercell. We proceed by projecting these $3ZN$ modes onto a set of N $\mathbf{k}$ -points as allowed by the dimensions of the supercell. For isotropic supercells of length $L = \sqrt[3]{N}$, for example, the allowed $\mathbf{k}$ -points (given in reduced form) are

$$\mathbf{k} = \left(\frac{n_1}{L}, \frac{n_2}{L}, \frac{n_3}{L} \right); \quad n_i \in \{0, 1, \dots, L-1\}. \quad (3)$$

Hence finer $\mathbf{k}$ -meshes require larger supercells. The projection ρ for each $\mathbf{k}$ is determined for all ω by the relation

$$\rho(\mathbf{k}, \omega) = \sum_{\nu} \left\{ \frac{\delta[\omega - \omega(\nu)]}{N} \times \sum_{\alpha} \left| \sum_{jl} e_{jl}^\alpha(\nu) \exp[i\mathbf{k} \cdot \mathbf{r}(jl)] \right|^2 \right\}, \quad (4)$$

where $\mathbf{r}(jl)$ is the position vector for atom-cell jl in the supercell. Our formalism here is analogous to the structure factor expression given in Eq. (21) of Ref. [30]. It is necessary to average over symmetry-equivalent $\mathbf{k}$ points, with the accuracy of $\rho(\mathbf{k}, \nu)$ being improved by further averaging over multiple independent configurations (we typically use five).

We demonstrate the consistency of this approach with conventional lattice dynamical calculations using a periodic simple cubic lattice. This example will later correspond to the VCA limit for a set of binary alloys that we consider. Figure 1a shows the harmonic phonon dispersion relations obtained using conventional lattice dynamical methods parameterized as follows. We consider a single “average” atom (mass m) in a primitive cubic unit cell (lattice parameter a) that interacts with its six nearest neighbors (separated by $\langle 100 \rangle$ lattice vectors) via effective harmonic bond stretching and bond bending terms:

$$E_{\text{harm}} = \frac{1}{2} k_{\text{harm}} (r - r_0)^2; \quad (5)$$

$$E_{\text{angle}} = \frac{1}{2} k_{\text{angle}} (\theta - \theta_0)^2. \quad (6)$$

The actual parameters used are listed in Table 1; these have been chosen to ensure elastic stability and broad dispersion in phonon energies.

The corresponding SCLD phonon dispersion curves obtained using the same parameterization for $10 \times 10 \times 10$ and $20 \times 20 \times 20$ supercells are shown in Fig. 1b and c. Because there is no disorder in these supercell configurations, then the projections $\rho(\mathbf{k}, \omega)$ take the discrete integral values 0, 1, ... (strictly). The match between SCLD and conventional lattice dynamical calculations is exact, with the only difference

Table 1 A parameter summary for the virtual crystal approximant described in the text.

parameter	VCA value
$a/\text{\AA}$	10
m/amu	60
$k_{\text{harm}}/\text{eV}\text{\AA}^{-2}$	10
$r_0/\text{\AA}$	10
$k_{\text{angle}}/\text{eV rad}^{-2}$	10
$\theta_0/^\circ$	90

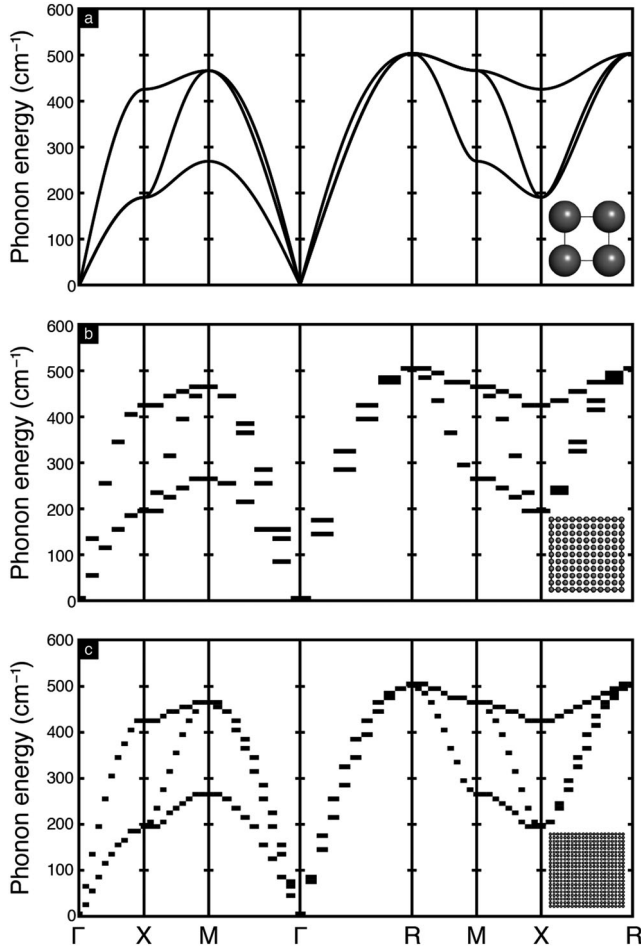


Figure 1 Consistency test for SCLD calculations using a periodic model system. (a) Phonon dispersion curves determined using conventional dynamical matrix calculations as implemented in GULP (Ref. [29]). The relevant parameterization is described in the text and in Table 1. The simple cubic cell contains a single atom; hence there are three (sometimes degenerate) branches of the phonon dispersion at each $\mathbf{k}$ -point. (b,c) The corresponding phonon dispersion curves determined using the SCLD approach described in the text for (b) $10 \times 10 \times 10$ and (c) $20 \times 20 \times 20$ supercells. Representations of the GULP unit cells are given in the bottom-right corner of each set of phonon dispersion curves

between the two being the finite $\mathbf{k}$ -grid on which the SCLD calculations are obtained.

3 Results Having established the viability of the SCLD approach in the mean-field limit of the VCA, we turn now to the key focus of our study: namely, determination of the intrinsic phonon broadening resulting from static disorder. Our implementation involves varying the masses $m(jl)$ and/or force-constants $\Phi_{\alpha\beta} \begin{pmatrix} jl & j'l' \\ 0 & \ell' \end{pmatrix} \equiv k_{\text{harm}}, k_{\text{angle}}$ through-out a disordered configuration, as envisaged in Section 2. For simplicity, we focus on a single family of related systems:

Table 2 The perturbed parameters in the mass and harmonic bond stiffness disordered alloys

parameter	mass disorder	force-constant disorder
m_A/amu	40	60
m_B/amu	80	60
$k_{\text{harm}}(A-A)/\text{eV}\text{\AA}^{-2}$	10	5
$k_{\text{harm}}(B-B)/\text{eV}\text{\AA}^{-2}$	10	15
$k_{\text{harm}}(A-B)/\text{eV}\text{\AA}^{-2}$	10	10

simple cubic binary (AB) alloys containing equal quantities of the two components.

3.1 Random disorder In our first case study, we consider the effect of random mass disorder. This is implemented by varying m_A and m_B parameters but retaining homogeneity in the $k_{\text{harm}}, k_{\text{angle}}$ terms [Table 2]. For a set of five independent configurations, each corresponding to a $10 \times 10 \times 10$ supercell of the simple cubic cell, we assigned atom sites to A and B components randomly such that each configuration contained equal numbers of A and B atoms. The corresponding phonon spectrum, determined using the SCLD approach and averaged across all five configurations, is shown in Fig. 2a. An immediate consequence of the presence of nontrivial disorder is the continuous behavior of the projection $\rho(\mathbf{k}, \omega)$, which now assumes non-integral values between 0 and 1. This spread in values of ρ reflects the intrinsic contribution to phonon broadening arising purely due

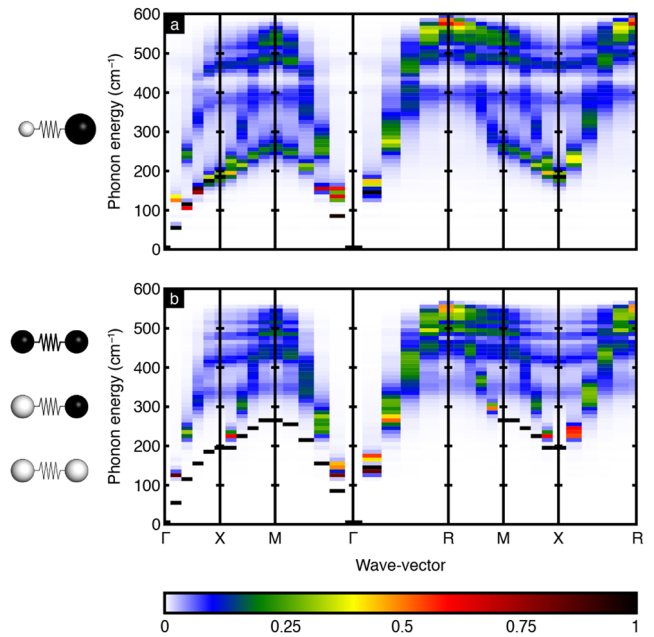


Figure 2 A study into the effect of mass and k_{harm} disorder in a random binary alloy. (a,b) Phonon dispersion curves determined through the SCLD approach using a $10 \times 10 \times 10$ supercell for (a) a mass disordered alloy and (b) an alloy with harmonic bond stretching force constant disorder.

to static disorder within the configuration. Moreover, additional branches appear to emerge (e.g., at the R point around 400 cm^{-1}), showing that the SCLD approach, unlike perturbation theory, is able to capture multiple effects simultaneously. Qualitatively similar behavior is observed for all ratios m_A/m_B , with the magnitude of phonon broadening a function of the deviation of this ratio away from unity. In comparing to experimental data one would need to take into account also the instrumental resolution function.

We performed similar calculations for an equivalent set of configurations but where we varied the strength of harmonic bond stretching force constants rather than atomic masses. The relevant parameters are again listed in Table 2 and the corresponding phonon dispersion relations are now shown in Fig. 2b. The choice in parameters reflects a stronger effective variation than in the mass disorder and while the overall extent of phonon broadening is roughly similar to that observed for the case of mass disorder, we find a number of qualitative differences that demonstrate the sensitivity of the dynamical matrix to different types of disorder. For example, whereas the phonon density of states vanishes near 450 cm^{-1} in the case of mass disorder, the excitation spectrum of the system with force-constant disorder is entirely gapless. Perhaps even more striking is the absence of any broadening for specific branches of the phonon dispersion in Fig. 2b, namely, the lowest-energy transverse acoustic branch for Γ -X, X-M, and Γ -M directions in reciprocal space. That these two types of disorder give rise to different broadening effects is unsurprising since they affect diagonal and off-diagonal elements of the dynamical matrix in different ways [27]. Our results for these canonical systems agree well with the conclusions of earlier studies [28, 30].

3.2 Correlated disorder Our next step, and the ultimate goal of our study, was to explore the effect of including correlations in the distribution of A and B sites (while maintaining stoichiometry). We consider here the very simplest type of occupational correlation, corresponding to avoidance of like constituents on neighboring sites; in zeolite chemistry this is the Lowenstein rule [31]. The extent of correlation is quantified by the order parameter

$$\phi = \frac{N_{AB} - (N_{AA} + N_{BB})}{3N}, \quad (7)$$

where N_{AB} is the number of nearest neighbor contacts between atoms of types A and B, and N is the total number of atoms (= supercell size, in this case). A statistical distribution of A and B sites gives $N_{AA} = N_{BB} = 3N/4$, $N_{AB} = 3N/2$ and hence $\phi = 0$. If A-A/B-B avoidance is complete then $N_{AA} = N_{BB} = 0$, $N_{AB} = 3N$ and $\phi = 1$; this state corresponds to rocksalt-type ordering of A and B sites.

Using a custom Monte Carlo algorithm, we generated an ensemble of configurations corresponding to the order parameter values $\phi = 0, \frac{1}{4}, \frac{1}{2}, \frac{3}{4}, 1$. Each configuration represented a $12 \times 12 \times 12$ supercell of the primitive cubic cell. In almost every case we prepared five independent configura-

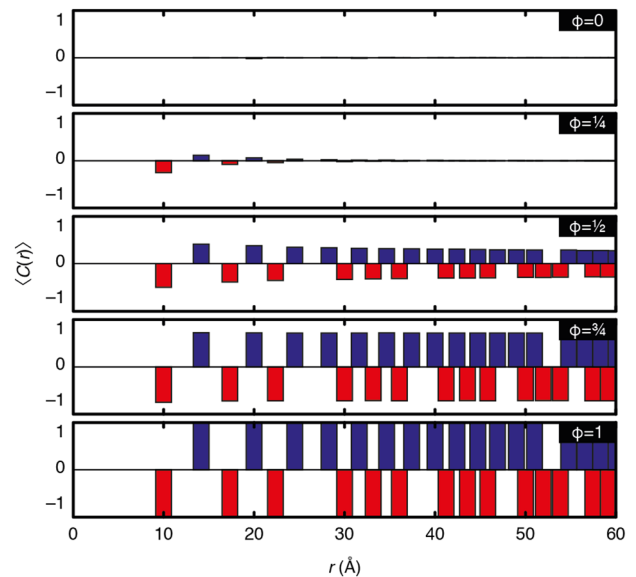


Figure 3 Average correlation functions $\langle C(r) \rangle$ obtained from the five independent configurations at each given ϕ value. Positive correlations, A-A and B-B, are shown in blue with negative correlations, A-B, shown in red.

tions to improve counting statistics; the exception was the case $\phi = 1$, which is ordered. As a check of longer-range correlations we calculated the correlation function

$$C(r) = \frac{1}{Nz(r)} \sum_{i,j|r_{ij}=r} e(i)e(j), \quad (8)$$

for each configuration. Here, $e(i) = \pm 1$ denotes whether site i is occupied by an A or B atom, N is the total number of atoms, and the sum is taken over the $z(r)$ neighbors j of site i at distance r . The average behavior of $C(r)$ for a given ϕ value is shown in Fig. 3. For each configuration, we calculated the corresponding phonon dispersion relation using our SCLD approach, averaging over configurations corresponding to equivalent values of the order parameter. For these various calculations, we used the “mass disorder” parameters given in Table 2. Consequently we expect the form of the phonon dispersion for the $\phi = 0$ configurations to resemble closely that determined in the “random disorder” section above [Fig. 2a].

The resulting dispersion curves are shown in Fig. 4. We do indeed observe good consistency between our results for $\phi = 0$ [Fig. 4a] and those given in Fig. 2, noting for completeness that the $\mathbf{k}$ -grid is slightly denser for the former than for the latter. Our key result, however, is the consistent and physically sensible evolution of the phonon spectrum as the strength of correlations increases. We find a steady decrease in phonon broadening with increasing ϕ that accompanies the opening of an excitation gap near 400 cm^{-1} . Hence, in a real system, the nature of the density of states in this region of the phonon spectrum is likely to be highly sensitive to the degree of site ordering. Also clear is the emergence

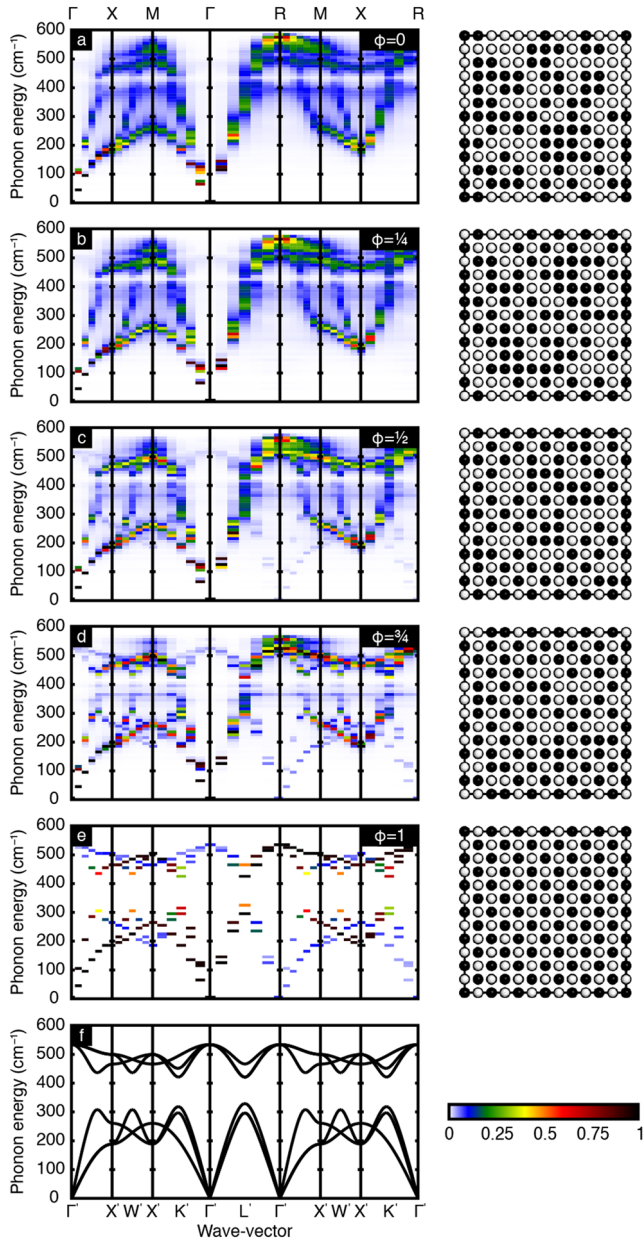


Figure 4 Investigation into the effect of correlated disorder on phonon band broadening. (a–e) Phonon dispersion curves determined through the SCLD method for $12 \times 12 \times 12$ supercells of a mass disordered alloy with ϕ values of (a) 0.00, (b) 0.25, (c) 0.50, (d) 0.75 and (e) 1.00 – the ordered NaCl structure. (f) Phonon dispersion curves determined using the conventional dynamical matrix calculations in GULP for the $\phi = 1.00$ structure. The differing wave-vector axis labels at the top and bottom of the figure refer to the high symmetry points in the primitive cubic and face centered cubic Brillouin zones, respectively. The color scale is a measure of the projection ρ at each $\mathbf{k}$ -point.

of a new set of phonon branches that in the case of $\phi = 1$ establishes the original zone corner $\mathbf{k} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (R point) as a new zone center (denoted in Fig. 4 as Γ^*). This behavior is entirely physical: the ordered $\phi = 1$ configuration has

a face-centered cubic unit cell with lattice parameter double that of the original primitive cubic cell. Hence, the point $\mathbf{k} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ is now a reciprocal lattice vector. The harmonic phonon relation can be calculated exactly for this state and is shown in Fig. 4f; the match to our SCLD result in Fig. 4e is again exact.

We note that the projection magnitude $\rho(\mathbf{k}, \omega)$ for the secondary (face-centered) phonon branches is much smaller than that for the primary branches. This difference reflects the mass difference between A and B atoms. It is straightforward to show, using standard lattice dynamical theory [20], that the projections of the acoustic and optic branches at the zone center are given by

$$\rho(\mathbf{k} = 0, \text{acoustic}) = \frac{1}{2} + \frac{\sqrt{m_A m_B}}{m_A + m_B}, \quad (9)$$

$$\rho(\mathbf{k} = 0, \text{optic}) = \frac{1}{2} - \frac{\sqrt{m_A m_B}}{m_A + m_B}. \quad (10)$$

Hence, in the limit of large mass difference between A and B atoms, the projections approach $\rho \rightarrow \frac{1}{2}$; conversely, for vanishingly small mass differences, the “optic” component also vanishes and the phonon dispersion reverts to that observed for a single component system. In our particular case, the values of m_A and m_B given in Table 2 correspond to projection values of 97% (acoustic) and 3% (optic), as shown in Fig. 4e.

While we have focussed here on an extremely simple case of correlated disorder, the approach we have developed is straightforwardly applied to substantially more complicated cases. Our particular eventual interest is in strongly-correlated systems such as the various “procrystalline” families described in Ref. [16]. We note that these systems include examples where the source of disorder is electronic in nature, such as the correlated second-order Jahn Teller displacements observed in cubic BaTiO₃ [19, 32]. We anticipate that application of SCLD methods to such systems may help bridge the ostensibly unrelated concepts of disorder- and anharmonicity-dependent phonon broadening.

4 Concluding remarks Access to computationally tractable calculation approaches for determining phonon relations in disordered materials opens up the attractive possibility of iterative comparison with experimental inelastic neutron scattering and/or inelastic X-ray scattering measurements. This offers a means of refining both the form of structural disorder and the perturbations of effective interaction parameters from the experimental phonon spectrum. Such an approach would complement conventional elastic scattering measurements as a method of characterizing disorder [33], with the added advantage of providing insight into the effect of local symmetry breaking on local interaction strengths. Quantitative comparison with experimental data would require accurate characterization of the experimental resolution function, with care taken also to ensure appropriate treatment of polarization effects (e.g., LO/TO splitting).

We conclude with two final points of potential relevance to subsequent applications of SCLD methods. First, the absence of explicit symmetry constraints in the SCLD approach allows in principle for the investigation of infrared/Raman selection rule violations in disordered materials, including canonical systems such as water ice [34–37]. And, second, we note that the phonon broadening we observe is of course a signature of the breakdown of the plane-wave description of vibrational states in these disordered solids. Exploration of the localization (or otherwise) of the corresponding eigenvectors may provide valuable insight into the relationship of these vibrational states and the diffusons implicated in thermal transport in glasses [30, 38].

Acknowledgements A.R.O., A.S., and A.L.G. gratefully acknowledge financial support from the European Research Council (Grant 279705), from the Diamond Light Source, UK to A.R.O., and to A.S. from the Leverhulme Trust (Grant RPG-2015-292) and the Swiss National Science Foundation (Grant P2EZP2_155608).

References

- [1] E. S. Toberer, L. L. Baranowski, and C. Dames, *Annu. Rev. Mater. Res.* **42**, 179 (2012).
- [2] D. G. Cahill and R. O. Pohl, *Annu. Rev. Phys. Chem.* **39**, 93 (1988).
- [3] G. J. Snyder and E. S. Toberer, *Nature Mater.* **7**, 105 (2008).
- [4] J. Yang, L. Xi, W. Qiu, L. Wu, X. Shi, L. Chen, J. Yang, W. Zhang, C. Uher, and D. J. Singh, *NPJ Comput. Mater.* **2**, 15015 (2016).
- [5] W. G. Zeier, J. Schmitt, G. Hautier, U. Aydemir, Z. M. Gibbs, C. Felser, and G. J. Snyder, *Nature Rev. Mater.* **1**, 16032 (2016).
- [6] O. Delaire, J. Ma, K. Marty, A. F. May, M. A. McGuire, M.-H. Du, D. J. Singh, A. Podlesnyak, G. Ehlers, M. D. Lumsden, and B. C. Sales, *Nature Mater.* **10**, 614 (2011).
- [7] L.-D. Zhao, S.-H. Lo, Y. Zhang, H. Sun, G. Tan, C. Uher, C. Wolverton, V. P. Dravid, and M. G. Kanatzidis, *Nature* **508**, 373 (2014).
- [8] J. Hlinka, S. Kamba, J. Petzelt, J. Kulda, C. A. Randall, and S. J. Zhang, *Phys. Rev. Lett.* **91**, 107602 (2003).
- [9] R. A. Downie, D. A. MacLaren, R. I. Smith, and J. W. G. Bos, *Chem. Commun.* **49**, 4184 (2013).
- [10] M. Asaad, J. Buckman, R. I. Smith, and J. W. G. Bos, *RSC Adv.* **6**, 56511 (2016).
- [11] H. Xie, H. Wang, C. Fu, Y. Liu, G. J. Snyder, X. Zhao, and T. Zhu, *Sci. Rep.* **4**, 6888 (2014).
- [12] C. Fu, S. Bai, Y. Liu, Y. Tang, L. Chen, X. Zhao, and T. Zhu, *Nature Commun.* **6**, 9144 (2015).
- [13] A. L. Pope and T. M. Tritt, *Thermal conductivity: Theory, Properties and Applications*, 1st ed. (Kluwer Academic Publishers/Plenum Publishers, New York, 2004).
- [14] E. Courtens and R. Vacher, Acoustic-like excitations in strongly disordered media, in: *From Quasicrystals to More Complex Systems* (EDP Sciences/Springer-Verlag, Berlin, 2000).
- [15] D. A. Keen and A. L. Goodwin, *Nature* **521**, 303 (2015).
- [16] A. R. Overy, A. B. Cairns, M. J. Cliffe, A. Simonov, M. G. Tucker, and A. L. Goodwin, *Nature Commun.* **7**, 10445 (2016).
- [17] L. Pauling, *J. Am. Chem. Soc.* **57**, 2680 (1935).
- [18] H. D. Megaw, *Proc. R. Soc. A* **189**, 261 (1947).
- [19] M. S. Senn, D. A. Keen, T. C. A. Lucas, J. A. Hriljac, and A. L. Goodwin, *Phys. Rev. Lett.* **116**, 207602 (2016).
- [20] M. T. Dove, *Introduction to Lattice Dynamics*, 1st ed. (Cambridge University Press, Cambridge, 1993).
- [21] B. Abeles, *Phys. Rev.* **131**, 1906 (1963).
- [22] P. G. Klemens, *Proc. Phys. Soc. A* **68**, 1113 (1955).
- [23] P. G. Klemens, *Proc. Phys. Soc. A* **70**, 833 (1957).
- [24] J. Callaway, *Phys. Rev.* **113**, 1046 (1959).
- [25] D. C. Mattis and J. Bardeen, *Phys. Rev.* **111**, 412 (1958).
- [26] W. A. Kamitakahara and B. N. Brockhouse, *Phys. Rev. B* **10**, 1200 (1974).
- [27] A. Alam, R. K. Chouhan, and A. Mookerjee, *Phys. Rev. B* **83**, 054201 (2011).
- [28] J. M. Larkin and A. J. H. McGaughey, *J. Appl. Phys.* **114**, 023507 (2013).
- [29] J. D. Gale, *Faraday Trans.* **93**, 629 (1997).
- [30] Y. M. Beltukov, V. I. Kozub, and D. A. Parshin, *Phys. Rev. B* **87**, 134203 (2013).
- [31] W. Löwenstein, *Am. Miner.* **39**, 92 (1954).
- [32] R. Comès, M. Lambert, and A. Guinier, *Acta Crystallogr. A* **26**, 244 (1970).
- [33] T. R. Welberry and T. Weber, *Crystallogr. Rev.* **22**, 2 (2016).
- [34] H. Uwe, K. B. Lyons, H. L. Carter, and P. A. Fleury, *Phys. Rev. B* **33**, 6436 (1986).
- [35] K. Inoue, A. Hasegawa, K. Watanabe, H. Yamaguchi, and H. Uwe, *Phys. Rev. B* **38**, 6352 (1988).
- [36] H. Fukazawa and S. Mae, *Phys. Ice Core Rec.*, 25 (2000).
- [37] P. T. T. Wong and E. Whalley, *J. Chem. Phys.* **65**, 829 (1976).
- [38] K. Prasai, P. Biswas, and D. A. Drabold, *Semicond. Sci. Technol.* **31**, 073002 (2016).



Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jsscUniaxial negative thermal expansion and metallophilicity in $\text{Cu}_3[\text{Co}(\text{CN})_6]$ A.F. Sapnik^a, X. Liu^b, H.L.B. Boström^a, C.S. Coates^a, A.R. Overy^{a,c}, E.M. Reynolds^a,
A. Tkatchenko^d, A.L. Goodwin^{a,*}^a Department of Chemistry, University of Oxford, Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, UK^b State Key Laboratory of Mechanics and Control of Mechanical Structures, Key Laboratory for Intelligent Nano Materials and Devices of Ministry of Education, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China^c Diamond Light Source, Chilton, Oxfordshire OX11 0DE, UK^d Physics and Materials Science Research Unit, University of Luxembourg, L-1511, Luxembourg

ARTICLE INFO

Keywords:

Negative thermal expansion
Framework materials
Metallophilic interactions

ABSTRACT

We report the synthesis and structural characterisation of the molecular framework copper(I) hexacyanocobaltate(III), $\text{Cu}_3[\text{Co}(\text{CN})_6]$, which we find to be isostructural to $\text{H}_3[\text{Co}(\text{CN})_6]$ and the colossal negative thermal expansion material $\text{Ag}_3[\text{Co}(\text{CN})_6]$. Using synchrotron X-ray powder diffraction measurements, we find strong positive and negative thermal expansion behaviour respectively perpendicular and parallel to the trigonal crystal axis: $\alpha_a = 25.4(5) \text{ MK}^{-1}$ and $\alpha_c = -43.5(8) \text{ MK}^{-1}$. These opposing effects collectively result in a volume expansivity $\alpha_V = 7.4(11) \text{ MK}^{-1}$ that is remarkably small for an anisotropic molecular framework. This thermal response is discussed in the context of the behaviour of the analogous H- and Ag-containing systems. We make use of density-functional theory with many-body dispersion interactions (DFT + MBD) to demonstrate that $\text{Cu}^+ \dots \text{Cu}^+$ metallophilic ('cuprophilic') interactions are significantly weaker in $\text{Cu}_3[\text{Co}(\text{CN})_6]$ than $\text{Ag}^+ \dots \text{Ag}^+$ interactions in $\text{Ag}_3[\text{Co}(\text{CN})_6]$, but that this lowering of energy scale counterintuitively translates to a more moderate—rather than enhanced—degree of structural flexibility. The same conclusion is drawn from consideration of a simple GULP model, which we also present here. Our results demonstrate that strong interactions can actually be exploited in the design of ultra-responsive materials if those interactions are set up to act in tension.

1. Introduction

The development of responsive materials often exploits weak interactions as key design elements because lower interaction energies heighten the sensitivity of a material to external perturbations [1–4]. It is no accident, for example, that the weak inter-molecular forces in molecular crystals generally allow more extreme responses to changes in temperature [5,6] and pressure [7,8] than is possible in conventional inorganic ceramics, the structures of which are held together by strong ionic and covalent bonding networks. In this context, supramolecular interactions assume a particular importance, given that their energy scales are so much lower than those of electrostatic or covalent interactions. Hence the prevalence of hydrogen-bonding [9], halogen-bonding [10], π – π [11], van der Waals (vdW) [5], host–guest [12,13], and metallophilic [14] interactions amongst many of the important materials in the field.

Thermal expansion behaviour is a straightforward measure of responsiveness: it quantifies the effect of temperature on the linear

dimensions of a material [15]. Compounds with large thermal expansion coefficients often show extreme and counterintuitive responses to pressure [16,17], and may harbour various other anomalous elastic properties, such as negative Poisson's ratios [18] or thermosallient effects [19,20]. So it is perhaps unsurprising that some of the most extreme ('colossal') thermal expansion known has been observed in framework materials whose lattice dimensions are a function of weak metallophilic interactions [14,17,21]. The canonical system of this type is $\text{Ag}_3[\text{Co}(\text{CN})_6]$, which adopts a lattice structure [22] that can flex in such a way as to vary argentophilic $\text{Ag}^+ \dots \text{Ag}^+$ separations without affecting covalent interactions within the lattice itself [23,24]. A geometric consequence of this flexing behaviour is that the positive thermal expansion (PTE) of argentophilic interactions (*i.e.* increase in separation with increasing temperature) is translated into a negative thermal expansion (NTE) effect in a perpendicular direction, Fig. 1. The same mechanism operates under application of hydrostatic pressure, such that volume compression actually results in linear expansion for a particular set of directions [17]—so-called negative

* Corresponding author.

E-mail address: andrew.goodwin@chem.ox.ac.uk (A.L. Goodwin).<http://dx.doi.org/10.1016/j.jssc.2017.10.009>

Received 5 September 2017; Received in revised form 3 October 2017; Accepted 5 October 2017

Available online 07 October 2017

0022-4596/ © 2017 Elsevier Inc. All rights reserved.

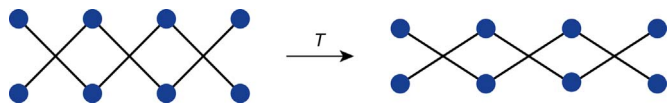


Fig. 1. “Wine-rack” mechanism for anisotropic thermal expansion in flexible framework materials. Horizontal expansion couples to vertical contraction *via* lattice flexing.

linear compressibility (NLC) [25–27]. NTE and NLC are valuable material properties, exploitable in the design of a thermal composites used in optical devices and next-generation pressure sensors.

In seeking to design even more responsive analogues of $\text{Ag}_3[\text{Co}(\text{CN})_6]$, we considered the possibility of replacing Ag by Cu. Metallophilic interactions involving Cu^+ ions are perhaps less well studied than argentophilic and aurophilic interactions, but are expected to be weaker given the reduced polarisability of the 3d shell [28,29]. Hence, by the arguments discussed above, $\text{Cu}_3[\text{Co}(\text{CN})_6]$ has always been an obvious candidate for extreme thermomechanical response. To the best of our knowledge, this system has never previously been reported: the difficulty of preparing the phase is likely a consequence of the propensity for Cu^+ to disproportionate under the aqueous reaction conditions used to prepare the family of materials related to $\text{Ag}_3[\text{Co}(\text{CN})_6]$ [23]. We have recently exploited the Cu^{2+} reduction protocol developed in Ref. [30] to allow access to otherwise unrealisable Cu(I)-containing frameworks [31], suggesting that a similar synthetic approach may provide an alternative synthetic entry point to $\text{Cu}_3[\text{Co}(\text{CN})_6]$.

Here we validate such an approach, reporting the synthesis, crystal structure, and thermal expansion behaviour of $\text{Cu}_3[\text{Co}(\text{CN})_6]$. Using a combination of high-resolution synchrotron X-ray diffraction measurements and Rietveld refinement, we show the system to be isostructural with $\text{Ag}_3[\text{Co}(\text{CN})_6]$ and $\text{H}_3[\text{Co}(\text{CN})_6]$ [22,32–34]. Variable-temperature (100–598 K) X-ray diffraction measurements allow determination of the corresponding coefficients of thermal expansion $\alpha_\ell = (\partial \ln \ell / \partial T)_p$, which we find to be substantially less extreme than those of $\text{Ag}_3[\text{Co}(\text{CN})_6]$ (even if they remain large in the context of the behaviour of conventional inorganic solids [35]). In particular, our data give $\alpha_a = 25.4(5) \text{ MK}^{-1}$ and $\alpha_c = -43.5(8) \text{ MK}^{-1}$; cf $\alpha_a = 144(9) \text{ MK}^{-1}$ and $\alpha_c = -126(4) \text{ MK}^{-1}$ for $\text{Ag}_3[\text{Co}(\text{CN})_6]$ [23]. In order to rationalise this more moderate thermomechanical response in terms of the relative strengths of $\text{Cu}^+ \dots \text{Cu}^+$ and $\text{Ag}^+ \dots \text{Ag}^+$ metallophilic interactions, we carry out a series of *ab initio* calculations. Our analysis suggests (i) that cuprophilic interactions are indeed weaker than argentophilic interactions in this family, and (ii) the more extreme thermomechanical response of the Ag-containing compound is a result of the balance of metallophilic and electrostatic interaction energies rather than a signature of particularly weak argentophilicity. Calculations using a highly simplified interaction model relevant to the entire $\text{A}_3[\text{Co}(\text{CN})_6]$ structural family lead to the same conclusions. Our results suggest that *competing* interactions—rather than low-energy interactions *per se*—can be key in the design of ultra-responsive materials.

2. Methods

All reagents were obtained from commercial suppliers and used as received.

2.1. Copper(I) hexacyanocobaltate(III)

We prepared polycrystalline samples of copper(I) hexacyanocobaltate(III) following a modification of the reduction protocol reported in Refs. [30,31]. A saturated aqueous solution of copper(II) sulfate (Sigma Aldrich, 99%; 0.177 g) was added dropwise to a concentrated aqueous solution of sodium bisulfite (Sigma Aldrich, 0.058 g), present in stoichiometric excess, to afford a mint-green solution. The solution was stirred for 30 min, after which time an aqueous solution of potassium hexacyanocobaltate(III) (Sigma Aldrich,

97%, 0.123 g; stoichiometric with respect to copper) was added dropwise to afford a pale blue precipitate. The solution was stirred for a further 2 h, and the pale-blue solid product formed was isolated by filtration, washing (H_2O) and drying under vacuum. The solid contained a mixture of copper(I) hexacyanocobaltate(III) and Prussian-blue-structured potassium copper(II) hexacyanocobaltate(III), a seemingly inescapable by-product of this synthetic strategy.

Copper(I) hexacyanocobaltate(III) could also be obtained in impure form using mechanochemical synthesis. Stoichiometric quantities of solid tetrakis(acetonitrile)copper(I) hexafluorophosphate (Chem Cruz, 98%, 0.413 g) and potassium hexacyanocobaltate (Sigma Aldrich, 97%, 0.123 g) were combined in an agate mortar, and intimately mixed *via* solid-state grinding for 30 min. An obvious colour change from white to pale blue occurred during this process. The resulting solid was washed (H_2O) and dried to afford a mixture of copper(I) hexacyanocobaltate(III), potassium copper(II) hexacyanocobaltate(III) and at least one further unidentified product. Given the reduced purity of this product, the solution-phase product described above was used for all diffraction measurements carried out in this study.

2.2. Powder X-ray diffraction

High-resolution synchrotron X-ray powder diffraction measurements were carried out using the I11 beamline at the Diamond Light Source. A finely-ground sample of copper(I) hexacyanocobaltate(III), prepared as above, was loaded into a borosilicate capillary (0.5 mm diameter) and mounted on the diffractometer. Diffraction patterns were recorded using the Mythen2 point sensitive detector over the angular range $2\theta = 2\text{--}92^\circ$, using an X-ray wavelength $\lambda = 0.826210 \text{ \AA}$ calibrated by refinement of a silicon NIST 640c standard. Each measurement consisted of two scans of 5 s exposure, offset relative to one another by $\Delta 2\theta = 0.25^\circ$. During preliminary measurements we found the sample to be strongly sensitive to damage by the synchrotron X-ray beam. Consequently, our eventual data collection strategy involved translation of the capillary between measurements such that every measurement was carried out on a pristine sample. The sample temperature was controlled using an Oxford Cryostream (100–500 K) and a Cyberstar hot air blower (523–598 K). Diffraction patterns were measured at intervals of 25 K between 100 and 500 K and again between 523 and 598 K. A ramp rate of 0.1 K s^{-1} was used between successive measurements, with an equilibration time of 60 s at each temperature point.

Both Pawley and Rietveld refinements were carried out using TOPAS Academic (version 4.1) [36]. We employed a modified Thompson–Cox–Hasting pseudo-Voigt (TCHZ) peak shape, combined with a simple axial divergence correction and a Stephens anisotropic peak broadening term [37]. The potassium copper(II) hexacyanocobaltate(III) impurity phase was modelled using Pawley refinement of the $Fm\bar{3}m$ double-metal cyanide cell ($a \sim 10 \text{ \AA}$) [38]. Rietveld refinement of the $\text{Cu}_3[\text{Co}(\text{CN})_6]$ phase made use of a starting model based on the known structure of $\text{Ag}_3[\text{Co}(\text{CN})_6]$ [22]. Refinement was stable for all temperature points, provided that Co–C/C–N bond distance restraints and a single isotropic displacement parameter for all atom types were used in the Rietveld model. Sequential (seed-batch) Rietveld refinements, where the starting structural parameters for each temperature point were those used at the preceding temperature, provided structural models with physically-sensible temperature dependencies for $T \leq 450 \text{ K}$. For the temperature regime $450 \leq T \leq 598 \text{ K}$, we found that the positional coordinates of the C and N atoms and the value of B_{iso} showed strong covariance, and hence we have reduced confidence in the absolute values of these parameters. This regime corresponds to the temperature range over which decomposition of the $\text{KCu}[\text{Co}(\text{CN})_6]$ phase appears to set in.

2.3. Thermal expansivity determination

Thermal expansivities were calculated using the PASCAL software

[39]. We employed estimated temperature uncertainties of 5 K and fitted the principal axis expansivities using linear functions. For internal consistency with the uniaxial expansivities, the volume expansivity was determined using the trace of the expansivity tensor [40] rather than *via* the direct V – T fit given by PASCAL [39].

2.4. Ab initio calculations

Ab initio calculations were performed within the FHI-aims code [41], using the numeric atom-centred orbital tier 1 basis set for the wavefunction and a $5 \times 5 \times 5$ k -point mesh for the Brillouin zone sampling. The Perdew–Burke–Ernzerhof (PBE) functional [42] was used to model the semilocal exchange–correlation energy. To describe the non-local dispersion energies, we used both the interatomic pairwise Tkatchenko–Scheffler (TS) method [43], as well as the many-body dispersion (MBD) method, which includes many-body dipolar interatomic interactions to all orders in perturbation theory [44,45]. The lattice constants were obtained from unit cell relaxations with cell angles fixed to experimental values. Full *a posteriori* relaxation of the unit cell proved the reliability of this scheme.

2.5. GULP calculations

The GULP software (version 4.4) [46] was used to calculate equilibrium cell dimensions for a series of simple interaction potential models. Cell optimisations were carried out under constant pressure conditions $p = 0$ and at $T = 0$, with strains constrained by symmetry. Dispersion interactions were modelled using a Buckingham potential with vanishingly small repulsive term, and the ‘c6’ flag was activated to employ Ewald-type summation. For all calculations, checks were carried out to ensure optimisation convergence and to verify the conservation of angle terms in the parameterisation.

3. Results and discussion

3.1. Crystal structure of $\text{Cu}_3[\text{Co}(\text{CN})_6]$

The ambient-temperature X-ray powder diffraction pattern of our $\text{Cu}_3[\text{Co}(\text{CN})_6]$ sample is shown in Fig. 2. We could account for the entire diffraction pattern using two components, one based on the $\text{Ag}_3[\text{Co}(\text{CN})_6]$ structure-type (space group symmetry $P\bar{3}1m$) and one with the cubic Prussian blue structure (space group symmetry $Fm\bar{3}m$).

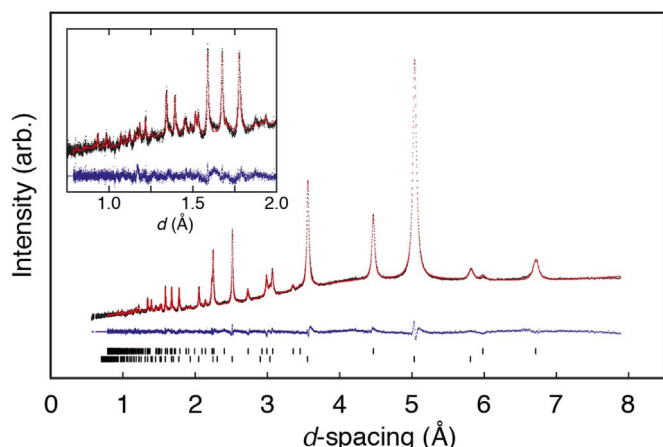


Fig. 2. X-ray powder diffraction behaviour and its interpretation in $\text{Cu}_3[\text{Co}(\text{CN})_6]$. Experimental data are shown as black points, Rietveld fit as red points, and the difference function (data – fit) as a solid blue line. Tick marks denote the positions of symmetry-allowed reflections for the $\text{Cu}_3[\text{Co}(\text{CN})_6]$ (upper marks) and impurity $\text{KCu}[\text{Co}(\text{CN})_6]$ (lower marks) phases. The inset shows a magnified representation of the fit at low- d (high- Q). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

This second phase would be consistent with the formation of $\text{KCu}[\text{Co}(\text{CN})_6]$ during synthesis, which is certainly feasible on chemical grounds [47,48]. A Pawley fit using this two-phase model confirms our assignment of space group symmetries and rules out the presence of any additional crystalline phases. We note that there is good (if fortuitous) distinction between the diffraction profiles of the two phases present, which allows us to clearly distinguish the corresponding lattice parameters and their thermal expansion behaviour (see SI).

Having established the space group symmetry of $\text{Cu}_3[\text{Co}(\text{CN})_6]$ we proceeded to carry out a Rietveld refinement, employing a starting model based on the lattice parameters obtained during Pawley fitting and the published atom coordinates of $\text{Ag}_3[\text{Co}(\text{CN})_6]$ [22]. We continued to model the $\text{KCu}[\text{Co}(\text{CN})_6]$ phase using a Pawley fit—indeed this is the case for all subsequent refinements and is not discussed further. We found good stability in the refinement of our structural model of $\text{Cu}_3[\text{Co}(\text{CN})_6]$, obtaining a R -value of 3.029%; the corresponding fit is shown in Fig. 2 and the relevant structural details are summarised in Table 1. A representation of the crystal structure itself is given in Fig. 3. All refined bond lengths are chemically sensible: we find a Co–C distance of 1.832(11) Å, which is similar to that in $\text{Ag}_3[\text{Co}(\text{CN})_6]$ ($d(\text{Co}–\text{C}) = 1.895$ Å) [22]; likewise the Cu–N separation of 1.887(10) Å is comparable to that found in CuCN ($d(\text{Cu}–\text{C}/\text{N}) = 1.839(9)–1.872(12)$ Å) [49].

A property of the particular space group symmetry of $\text{Cu}_3[\text{Co}(\text{CN})_6]$ is that the $\text{Cu}^+ \dots \text{Cu}^+$ separation is directly related to the lattice parameters:

$$r_{\text{Cu} \dots \text{Cu}} = \frac{a}{2}. \quad (1)$$

Hence we find $r_{\text{Cu} \dots \text{Cu}} = 3.4543(5)$ Å, which lies at the very upper bound of $\text{Cu}^+ \dots \text{Cu}^+$ separations for which cuprophilic interactions are considered relevant [50]. One crude measure of the strength of metallophilic interactions is to consider the ratio of the observed interatomic distance to the sum of the corresponding vdW radii [28]. Using our room-temperature lattice parameters and the vdW radii given in Ref. [51] we obtain a ratio of 1.00 for $\text{Cu}_3[\text{Co}(\text{CN})_6]$, which is remarkably similar to the corresponding value for $\text{Ag}_3[\text{Co}(\text{CN})_6]$ (0.99) [23]. So, at face value, one might expect comparable metallophilic interaction strengths for the two systems.

3.2. Thermal expansion behaviour

Having collected a series of X-ray diffraction patterns over the temperature range 100–598 K, we carried out Rietveld refinements for each data set using the same approach described above. We obtained satisfactory refinements for all temperatures, albeit with some signs of increased uncertainties at the very highest temperatures—i.e., close to the onset of decomposition of the Prussian blue phase. The temperature dependence of the lattice parameters, illustrated in Fig. 4(a), was

Table 1

Structural details for $\text{Cu}_3[\text{Co}(\text{CN})_6]$ obtained by Pawley/Rietveld refinement against X-ray powder diffraction data collected at 300 K and estimated 0 K values extracted from linear fits to 100–598 K refinements. Atom positions are Co (0, 0, 0), Ag ($\frac{1}{2}$, 0, $\frac{1}{2}$), C (x_{C} , 0, z_{C}), N (x_{N} , 0, z_{N}).

	300 K (experimental)	0 K (estimated)
Crystal system	Trigonal	Trigonal
Space group	$P\bar{3}1m$	$P\bar{3}1m$
a (Å)	6.9085(10)	6.855(19)
c (Å)	6.7077(16)	6.797(19)
V (Å ³)	277.25(8)	276.6(17)
x_{C}	0.2177(15)	0.2167
z_{C}	0.1566(14)	0.1533
x_{N}	0.3161(15)	0.3182
z_{N}	0.2920(14)	0.2887
B_{iso} (Å ²)	3.91(14)	–

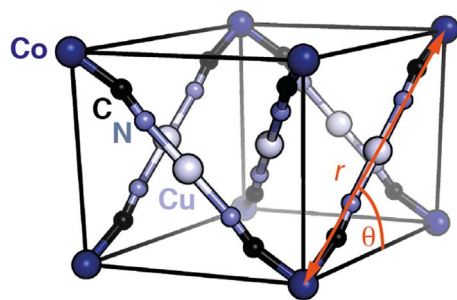


Fig. 3. Structural model for $\text{Cu}_3[\text{Co}(\text{CN})_6]$ determined using Rietveld refinement of X-ray powder diffraction data collected at 298 K. Co atoms shown in dark blue, Cu atoms in blue–white, N atoms in blue, and C atoms in black. The XBUs r and θ —shown here in orange—correspond to the framework strut length and hingeing angle, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

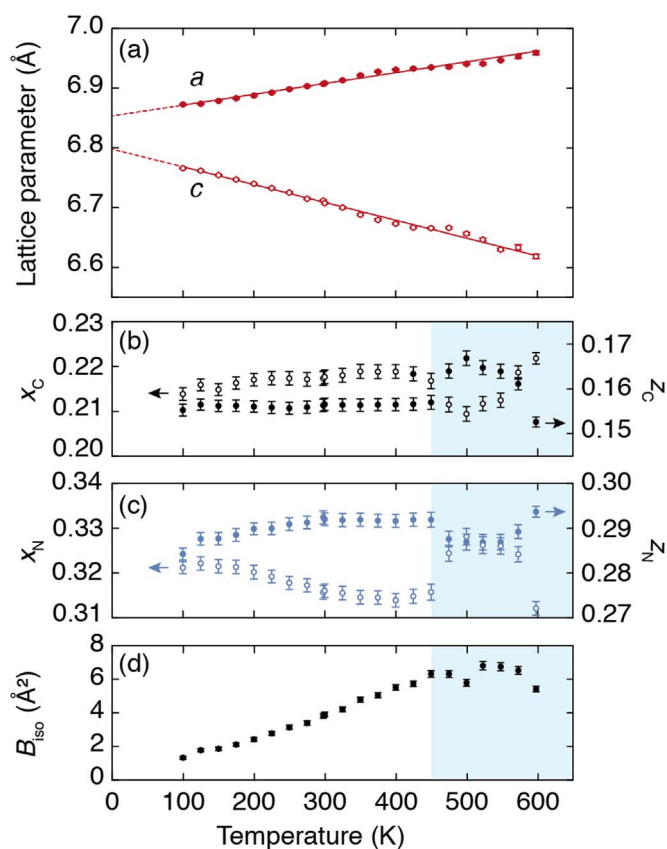


Fig. 4. Temperature dependence of structural parameters of $\text{Cu}_3[\text{Co}(\text{CN})_6]$ as determined using variable-temperature X-ray powder diffraction. (a) Lattice parameters a and c (filled and open symbols, respectively), together with the linear fits (solid lines) used to determine the uniaxial coefficients of thermal expansion. The fits are extrapolated to 0 K (dashed lines) to give the corresponding ‘0 K estimates’ discussed in the text. (b, c) Positional coordinates for the C and N atoms, showing smooth variation over the temperature range 100–450 K for which reliable Rietveld refinements were obtained. The temperature regime 450–600 K is shaded as refinements in this regime gave reliable lattice parameters but unreliable positional coordinates and atomic displacement parameters. (d) Isotropic atomic displacement parameter $B_{\text{iso}} = 8\pi^2\langle u^2 \rangle$ used to model thermal displacements for all atoms.

observed to be approximately linear over this entire temperature range. As in nearly all members of this structural family, $\text{Cu}_3[\text{Co}(\text{CN})_6]$ exhibits NTE effect parallel to the c crystal axis, and PTE effects in perpendicular directions (i.e., including the a and b crystal axes). Hence the basic thermomechanical response of this system can be understood in terms of the same ‘wine-rack’ mechanism illustrated in Fig. 1. The remaining structural parameters x_{C} , z_{C} , x_{N} , z_{N} , B_{iso} also show linear temperature dependencies [Fig. 4(b–d)]; taken together

Table 2

Experimental coefficients of thermal expansion for $\text{A}_3[\text{Co}(\text{CN})_6]$ systems.

A	α_a (MK^{-1})	α_c (MK^{-1})	α_v (MK^{-1})	ΔT (K)	Ref.
H	12.0(4)	−8.8(3)	15.1(6)	4–300	[34]
Cu	25.4(5)	−43.5(8)	7.4(11)	100–598	This work
Ag	145.9(6)	−122.1(3)	169.8(9)	16–500	[23]

these values allow us to estimate a set of 0 K structural parameters that may prove useful for comparison against *e.g. ab initio* studies [Table 1]. We note that this estimation necessarily discounts the reduction in magnitude of thermal expansion behaviour required as $T \rightarrow 0$ K [52]. For the related systems $\text{D}_3[\text{Co}(\text{CN})_6]$ and $\text{Ag}_3[\text{Co}(\text{CN})_6]$, where accurate lattice parameter data exist for temperatures substantially lower than the range we are able to study here (i.e., $T \ll 20$ K), the error introduced by extrapolating only from data collected at $T > 100$ K is less than 0.3% [14,23]. This threshold is the basis for the estimated uncertainties given for the calculated 0 K lattice parameters in Table 1.

Coefficients of thermal expansion were determined using linear fits to the lattice parameter data [39], and are given in Table 2. What is immediately apparent is that the magnitudes of both PTE and NTE effects in $\text{Cu}_3[\text{Co}(\text{CN})_6]$ are substantially smaller than those in the Ag-containing system. Consequently, $\text{Cu}_3[\text{Co}(\text{CN})_6]$ is not a colossal thermal expansion material, and its thermomechanical response shares more in common with other Cu-containing networks such as $\alpha\text{-Cu}[\text{C}(\text{CN})_3]$ (Ref. [31]) and CuCN (Ref. [53]) than with $\text{Ag}_3[\text{Co}(\text{CN})_6]$ and $\text{Ag}_3[\text{Fe}(\text{CN})_6]$ [14]. We will come to rationalise the differences in behaviour of the copper(I) and silver(I) hexacyanocobaltates below, but include first some additional analysis of the trends in lattice parameters we observe using our newly-measured data.

The ‘wine-rack’ mechanism that is thermally activated in this system can be interrogated directly using the so-called mechanical building unit (XBU) approach [2]. We make use of the pair of transformations

$$r = \frac{1}{2}\sqrt{a^2 + c^2}, \quad (2)$$

$$\theta = \tan^{-1}\left(\frac{c}{a}\right), \quad (3)$$

which relate the unit cell dimensions to the framework strut length r and framework angle θ [Fig. 3]. Using these same relationships, we can recast the lattice expansivities in terms of XBU expansivities, obtaining $\alpha_r = -8.2 \text{ MK}^{-1}$ and $\alpha_\theta = 43.1 \text{ MK}^{-1}$. Hence the bulk of the thermal expansion response can be accounted for by changes in the framework geometry ($|\alpha_\theta| \gg |\alpha_r|$); the lattice expansivities attributable to this flexing mechanism alone are $\alpha'_a = 33.5 \text{ MK}^{-1}$ and $\alpha'_c = -35.7 \text{ MK}^{-1}$, where we use the prime notation to indicate calculation from α_θ . The observation $\alpha_r < 0$ indicates that the Co–CN–Cu–NC–Co ‘struts’ from which the framework structure of $\text{Cu}_3[\text{Co}(\text{CN})_6]$ is assembled actually contract with increasing temperature. This behaviour is likely due to thermal activation of transverse vibrational modes where lateral displacements of the chain (maximal at the Cu site) require shortening of the Co...Co vector [52,54]. Such a mechanism is implicated in the uniaxial NTE of CuCN itself ($\alpha_{\text{chain}} = -32.1 \text{ MK}^{-1}$, Ref. [49,53]), and is presumably tempered here somewhat relative to that system by the increased strength of $\text{Co}^{\text{III}}\text{–Cu}$ vs $\text{Cu}^{\text{I}}\text{–C}$ bonds [47].

One consequence of the negative value of α_r is that the volume coefficient of thermal expansion of $\text{Cu}_3[\text{Co}(\text{CN})_6]$ is unusually small for systems in this particular family. Formally, this situation arises because of the fortuitous equivalence $\alpha_v \approx -\frac{1}{3}|\alpha'_r|$, which is the geometric requirement for $\alpha_v \rightarrow 0$.¹ Hence this material has the unusual property

¹ Note that $\alpha_i = \alpha'_i + \alpha_r$, and hence $\alpha_v \sim \alpha'_a + 3\alpha_r$.

of (approximately) temperature-independent density despite its relatively large linear thermal expansivities. At face value, this property may be expected to result in unusually extreme uniaxial compressibilities under application of hydrostatic pressure, since small changes in volume would appear to be linked to large changes in lattice dimensions. However, we anticipate by analogy to related systems that the XBU compressibility K_r is actually positive rather than negative, and so a small α_v need not require a large bulk modulus [2,55]. Nevertheless we expect the particular uniaxial compressibility corresponding to the c crystal axis to be negative, and so investigation of the NLC behaviour of $\text{Cu}_3[\text{Co}(\text{CN})_6]$ could prove a fruitful avenue of future research.

3.3. *Ab initio* calculations

The observation of more moderate thermal expansion behaviour in $\text{Cu}_3[\text{Co}(\text{CN})_6]$ relative to that in $\text{Ag}_3[\text{Co}(\text{CN})_6]$ poses a simple question: does this situation arise because cuprophilic interactions are actually *stronger* than argentophilic interactions, and hence less susceptible to changes in temperature?

In order to answer this question, we turn to *ab initio* calculations, which if carried out so as to include consideration of vdW interactions allow direct quantification of the metallophilic interactions in both compounds. We begin by reporting the 0 K structure for $\text{Cu}_3[\text{Co}(\text{CN})_6]$ obtained computationally and demonstrate that the inclusion of dispersive interactions is necessary to improve consistency with our experimental results. By mapping out the potential energy surface (PES) for all three $\text{A}_3[\text{Co}(\text{CN})_6]$ systems ($\text{A} = \text{H}, \text{Cu}, \text{Ag}$) across a variety of lattice strains and then taking into account the variation in vdW energies at each point, we extract the free-atom and in-solid (effective) C_6 coefficients. The value of these coefficients for each atom type A acts as a measure of the strength of metallophilic interactions in the corresponding $\text{A}_3[\text{Co}(\text{CN})_6]$ system.

The unit cell dimensions obtained in our DFT + vdW calculations are given in Table 3. The influence of dispersion energy on the lattice constants is large, just as is now known to be the case for $\text{Ag}_3[\text{Co}(\text{CN})_6]$ [56]. Our PBE calculation without vdW interactions overestimates a and underestimates c . Upon including dispersion interactions the lattice constants move closer to the experimental values. We note that the enhanced cohesive MBD energy for $\text{Cu}_3[\text{Co}(\text{CN})_6]$ arises from the collective effect of vdW interactions and the self-consistent polarisation in the unit cell [56]. The agreement with experiment is somewhat less exact than for $\text{Ag}_3[\text{Co}(\text{CN})_6]$ [56]; possible reasons include (i) the approximations implicit in extrapolating our $T > 100$ K experimental data to 0 K, (ii) the need for a higher-level hybrid DFT base functional, and (iii) the sensitivity of the dispersion energy at short interatomic distances to the parameterisation of the damping function.

In Fig. 5 we show a representative section of the PES for the three calculation regimes, and Fig. 6 shows the TS and MBD vdW energies as a function of the individual a and c lattice constants. Our results make clear that the vdW energy depends more strongly on a than it does on c .

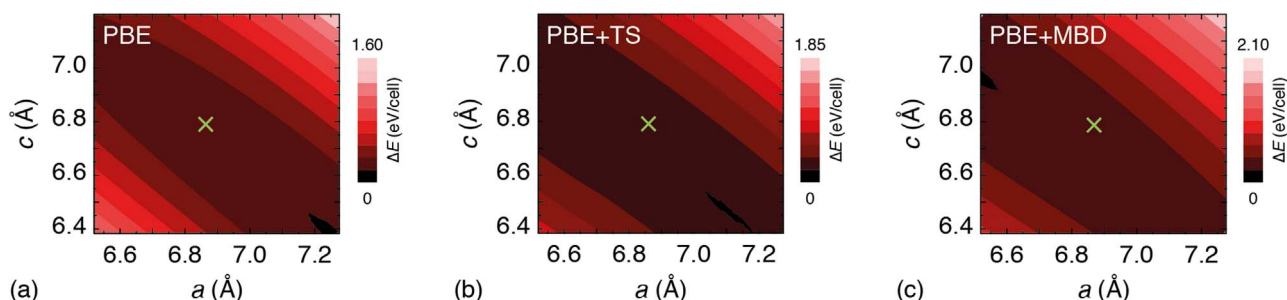


Fig. 5. The (a) PBE, (b) PBE + TS, and (c) PBE + MBD potential energy surfaces of $\text{Cu}_3[\text{Co}(\text{CN})_6]$ as a function of unit cell dimensions. The experimental lattice constants are indicated by crosses. Energies are given relative to the ground state in each case.

Table 3

Comparison between experimental and *ab initio* lattice parameters for $\text{Cu}[\text{Co}(\text{CN})_6]$. The difference term Δ corresponds to the sum of absolute cell strains $\sum_i |(x_{i,\text{calc}} - x_{i,\text{exp}})/x_{i,\text{exp}}|$.

	exp. (0 K)	PBE	TS	MBD
a (Å)	6.855	7.267	7.130	6.495
c (Å)	6.797	6.365	6.432	6.978
V (Å ³)	276.6	291.06	283.00	254.98
Δ (%)	0	18.4	13.4	13.2

Since the framework strut length r is more rigid than the framework angle θ , then to lower the total energy the lattice simply contracts along a (and b) while expanding along c . Hence the same mechanism explains the qualitative change in lattice constants observed both as a result of using different vdW calculation methods and as a result of an increase in the polarisability of atom A . Indeed because the MBD energy depends almost linearly on the lattice constants it behaves as an effective pressure on the lattice, equivalent to 1.22 GPa along a and 1.76 GPa along c .

To compare the strength of cuprophilic interactions in $\text{Cu}_3[\text{Co}(\text{CN})_6]$ with that of argentophilic interactions in $\text{Ag}_3[\text{Co}(\text{CN})_6]$ we further analysed our DFT + vdW results. Our basic approach was to parameterise the vdW contribution to the TS-vdW energy in terms of dispersion coefficients C_6 and vdW radii R_0 for each atom type. In the PBE + TS calculations, the free-atom C_6 coefficient and vdW radii R_0 are used as the initial input parameters. The effect of the local chemical environment is taken into account by calculating the effective in-solid C_6 and R_0 as described in Ref. [43]. Table 4 lists our results for the free-atom vdW parameters and the effective parameters for $\text{A}_3[\text{Co}(\text{CN})_6]$ ($\text{A} = \text{Ag}, \text{Cu}, \text{H}$) at the experimental lattice constants. We find that the argentophilic interactions are indeed stronger than cuprophilic interactions in these systems, as both the free-atom and effective C_6 values are larger by $\sim 40\%$ for Ag relative to Cu. For completeness we note that the effect of the local chemical environment on the C_6 coefficients is to reduce the dispersion coefficients.

3.4. GULP calculations

We supplement these high-level *ab initio* results with a series of extremely simple model calculations that also allow us to estimate the relative strengths of metallophilic interactions in $\text{Cu}_3[\text{Co}(\text{CN})_6]$ and $\text{Ag}_3[\text{Co}(\text{CN})_6]$. The approach we use is to develop the very simplest abstraction of all three $\text{A}_3[\text{Co}(\text{CN})_6]$ systems ($\text{A} = \text{H}, \text{Cu}, \text{Ag}$) that captures the key interactions responsible for their thermomechanical response. We parameterise this model with sufficiently few variables that six experimental observables (the two independent lattice parameters for each of the three systems) can be used to estimate metallophilic interaction strengths in the $\text{A} = \text{Cu}, \text{Ag}$ compounds.

The same structural model is used for all three systems: $P\bar{3}1m$ crystal symmetry, with a single anion (mass $m = m(\text{CoC}_6\text{N}_6)$) of charge $-1.5e$ at position (0, 0, 0) and a cation ($m = m(\text{A})$) with charge $+0.5e$ at

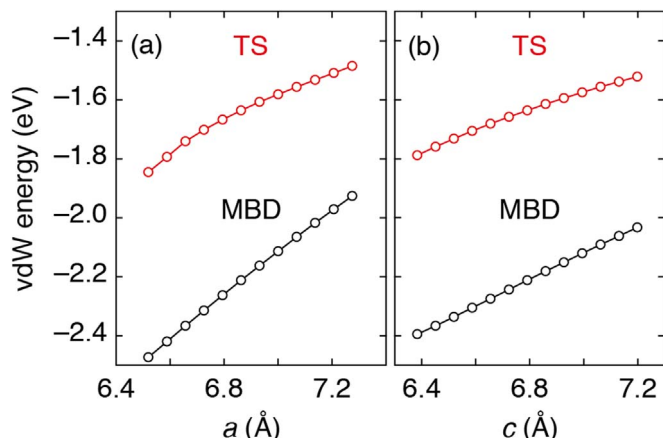


Fig. 6. The TS and MBD vdW energies in $\text{Cu}_3[\text{Co}(\text{CN})_6]$ per unit cell (a) as a function of lattice constant a with c fixed to experimental values and (b) as a function of c with a fixed to experimental values.

Table 4

The PBE + TS free-atom and in-solid vdW parameters for A atoms in $\text{A}_3[\text{Co}(\text{CN})_6]$ (A = Ag, Cu, H) at experimental lattice constants.

	C_6 (hartree bohr ⁶)		R_0 (bohr)	
	free-atom	in-solid	free-atom	in-solid
$\text{Ag}_3[\text{Co}(\text{CN})_6]$	339.00	295.73	3.82	3.73
$\text{Cu}_3[\text{Co}(\text{CN})_6]$	235.00	207.03	3.76	3.64
$\text{H}_3[\text{Co}(\text{CN})_6]$	6.50	4.28	3.10	2.89

position $(\frac{1}{2}, 0, \frac{1}{2})$ [Fig. 7(a)]. These charges reflect the approximate Mulliken charges determined for $\text{H}_3[\text{Co}(\text{CN})_6]$ and $\text{Ag}_3[\text{Co}(\text{CN})_6]$ in Ref. [57] and are consistent with the Hirshfeld and Bader charges obtained in our own *ab initio* calculations (see SI). We refer to the anion using the symbol X (formally this corresponds to the $[\text{Co}(\text{CN})_6]^{3-}$ ion), giving the unit cell composition A_3X . This structural model is then decorated with three interaction potentials: first, a harmonic bond potential between neighbouring A and X sites with force-constant k_r ; second, a harmonic bond-angle potential governing A–X–A triplets with force-constant k_θ ; and, third, (in the case of Cu and Ag systems) dispersive interactions between neighbouring A sites intended to reflect the empirical $\frac{1}{r^6}$ -dependence of metalphilic interactions [58]. The prefactor C_6 of this dispersive term quantifies the strength of metalphilic interactions.

In order to reduce the number of parameters involved in this model, we make the following assumptions. First, we take the effective charges at X and A sites to be system-independent. We justify this assumption by noting that the Mulliken charges reported for $\text{H}_3[\text{Co}(\text{CN})_6]$ and $\text{Ag}_3[\text{Co}(\text{CN})_6]$ vary more greatly by calculation method than they do between systems [57]; the A = Cu case is intermediate to the A = H and A = Ag cases (see SI). Second, we take the flexing stiffness k_θ and equilibrium angle θ_0 also to be system-independent, with θ_0 as close to 90° as possible. This is probably reasonable given that both terms will be governed by the chemistry of the $[\text{Co}(\text{CN})_6]^{3-}$ anion, which is common to all three systems. Third, we take the (system-dependent) values of r_0 as the sum of bond lengths $d(\text{Co} - \text{C}) + d(\text{C} - \text{N}) + d(\text{N} - \text{A})$ determined crystallographically: we use the values from Ref. [34] for A = H, from Ref. [17] for A = Ag, and from our present study for A = Cu.

We proceeded to determine a set of parameters k_r , k_θ , θ_0 that, when used to drive geometry optimisation, result in the closest possible agreement between 0 K (derived from experiment) and relaxed cell parameters for A = H. Our results are listed in Table 5, together with a

comparison of the experimental and simulated lattice parameters; the corresponding match in framework geometry is illustrated in Fig. 7.² We note that we do not attach any particular physical meaning to the parameter values in our model, since (in particular) the charge distribution we use is heavily simplified. Nevertheless it is reassuring that even this simple model allows robust geometry optimisation to a physically-sensible state.

Having used the geometry of the A = H system to determine all of the system-independent parameter values, we proceeded to optimise the geometry of analogous models for A = Cu and Ag. In each case the value of r_0 was updated according to the experimental bond lengths, and only the value of C_6 was varied in order to obtain the closest match between calculated and experimental (0 K extrapolated) lattice parameters. The corresponding parameter values and optimised cell dimensions are again summarised in Table 5; we note that the level of agreement ($< 2\%$) is encouraging given the simplicity of the GULP model we have used. Also encouraging is that, for both compounds, the a lattice parameters are overestimated in the absence of a metalphilic contribution to the lattice enthalpy. This indicates that the electrostatic contribution to the free energy (the single component of our model acting to increase a) operates in tension with the metalphilic interactions. While we do not attach any importance to the absolute values of the C_6 parameters that emerge from our calculations, what we do think is meaningful is the observation that C_6 is larger for A = Ag than for A = Cu. In other words, the experimental unit cell dimensions for $\text{Cu}_3[\text{Co}(\text{CN})_6]$ and $\text{Ag}_3[\text{Co}(\text{CN})_6]$ are consistent with stronger argentophilic interactions in the latter than cuprophilic interactions in the former. Moreover, the ratio of cuprophilic:argentophilic interaction strengths we deduce from our simple GULP model is essentially the same as that obtained in our *ab initio* calculations: $C_6(\text{Cu})/C_6(\text{Ag}) = 61\%$ vs 70% , respectively.

3.5. Flexibility from competing interactions

So our various calculations converge on the same scenario whereby cuprophilic interactions in $\text{Cu}_3[\text{Co}(\text{CN})_6]$ are weaker than argentophilic interactions in $\text{Ag}_3[\text{Co}(\text{CN})_6]$ by 30–40%. One obvious question remains: how is this observation consistent with the more moderate thermal expansion behaviour of the Cu-containing compound?

To address this question we exploit the approximate proportionality between thermal expansivities and isothermal compressibilities noted in Refs. [17,27,59]:

$$\alpha_i \simeq \frac{C_T}{V} \hat{\gamma} K_i. \quad (4)$$

Here C_T is the isothermal specific heat, V the molar volume, $\hat{\gamma}$ the mean effective Grüneisen parameter and K_i the uniaxial compressibilities. We estimate that the pre-factor $C_T \hat{\gamma}/V$ varies by not more than $\sim 25\%$ between the A = Cu and A = Ag systems,³ such that a comparison of compressibilities for the two compounds provides a reasonable first-order approximation to the relative thermal expansivities. We concern ourselves with compressibilities rather than expansivities since the former are obtainable directly from the calculations (both *ab initio* and GULP) described above. The relative compressibilities for all three compounds are illustrated graphically in Fig. 8. What is evident is that the Cu-containing compound exhibits intermediate behaviour to the H- and Ag-containing systems, despite its relatively weaker metalphilic

² We found the quality of fit was relatively insensitive to changes in k_r of up to ca 25% of its value. Variations in this parameter did affect the absolute values of the compressibilities determined subsequently; however the same trend in magnitudes of compressibilities shown in Fig. 8 was found in all cases.

³ Here we have made use of three relationships: first, that $\hat{\gamma}$ appears to be relatively system-independent [57]; second, that the ratio of the C_T values for A = Cu and Ag will be approximately equal to the ratio of the $\sqrt{m}$ terms, since the low-energy phonon dispersion will be dominated by heavy-atom displacements; and third, we use the experimental molar volumes.

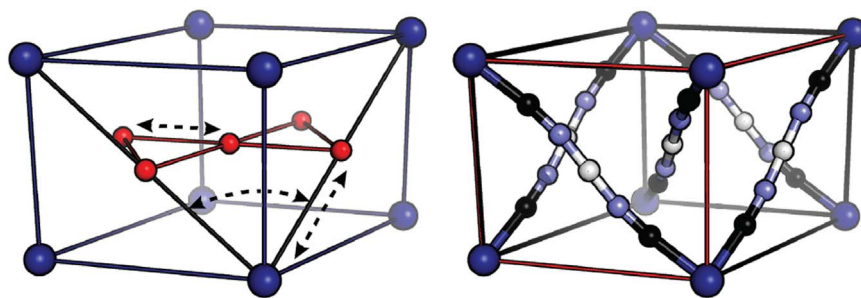


Fig. 7. GULP model for $A_3[Co(CN)_6]$ systems and the corresponding match in $H_3[Co(CN)_6]$ geometry used to estimate its interaction potential parameters. (Left) The model consists of X atoms at the Co site (large blue spheres; formal charge $-1.5e$) and A atoms at the H/Cu/Ag site (red spheres; formal charge $+0.5e$). The model includes three interatomic potentials in addition to Coulomb interactions: harmonic Co–A ‘bond stretching’ interactions, harmonic A–Co–A ‘bond bending’ interactions, and r^{-6} dispersive interactions between A sites. (Right) Match between experimental unit cell dimensions (solid black lines) of $H_3[Co(CN)_6]$ (Ref. [34]) and relaxed cell in our GULP model (solid red lines) for the parameter values given in Table 5. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 5

GULP model parameters and comparison between calculated and observed lattice parameters. Refined parameters are shown in bold.

	$H_3[Co(CN)_6]$	$Cu_3[Co(CN)_6]$	$Ag_3[Co(CN)_6]$
k_r (eV/Å ²)	400	400	400
r_0 (Å)	4.319	4.867	5.070
k_θ (eV/rad ²)	47	47	47
θ_0 (°)	89	89	89
C_6 (eV Å ⁶)	0	8810	14,400
a (Å)	6.450	6.901	6.812
a_{expt}^0 K (Å)	6.409	6.855	6.740
$\Delta a/a$ (%)	+ 0.6%	+ 0.7%	+ 1.1%
c (Å)	5.749	6.842	7.474
c_{expt}^0 K (Å)	5.713	6.797	7.390
$\Delta c/c$ (%)	+ 0.6%	+ 0.7%	+ 1.1%

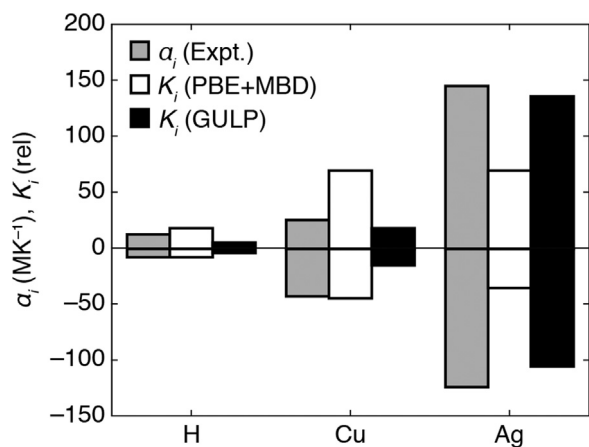


Fig. 8. Trends in calculated uniaxial compressibilities (white bars = *ab initio*; black bars = GULP; data normalised for comparison) and lattice expansivities (grey bars = values taken from Refs. [23,34] and this study) for $A_3[Co(CN)_6]$ compounds.

interactions. The qualitative similarity to the relative thermal expansivities is striking, particularly given the (necessary) omission of anharmonic contributions from our calculations which likely contribute substantially to the experimental behaviour [60].

4. Concluding remarks

We are led to the counterintuitive conclusion that stronger interactions can actually make a material more compliant: $Ag_3[Co(CN)_6]$ exhibits colossal thermomechanical responses but $Cu_3[Co(CN)_6]$ does not, despite the energy scale associated with metallophilic interactions

being larger in the former than in the latter. Of course the key here is that metallophilic interactions are net attractive, and act in tension with the (repulsive) electrostatic component [61,62]. Any effective harmonic potential can be made increasingly shallow by the addition of attractive r^{-6} terms, as illustrated in Fig. 9. This is the nub of the physics at play in this family: in the absence of metallophilic interactions, the frameworks are not especially mechanically responsive but they do become so as metallophilicity is introduced.

Hence the conventional materials design rules are reversed, and we anticipate that the member of the $A_3[Co(CN)_6]$ family likely to show the most extreme thermomechanical response is actually the as-yet-unrealised compound $Au_3[Co(CN)_6]$. It was shown in Ref. [57] that this system is likely to have a particularly compliant structure, although the degree of compliance will depend heavily on the strength of the aurophilic interaction contribution to the lattice enthalpy. Given the notorious difficulty of accessing aqueous Au(I) chemistry, it is not yet clear how $Au_3[Co(CN)_6]$ might be accessed synthetically. A viable alternative is the (also unrealised) compound $Fe[Au(CN)_2]_3$ —i.e., with Co(III) replaced by Fe(III) and the CN ion orientations reversed—which by analogy to $Fe[Ag(CN)_2]_3$ should in principle be accessible *via* reaction of aqueous Fe^{3+} containing solutions with $KAu(CN)_2$ [63]. The observation [14] of qualitatively similar ‘colossal’ thermal expansion in $Ag_3[Co(CN)_6]$ and $Ag_3[Fe(CN)_6]$ suggests that chemical substitution at the trivalent metal site is unlikely to influence the degree of thermomechanical response observed.

With respect to $Cu_3[Co(CN)_6]$, further spectroscopic and lattice dynamical studies will likely prove valuable in understanding more deeply the microscopic origin of its NTE response, as has been the case for the other materials in this family [64,65]. While it has not been computationally feasible in our study to extend the MBD calculations to finite temperatures, a clear computational challenge for future investigations is the calculation of the phonon dispersion relation and thermal expansivity tensor of $Cu_3[Co(CN)_6]$, including MBD effects.

From a computational perspective, one key implication of our study is the importance of obtaining accurate descriptions of vdW interactions in compliant framework materials. This importance is particularly

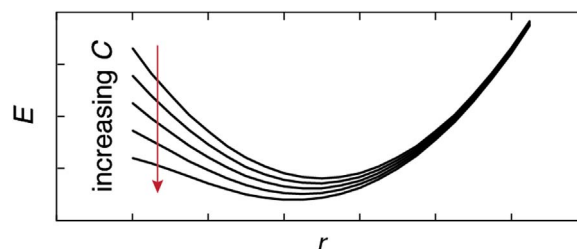


Fig. 9. Flattening of an effective interaction potential $E = \frac{1}{2}k(r - r_0)^2 + C_6r^{-6}$ with increasing dispersion interaction strength C_6 . Reduced curvature leads to more extreme expansivity and compressibility behaviour.

acute for systems such as $\text{Cu}_3[\text{Co}(\text{CN})_6]$ and $\text{Ag}_3[\text{Co}(\text{CN})_6]$ where the PES is anomalously shallow as a result of competition between vdW and electrostatic contributions. As flagged above, a key challenge in this regard is the treatment of finite-temperature effects; *i.e.* anharmonicity. We anticipate that the discovery of anomalous mechanics in increasingly many systems based on vdW-type interactions [66,67] will motivate further research effort along precisely these lines.

Acknowledgements

The synchrotron diffraction measurements were carried out at the Diamond Light Source (I11 Beamline). We are extremely grateful for the award of a Block Allocation Grant, which made this work possible, and for the assistance in data collection provided by S.J. Cassidy (Oxford) and the I11 beamline staff. A.F.S., A.R.O. and A.L.G. gratefully acknowledge funding through the European Research Council (Grant 279705). C.S.C. and A.L.G. acknowledge funding through the Leverhulme Trust (Grant RPG-2015-292). A.R.O. thanks the Diamond Light Source for a Studentship. This project received funding from the European Union (EU) Horizon 2020 Research and Innovation Programme under Marie Skłodowska-Curie Grant Agreement 641887 (project acronym DEFNET).

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.jssc.2017.10.009>.

References

- [1] F.-X. Coudert, Responsive metal-organic frameworks and framework materials: under pressure, taking the heat, in the spotlight, with friends, *Chem. Mater.* 27 (2015) 1905–1916.
- [2] J.M. Ogborn, I.E. Collings, S.A. Moggach, A.L. Thompson, A.L. Goodwin, Supramolecular mechanics in a metal-organic framework, *Chem. Sci.* 3 (2012) 3011–3017.
- [3] S. Horike, S. Shimomura, S. Kitagawa, Soft porous crystals, *Nat. Chem.* 1 (2009) 695–704.
- [4] G.R. Krishna, R. Devarapalli, G. Lal, C.M. Reddy, Mechanically flexible organic crystals achieved by introducing weak interactions in structure: supramolecular shape synthons, *J. Am. Chem. Soc.* 138 (2016) 13561–13567.
- [5] D. Das, T. Jacobs, L.J. Barbour, Exceptionally large positive and negative anisotropic thermal expansion of an organic crystalline material, *Nat. Mater.* 9 (2010) 36–39.
- [6] A.L. Goodwin, Organic crystals: packing down, *Nat. Mater.* 9 (2010) 7–8.
- [7] H.J. Shepherd, T. Palamarcu, P. Rosa, P. Guionneau, G. Molnár, J.-F. Létard, A. Bousseksou, Antagonism between extreme negative linear compressibility and spin crossover in $[\text{Fe}(\text{dpp})_2(\text{NCS})_2]\cdot\text{py}$, *Angew. Chem. Int. Ed.* 51 (2012) 3910–3914.
- [8] S.G. Duyker, V.K. Peterson, G.J. Kearley, A.J. Studer, C.J. Kepert, Extreme compressibility in $\text{LnFe}(\text{CN})_6$ coordination framework materials via molecular gears and torsion springs, *Nat. Chem.* 8 (2016) 270–275.
- [9] W. Li, A. Thirumurugan, P.T. Barton, Z. Lin, S. Henke, H.H.-M. Yeung, M.T. Wharmby, E.G. Bithell, C.J. Howard, A.K. Cheetham, Mechanical tunability via hydrogen bonding in metal-organic frameworks with the perovskite architecture, *J. Am. Chem. Soc.* 136 (2014) 7801–7804.
- [10] R.H. Jones, K.S. Knight, W.G. Marshall, J. Clews, R.J. Darton, D. Pyatt, S.J. Coles, P.N. Horton, Colossal thermal expansion and negative thermal expansion in simple halogen bonded complexes, *CrystEngComm* 16 (2014) 237–243.
- [11] P.G. Yot, Q. Ma, J. Haines, Q. Yang, A. Ghofri, T. Devic, C. Serre, V. Dmitriev, G. Férey, C. Zhong, G. Maurin, Large breathing of the MOF MIL-47(V^{tr}) under mechanical pressure: a joint experimental-modelling exploration, *Chem. Sci.* 3 (2012) 1100–1104.
- [12] E.R. Engel, V.J. Smith, C.X. Bezuidenhout, L.J. Barbour, Uniaxial negative thermal expansion facilitated by weak host-guest interactions, *Chem. Commun.* 50 (2014) 4238–4241.
- [13] F. Salles, G. Maurin, C. Serre, P.L. Llewellyn, C. Knöfel, H.J. Choi, Y. Filinchuk, L. Olivier, A. Vimont, J.R. Long, G. Férey, Multistep, N_2 breathing in the metal-organic framework $\text{Co}(1,4\text{-benzenedipyrzolate})$, *J. Am. Chem. Soc.* 132 (2010) 13782–13788.
- [14] A.L. Goodwin, D.A. Keen, M.G. Tucker, M.T. Dove, L. Peters, J.S.O. Evans, Argentophilicity-dependent colossal thermal expansion in extended Prussian Blue analogues, *J. Am. Chem. Soc.* 130 (2008) 9660–9661.
- [15] C.Y. Ho, R.E. Taylor, Thermal Expansion of Solids, ASM International, Ohio, 1998.
- [16] R. Krishnan (Ed.) Thermal Expansion of Crystals, Vol. 22 of International Series on the Science of the Solid State, Pergamon Press, Oxford, 1979.
- [17] A.L. Goodwin, D.A. Keen, M.G. Tucker, Large negative linear compressibility of $\text{Ag}_3[\text{Co}(\text{CN})_6]$, *Proc. Natl. Acad. Sci. USA* 105 (2008) 18708–18713.
- [18] G.N. Greaves, A.L. Greer, R.S. Lakes, T. Rouxel, Poisson's ratio and modern materials, *Nat. Mater.* 10 (2011) 823–837.
- [19] M.K. Panda, T. Runčevski, S. Chandra Sahoo, A.A. Belik, N.K. Nath, R.E. Dinnebier, P. Naumov, Colossal positive and negative thermal expansion and thermosensitive effect in a pentamorphic organometallic martensite, *Nat. Commun.* 5 (2014) 4811.
- [20] M.K. Panda, R. Centore, M. Causà, A. Tuzi, F. Borbone, P. Naumov, Strong and anomalous thermal expansion precedes the thermosensitive effect in dynamic molecular crystals, *Sci. Rep.* 6 (2016) 29610.
- [21] J.L. Korčok, M.J. Katz, D.B. Leznoff, Impact of metalophilicity on “colossal” positive and negative thermal expansion in a series of isostructural dicyanometallate coordination polymers, *J. Am. Chem. Soc.* 131 (2009) 4866–4871.
- [22] A. Ludi, H.U. Güdel, Die Kristallstruktur von $\text{Ag}_3\text{Co}(\text{CN})_6$, *Helv. Chim. Acta* 51 (1968) 1762–1765.
- [23] A.L. Goodwin, M. Calleja, M.J. Conterio, M.T. Dove, J.S.O. Evans, D.A. Keen, L. Peters, M.G. Tucker, Colossal positive and negative thermal expansion in the framework material $\text{Ag}_3[\text{Co}(\text{CN})_6]$, *Science* 319 (2008) 794–797.
- [24] M.J. Conterio, A.L. Goodwin, M.G. Tucker, D.A. Keen, M.T. Dove, L. Peters, J.S.O. Evans, Local structure in $\text{Ag}_3[\text{Co}(\text{CN})_6]$: colossal thermal expansion, rigid unit modes and argentophilic interactions, *J. Phys.: Condens. Matter* 20 (2008) 255225.
- [25] R.H. Baughman, S. Stafström, C. Cui, S.O. Dantas, Materials with negative compressibilities in one or more dimensions, *Science* 279 (1998) 1522–1524.
- [26] R. Lakes, K.W. Wojciechowski, Negative compressibility, negative Poisson's ratio, and stability, *Phys. Stat. Sol. B* 245 (2008) 545–551.
- [27] A.B. Cairns, A.L. Goodwin, Negative linear compressibility, *Phys. Chem. Chem. Phys.* 17 (2015) 20449–20465.
- [28] M. Jansen, Homoatomic $d^{10}\text{--}d^{10}$ interactions: their effects on structure and chemical and physical properties, *Angew. Chem. Int. Ed. Engl.* 26 (1987) 1098–1110.
- [29] E. O'Grady, N. Kaltsoyannis, Does metalophilicity increase or decrease down group 11?? Computational investigations of $[\text{Cl-M-PH}_3]_2$ ($\text{M} = \text{Cu}, \text{Ag}, \text{Au}$, [111]), *Phys. Chem. Chem. Phys.* 6 (2004) 680–687.
- [30] K.E. Bessler, L.A.d.P. Calzavara, V.M. Deflon, E. Niquet, Bis(μ -tricyanomethanido) tetrakis(triphenylphosphine)dioctetate(I), *Acta Cryst. E* 57 (2001) m522–m523.
- [31] S.J. Hunt, M.J. Cliffe, J.A. Hill, A.B. Cairns, N.P. Funnell, A.L. Goodwin, Flexibility transition and guest-driven reconstruction in a ferroelastic metal-organic framework, *CrystEngComm* 17 (2016) 361–369.
- [32] L. Pauling, P. Pauling, A tritetracate crystal structure: trihydrogen cobaltcyanide and trisilver cobaltcyanide, *Proc. Natl. Acad. Sci. USA* 60 (1968) 362–367.
- [33] R. Haser, B. Bonnet, J. Roziere, Caractéristiques spectroscopiques des liaisons hydrogène N–H–N très fortes. Études des acides $\text{A}_3\text{M}(\text{CN})_6$, ($\text{A} = \text{H}, \text{D}; \text{M} = \text{Fe}, \text{Co}$) par spectroscopie de vibration, *J. Mol. Struct.* 40 (1977) 177–189.
- [34] D.A. Keen, M.T. Dove, J.S.O. Evans, A.L. Goodwin, L. Peters, M.G. Tucker, The hydrogen-bonding transition and isotope-dependent negative thermal expansion in $\text{H}_3\text{Co}(\text{CN})_6$, *J. Phys.: Condens. Matter* 22 (2010) 404202.
- [35] C. Lind, Two decades of negative thermal expansion research: where do we stand?, *Materials* 5 (2012) 1125–1154.
- [36] A.A. Coelho, TOPAS-academic, version 4.1 (computer software), Tech. rep., Coelho Software, Brisbane.
- [37] P.W. Stephens, Phenomenological model of anisotropic peak broadening in powder diffraction, *J. Appl. Cryst.* 32 (1999) 281–289.
- [38] A. Ratuszna, G. Malecki, Crystal structure of cubic $\text{KMe}[\text{M}(\text{CN})_6]_2$ and monoclinic $\text{Mn}_3[\text{Fe}(\text{CN})_6]_2$ with $\text{Me} = \text{Co}, \text{Ni}, \text{Cu}; \text{M} = \text{Co}, \text{Fe}$, *Mater. Sci. Forum* 321–324 (2000) 947–953.
- [39] M.J. Cliffe, A.L. Goodwin, PASCAL: a principal axis strain calculator for thermal expansion and compressibility determination, *J. Appl. Cryst.* 45 (2012) 1321–1329.
- [40] J.F. Nye, Physical Properties of Crystals, Oxford University Press, Oxford, 1957.
- [41] V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter, M. Scheffler, Ab initio molecular simulations with numeric atom-centered orbitals, *Comput. Phys. Commun.* 180 (2009) 2175–2196.
- [42] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* 77 (1996) 3865–3868.
- [43] A. Tkatchenko, M. Scheffler, Accurate molecular van der Waals interactions from ground-state electron density and free-atom reference data, *Phys. Rev. Lett.* 102 (2009) 073005.
- [44] A. Tkatchenko, R.A. DiStasio Jr., R. Car, M. Scheffler, Accurate and efficient method for many-body van der Waals interactions, *Phys. Rev. Lett.* 108 (2012) 236402.
- [45] A. Ambrosetti, A.M. Reilly, R.A. DiStasio Jr., A. Tkatchenko, Long-range correlation energy calculated from coupled atomic response functions, *J. Chem. Phys.* 140 (2014) 18A508.
- [46] J.D. Gale, GULP: a computer program for the symmetry-adapted simulation of solids, *J. Chem. Soc. Faraday Trans. 93* (1997) 629–637.
- [47] A.G. Sharpe, The Chemistry of Cyano Complexes of the Transition Metals, Academic Press, London, 1976.
- [48] A. Widmann, H. Kahlert, H. Wulff, F. Scholz, Electrochemical and mechanochemical formation of solid solutions of potassium copper(II)/zinc(II) hexacyanocobaltate(III)/hexacyanoferrate(III) $\text{KCu}_x\text{Zn}_{1-x}[\text{hcc}]_x[\text{hcf}]_{1-x}$, *J. Sol. St. Electrochem.* 9 (2005) 380–389.
- [49] S.J. Hibble, S.G. Eversfield, A.R. Cowley, A.M. Chippindale, Copper(I) cyanide: a simple compound with a complicated structure and surprising room-temperature reactivity, *Angew. Chem. Int. Ed.* 43 (2004) 628–630.
- [50] M.J. Katz, K. Sakai, D.B. Leznoff, The use of aurophilic and other metal-metal

- interactions as crystal engineering design elements to increase structural dimensionality, *Chem. Soc. Rev.* 37 (2008) 1884–1895.
- [51] S.S. Batsanov, Van der Waals radii of elements, *Inorg. Mater.* 37 (2001) 871–885.
- [52] G.D. Barerra, J.A.O. Bruno, T.H.K. Barron, N.L. Allan, Negative thermal expansion, *J. Phys.: Condens. Matter* 17 (2005) R217–R252.
- [53] S.J. Hibble, G.B. Wood, E.J. Biblé, A.H. Pohl, M.G. Tucker, A.C. Hannon, A.M. Chippindale, Structures and negative thermal expansion properties of the one-dimensional cyanides, CuCN, AgCN and AuCN, *Z. Krist.* 225 (2010) 457–462.
- [54] T.A. Mary, J.S.O. Evans, T. Vogt, A.W. Sleight, Negative thermal expansion from 0.3 to 1050 K in ZrW_2O_8 , *Science* 272 (1996) 90–92.
- [55] J. Adamson, T.C. Lucas, A.B. Cairns, N.P. Funnell, M.G. Tucker, A.K. Kleppe, J.A. Hriljac, A.L. Goodwin, Competing hydrostatic compression mechanisms in nickel cyanide, *Physica B* 479 (2015) 35–40.
- [56] X. Liu, J. Hermann, A. Tkatchenko, Many-body stabilization of non-covalent interactions: structure, stability, and mechanics of $\text{Ag}_3\text{Co}(\text{CN})_6$ framework, *J. Chem. Phys.* 145 (2016) 241101.
- [57] M. Calleja, A.L. Goodwin, M.T. Dove, Origin of the colossal positive and negative thermal expansion in $\text{Ag}_3[\text{Co}(\text{CN})_6]$: an ab initio density functional theory study, *J. Phys.: Condens. Matter* 20 (2008) 255226.
- [58] L. Magnko, M. Schweizer, G. Rauhut, M. Schutz, H. Stoll, H.-J. Werner, A comparison of metallophilic attraction in $(\text{X-M-PH}_3)_2$ ($\text{M} = \text{Cu}, \text{Ag}, \text{Au}$; $\text{X} = \text{H}, \text{Cl}$)- PH_{32} ($\text{M} = \text{Cu}, \text{Ag}, \text{Au}$; $\text{X} = \text{H}, \text{Cl}$), *Phys. Chem. Chem. Phys.* 4 (2002) 1006–1013.
- [59] R.W. Munn, Role of the elastic constants in negative thermal expansion of axial solids, *J. Phys. C: Solid State Phys.* 5 (1972) 535–542.
- [60] M.T. Dove, H. Fang, Negative thermal expansion and associated anomalous physical properties: review of the lattice dynamics theoretical foundation, *Rep. Prog. Phys.* 79 (2016) 066503.
- [61] H. Fang, M.T. Dove, K. Refson, Ag–Ag dispersive interaction and physical properties of $\text{Ag}_3\text{Co}(\text{CN})_6$, *Phys. Rev. B* 90 (2014) 054302.
- [62] P. Hermet, J. Catafesta, J.-L. Bantignies, C. Levelut, D. Maurin, A.B. Cairns, A.L. Goodwin, J. Haines, Vibrational and thermal properties of $\text{Ag}_3[\text{Co}(\text{CN})_6]$ from first-principles calculations and infrared spectroscopy, *J. Phys. Chem. C* 117 (2013) 12848–12857.
- [63] J.A. Hill, A.B. Cairns, J.J.K. Lim, S.J. Cassidy, S.J. Clarke, A.L. Goodwin, Zero-strain reductive intercalation in a molecular framework, *CrystEngComm* 17 (2015) 2925–2928.
- [64] R. Mittal, M. Zbiri, H. Schober, S.N. Achary, A.K. Tyagi, S.L. Chaplot, Phonons and colossal thermal expansion behavior of $\text{Ag}_3\text{Co}(\text{CN})_6$ and $\text{Ag}_3\text{Fe}(\text{CN})_6$, *J. Phys.: Condens. Matter* 24 (2012) 505404.
- [65] K.K. Mishra, N. Salke, S.N. Achary, A.K. Tyagi, R. Rao, High pressure Raman spectroscopic study of $\text{H}_3\text{Co}(\text{CN})_6$, in: *AIP Conference Proceedings*, vol. 1591, 2014, p. 125.
- [66] A.B. Cairns, J. Catafesta, C. Levelut, J. Rouquette, A. van der Lee, L. Peters, A.L. Thompson, V. Dmitriev, J. Haines, A.L. Goodwin, Giant negative linear compressibility in zinc dicyanoaurate, *Nat. Mater.* 12 (2013) 212–216.
- [67] C.H. Woodall, C.M. Beavers, J. Christensen, L.E. Hatcher, M. Intissar, A. Parlett, S.J. Teat, C. Reber, P.R. Raithby, Hingeless negative linear compression in the mechanocromic gold complex $[(\text{C}_6\text{F}_5\text{Au})_2(\mu\text{-1,4-diisocyanobenzene})]$, *Angew. Chem. Int. Ed.* 52 (2013) 9691–9694.

Hybrid local-order mechanism for inversion symmetry breaking

Emma H. Wolpert,¹ Alistair R. Overy,^{1,2} Peter M. M. Thygesen,¹ Arkadiy Simonov,¹ Mark S. Senn,³
and Andrew L. Goodwin^{1,*}

¹*Department of Chemistry, University of Oxford, Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, United Kingdom*

²*Diamond Light Source, Chilton, Oxfordshire, OX11 0DE, United Kingdom*

³*Department of Chemistry, University of Warwick, Gibbet Hill, Coventry CV4 7AL, United Kingdom*



(Received 15 December 2017; revised manuscript received 21 March 2018; published 5 April 2018)

Using classical Monte Carlo simulations, we study a simple statistical mechanical model of relevance to the emergence of polarization from local displacements on the square and cubic lattices. Our model contains two key ingredients: a Kitaev-like orientation-dependent interaction between nearest neighbors and a steric term that acts between next-nearest neighbors. Taken by themselves, each of these two ingredients is incapable of driving long-range symmetry breaking, despite the presence of a broad feature in the corresponding heat-capacity functions. Instead, each component results in a “hidden” transition on cooling to a manifold of degenerate states; the two manifolds are different in the sense that they reflect distinct types of local order. Remarkably, their intersection, i.e., the ground state when both interaction terms are included in the Hamiltonian, supports a spontaneous polarization. In this way, our study demonstrates how local-order mechanisms might be combined to break global inversion symmetry in a manner conceptually similar to that operating in the “hybrid” improper ferroelectrics. We discuss the relevance of our analysis to the emergence of spontaneous polarization in well-studied ferroelectrics such as BaTiO₃ and KNbO₃.

DOI: [10.1103/PhysRevB.97.134106](https://doi.org/10.1103/PhysRevB.97.134106)

I. INTRODUCTION

Central to the study of ferroelectric materials is an understanding of the collective mechanisms responsible for inversion-symmetry breaking in solids [1,2]. For proper ferroelectrics (e.g., the long-studied PbTiO₃) [3], the key collective behavior is a single zone-center polar phonon that softens on cooling the paraelectric parent below the Curie temperature T_C . A conceptually similar picture emerges in improper ferroelectrics such as Gd₂(MoO₄)₃ and YMnO₃, where the polar phonon instability is driven by a nonpolar distortion that actually acts as the primary order parameter [4–6].

An important recent development in the field has been the *hybrid* improper ferroelectric (HIF) mechanism relevant to, e.g., Ca₃Mn₂O₇ [7–10]. The remarkable feature of this mechanism is that spontaneous polarization emerges *via* trilinear coupling to two nonpolar distortion modes. The important implication in the particular context of multiferroics is that polarization-magnetization coupling might be targeted through judicious combinations of nonpolar distortions (e.g., tilts or cation order) rather than attempting to reconcile the inherently antagonistic requirements for magnetic order (partially filled *d* orbitals) and polar instabilities (closed-shell *d*-electron configurations) [11]. Such “tilt-engineering” approaches have now been exploited to remarkable effect in the design of (Ca_{*y*}Sr_{1–*y*})_{1.15}Tb_{1.85}Fe₂O₇, which shows spontaneous polarization and magnetization at room temperature [12].

In all these mechanisms, the collective distortions responsible for inversion-symmetry breaking—be they polar instabilities, octahedral tilts, cation ordering, or vacancy ordering

processes—are each associated with individual irreducible representations of the parent crystal symmetry. In other words, polarization emerges as a result of the relation

$$\Gamma^- \subseteq \oplus_i \Phi_i^\pm, \quad (1)$$

where Γ^- is a (generic) polar distortion and the collective distortion space spanned by the direct sum is generated by a small and finite number of unstable distortion modes (possibly nonpolar) with irreducible representations $\Phi_i^\pm$. For proper ferroelectrics Eq. (1) reduces to $\Gamma^- = \Phi^-$. While this is the conventional picture for systems such as BaTiO₃ and KNbO₃ [13], recent total scattering measurements [14] have supported the hypothesis of Refs. [15,16] that the paraelectric/ferroelectric transition may be strongly order/disorder in nature. In this alternate picture the ferroelectric transition involves a complex reorganization of cation positions that cannot properly be described in terms of Eq. (1). This is because both the paraelectric (cubic) and polar (tetragonal) phases support different types of strongly correlated disorder that are not related to one another by activation of a small and finite set of distortion modes (Fig. 1). Instead, the two states are related by the presence or absence of a particular type of *local* order [14,16].

In this study, we explore the concept of establishing HIF mechanisms based on coupling of polarization to distortions arising from local order. Our approach is to develop a simple microscopic model containing just two ingredients, each of which drives its own form of local ordering to a nonpolar disordered phase with a manifold of degenerate ground states. These two ingredients are our local analogs of, e.g., the tilt and rotation distortions in the HIF mechanism of Ca₃Mn₂O₇ [8]. Whereas the individual HIF distortions are localized in **k** space and collective in direct space, the two ingredients of our

*andrew.goodwin@chem.ox.ac.uk

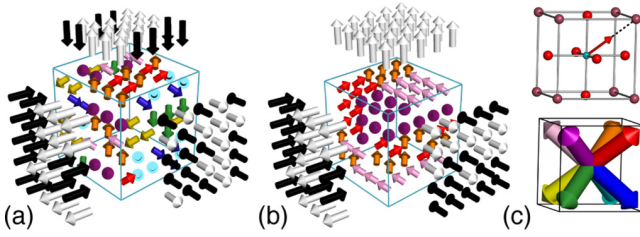


FIG. 1. Schematic representations of local and collective polarization in the (a) cubic and (b) tetragonal phases of BaTiO_3 and KNbO_3 [14]. The dipole moments within individual perovskite cells are shown as colored arrows. The collective polarization for a given column (parallel to any one of the three crystal axes) is shown as a black or white arrow. In both phases there is strong local order (common polarization projection along a given axis), but macroscopic inversion symmetry is broken only in the tetragonal phase. (c) Local polarization is driven by a second-order Jahn-Teller distortion of, e.g., the TiO_6 coordination environment in which the Ti atom (teal sphere) displaces towards a single corner of the corresponding unit cell (red arrow). The eight possible displacement vectors $\langle 111 \rangle$ are shown in various colors.

model drive order that is localized in $\mathbf{r}$ space and collective in reciprocal space. Using Monte Carlo (MC) simulations, we show that the full Hamiltonian has as its ground state a disordered, but polar, phase that is conceptually related to tetragonal BaTiO_3 or KNbO_3 . Hence a collective polar distortion emerges from coupling to two nonpolar local-order instabilities. The key implication of this result is that judicious control over local-order phenomena might offer an alternative route to as yet unexplored classes of ferroelectric materials.

Our paper is arranged as follows. We begin by introducing the general model at the heart of our study, relating its ingredients to simple physical interactions likely to be relevant to real materials. We describe our MC approach and proceed to establish the phase behavior of the two individual components of our Hamiltonian, demonstrating the existence of local-structure transitions in each case. Our focus then shifts to the behavior of the combined interaction model. We determine a general phase diagram and show explicitly the coupling of local order to macroscopic polarization. For ease of interpretation, we focus in these studies on a two-dimensional representation of the Hamiltonian. Nevertheless, our paper concludes with a discussion of the (straightforward) extension to three dimensions, which allows us to draw comparisons to physical systems such as BaTiO_3 and KNbO_3 .

II. RESULTS AND DISCUSSION

A. Interaction model

Our two-dimensional (2D) toy model concerns a square array of interacting sites. In order to make clear the eventual parallels to real [three-dimensional (3D)] ferroelectric compounds such as BaTiO_3 and KNbO_3 , we associate this 2D model with a fictitious lattice of composition ABO_2 [Fig. 2(a)]. The key degrees of freedom in this model are the displacements of individual B -site atoms associated with lattice sites $\mathbf{r}$. These displacements may take one of four equivalent vector states $\mathbf{e}$, which we associate with constant-magnitude off-center displacements polarized along the square diagonals [Fig. 2(a)];

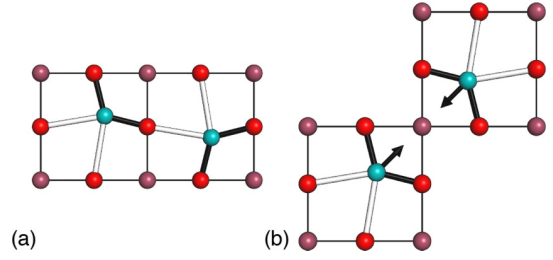


FIG. 2. (a) A square ABO_2 lattice with alternating strong (black) and weak (white) B -O bonds. A -site cations are shown in brown, B -site cations are in teal, and O atoms are in red. Note that each O atom is involved in exactly one strong and one weak B -O bond; this results in an alternating pattern of strong-weak-strong-... bonds along each axis. (b) The steric interaction term of Eq. (2) penalizes the displacement of two nearest-neighbor (diagonally related) B -site cations towards one another and hence towards a single common A -site cation.

hence $\mathbf{e}_{\mathbf{r}} \in \langle 11 \rangle$ in two dimensions. In a physical system, this local displacement may arise as a result of (by way of example) a second-order Jahn-Teller (SOJT) distortion or chemical bonding asymmetry; we consider the particular case where all local displacements are of equal magnitude and are strictly polarized along the cell diagonals.

Note that a simple coupling $J \mathbf{e}_{\mathbf{r}} \cdot \mathbf{e}_{\mathbf{r}'}$ between neighboring sites $\mathbf{r}, \mathbf{r}'$ would result in a polar instability for $J < 0$ but would give nonpolar antiferroelectric and disordered ground states for $J > 0$ and $J = 0$, respectively. The full Hamiltonian of our model does not include this particular interaction; instead, we have

$$\mathcal{H} = -J_1 \sum_{\mathbf{r}} (e_{\mathbf{r}}^x e_{\mathbf{r}+\mathbf{a}}^x + e_{\mathbf{r}}^y e_{\mathbf{r}+\mathbf{b}}^y) + J_2 \sum_{\mathbf{r}} \delta(\mathbf{e}_{\mathbf{r}} + \mathbf{e}_{\mathbf{r}+\mathbf{e}_{\mathbf{r}}}), \quad (2)$$

with $J_1, J_2 \geq 0$, δ being the Kronecker delta function, and $\mathbf{a}, \mathbf{b}$ being the lattice vectors.

The first term in Eq. (2) is conceptually related to the Kitaev model [17] of relevance to RuCl_3 and Na_2IrO_3 [18,19]: in both cases the interaction is bond dependent. It describes a discrete “compass” model [20,21] that separates the 2D lattice into a set of noninteracting one-dimensional (1D) Ising chains. Nearest neighbors separated by $\pm \mathbf{a}$ interact via the x component of their states (i.e., $e_{\mathbf{r}}^x, e_{\mathbf{r}+\mathbf{a}}^x$); likewise, those separated by $\pm \mathbf{b}$ interact via the y components $e_{\mathbf{r}}^y, e_{\mathbf{r}+\mathbf{b}}^y$. Since $J_1 > 0$, energy is minimized whenever neighboring states displace in the same direction relative to the axis along which they are connected. This interaction, if perhaps obscure at first sight, has a sound chemical basis for systems with SOJT distortions. Taking the example of a square ABO_2 lattice, such distortions would involve mixing of empty B d states with filled O p states to give a neighboring pair of strong B -O bonds for each B site; the requirement that each O atom is involved in exactly one strong B -O bond gives precisely the Kitaev-like interaction present in our model [Fig. 2(a)].

The second term in Eq. (2) penalizes next-nearest-neighbor displacements that act in direct opposition. This is a crude representation of the steric interaction that would arise from correlated B -site displacements towards a common A -site cation [Fig. 2(b)]. The same type of next-nearest-neighbor

displacement pattern is penalized by a dipolar interaction, which one might argue is a more physical ingredient in a Hamiltonian, but the corresponding ground state is ordered and hence unsuitable for the purposes of our study. We anticipate that screened dipolar interactions probably account for the interaction in some physical systems.

In this context and for ease of discussion, we hereafter denote the two components of Eq. (2) as “Kitaev” and “steric” interactions. We proceed to study the phase behavior these interactions drive, first in isolation and then in tandem.

B. Monte Carlo simulations

Our MC simulations made use of a custom-written code based on that employed in Ref. [22] and were carried out as follows. A starting configuration corresponding to a 30×30 supercell of the square unit cell was decorated randomly with states $\mathbf{e}_r \in \{[1, 1], [1, \bar{1}], [\bar{1}, 1], [\bar{1}, \bar{1}]\}$. We made use of periodic boundary conditions and followed the standard Metropolis Monte Carlo algorithm [23]; moves involved random reassignment of the state of a randomly selected site, and energies E were calculated for a given set of J_1, J_2 parameters according to Eq. (2). Simulations were started at high temperatures and slowly cooled. We ensured equilibration at each temperature step by discarding ten times as many moves as were required for the system to become uncorrelated from its initial state t_0 . We then performed a further $100t_0$ moves to calculate the specific heat from the fluctuation-dissipation relation

$$C = \frac{\langle E^2 \rangle - \langle E \rangle^2}{k_B T^2}, \quad (3)$$

where k_B is the Boltzmann constant. Results were averaged over five independent runs. We determined the qualitative influence of finite-size effects by repeating key simulations at different supercell dimensions.

C. Behavior of limiting cases

We begin by considering the phase behavior of the pure Kitaev ($J_2 = 0$) and pure steric ($J_1 = 0$) interaction models. In both cases our MC simulations identified the existence of a single broad anomaly in the specific heat that we will come to show accompanies a meaningful change in local structure (Fig. 3). The maximum of this anomaly occurs at $T/J_i \simeq \frac{1}{2}$. In each case there is no long-range symmetry breaking at any finite temperature: this is evident in the single-particle correlation function $\langle \mathbf{e} \rangle$, the magnitude of which vanishes within uncertainty for both models at all temperatures. This quantity is proportional to the bulk polarization magnitude, which is therefore also zero for both models at all temperatures.

Despite the absence of long-range symmetry breaking in either transition, our thermodynamic calculations clearly show the loss of configurational entropy on cooling that we associate with local-order processes. To illustrate this point we calculate two “local-order parameters” for each MC configuration:

$$\phi_K = \frac{1}{4} [(\mathbf{e}_r^x + \mathbf{e}_{r+a}^x)^2 + (\mathbf{e}_r^y + \mathbf{e}_{r+b}^y)^2 - 4], \quad (4)$$

$$\phi_s = 1 - 4\langle \delta(\mathbf{e}_r + \mathbf{e}_{r+\mathbf{e}_r}) \rangle, \quad (5)$$

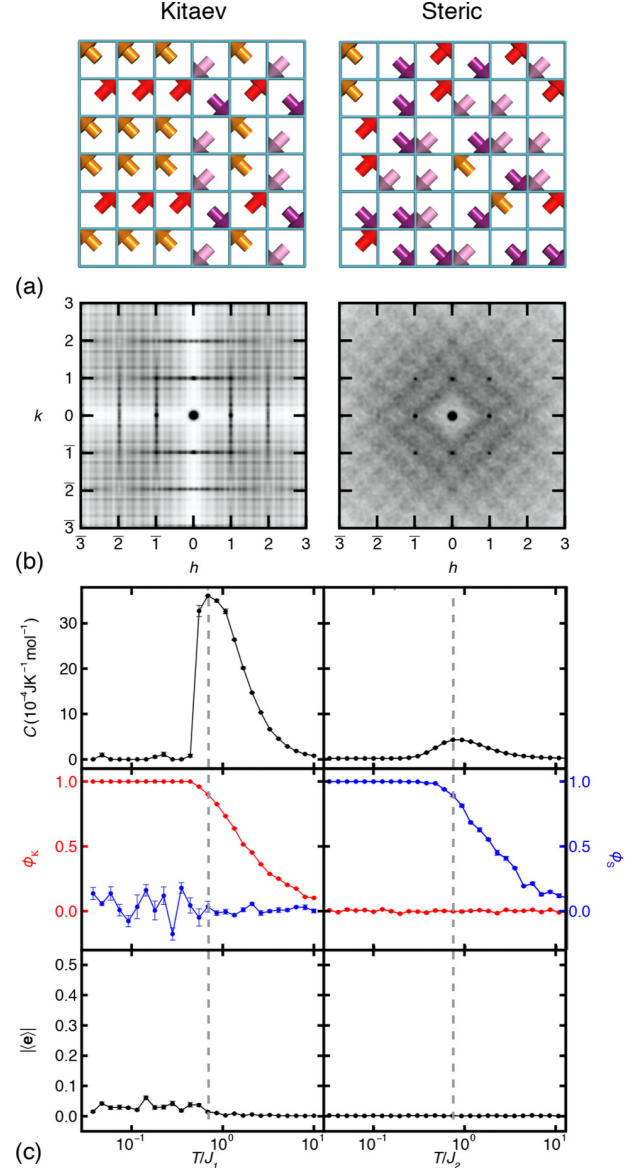


FIG. 3. Microscopic phase behavior in the single-term steric ($J_1 = 0$) and Kitaev ($J_2 = 0$) models described by Eq. (2). (a) Fragments of the low-temperature displacement configurations are disordered in both cases but contain different types of local order. The steric model contains no next-nearest-neighbor displacements of the form depicted in Fig. 2(b), and in the Kitaev model each row or column shares a common polarization along the corresponding row or column axis. (b) The corresponding single-crystal scattering patterns are sensitive to two-particle correlation functions and reflect nontrivial disorder of different types in the two low-temperature configurations. The Bragg intensities (a measure of the single-particle correlations) are identical in the two cases. (c) Thermodynamic and ordering behavior of the variable-temperature MC simulations. The top panels show the temperature dependence of the specific heat, with the position of its maximum indicated by a vertical dashed line. The middle panels show the temperature dependence of the local-order parameters ϕ_K (red) and ϕ_s (blue). Note the emergence of local order of (only) one type at temperatures below the corresponding specific-heat anomaly. The bottom panels show the macroscopic polarization magnitude $|\langle \mathbf{e} \rangle|$, which is zero within error for all MC temperatures.

with the average taken over all sites $\mathbf{r}$. By design, the value of ϕ_K is unity for any configuration in which all pairs of neighboring states displace in the same direction relative to the axis along which they are connected and zero for a random set of displacements $\mathbf{e}_r$. Likewise, a value $\phi_s = 1$ implies the complete absence of any next-nearest-neighbor displacements acting in direct opposition and $\phi_s = 0$ in the random case. The temperature dependence of these two parameters for the Kitaev and steric interaction models is shown in Fig. 3(c); we observe a clear progression from an uncorrelated paraelectric state ($\phi \sim 0$) at high temperatures to distinct locally ordered paraelectric states at temperatures below the relevant specific-heat anomalies.

The presence of different types of correlated disorder in the two limiting-case models at low temperatures is evident from the corresponding diffraction patterns [24] shown in Fig. 3(b). The Bragg intensities of the two models are identical, which is necessarily the case given the absence of any variation in single-particle correlation functions across the specific-heat anomalies. Instead, the two families of low-temperature states differ only in terms of the pair (and higher-order) correlation functions. In this sense the local-order transitions we observe are “hidden” [22,25] and are conceptually related to the spinice transition in, e.g., $\text{Ho}_2\text{Ti}_2\text{O}_7$ and the superstructure transition of some inclusion compounds [26,27]. Such transitions are not well described in terms of the conventional Landau paradigm and can sometimes be viewed instead as a Higgs transition of an emergent gauge theory [28].

Representative configurations themselves are illustrated in Fig. 3(a); we note that the Kitaev phase is related to the “ S_2C ” procristalline state as described in Ref. [29] and observed experimentally in perovskite oxynitrides [30,31]. This state supports strong 1D correlations along the lattice axes, as is evident in the diffraction pattern via the presence of continuous streaks of diffuse scattering perpendicular to the reciprocal lattice axes and is expected from the relationship to a decoupled 1D Ising model. Indeed, the specific-heat anomaly for this model [Fig. 3(c)] is equivalent to that obtained for the 1D Ising case. In both cases there is no strict long-range 1D order at low temperatures; rather, regions of medium-range 1D order [i.e., over many unit cells, with length scale proportional to $\exp(1/T)$] are separated by domain boundaries (Ising spin flips). With reference to our MC configurations, 1D order appears when the ordering length scale is commensurate with our simulation box size.

The low-temperature state of the steric interaction model is rather more disordered. This is evident in the diffraction pattern itself [Fig. 3(b)], for which the diffuse scattering component is only weakly structured throughout reciprocal space. Nevertheless, the state is not random; the form of local order present involves the complete absence of next-nearest-neighbor interactions of the type shown in Fig. 2(b).

So, by themselves, each of the Kitaev and steric interaction terms in Eq. (2) drives a nonpolar instability of the parent paraelectric state with respect to local ordering: these instabilities are localized in real space (i.e., strong local order) and collective in reciprocal space (i.e., associated with large families of $\mathbf{k}$ points). In particular, the phase behavior of both models cannot be described in terms of the activation of a small and finite set of collective (phononlike) distortion modes.

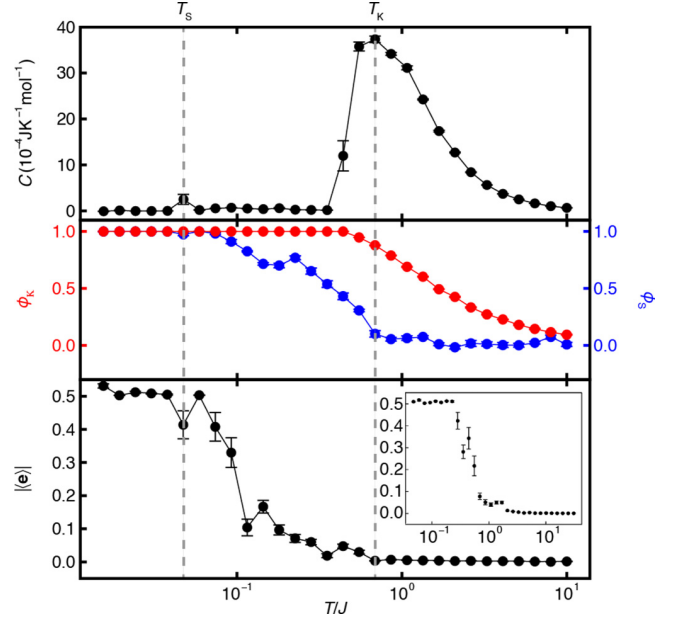


FIG. 4. Temperature dependence of thermodynamic and local-order parameters for the intermediate case ($\theta = \pi/35$). The heat capacity (top) shows two temperature anomalies; the higher one (at T_K) is associated with the onset of Kitaev-type local order, and the lower one (at T_s) is associated with the disappearance of local interactions of the type shown in Fig. 2(b). The temperature dependence of the local-order parameters is shown in the middle panel. The bottom panel shows the temperature dependence of the total polarization magnitude, which saturates on cooling below T_s . The inset shows the order parameter variation determined in a parallel simulation using a larger MC supercell (40×40 unit cells); clearly, the same behavior is observed.

D. Behavior of the intermediate case

We now consider the effect of coupling Kitaev and steric interactions by studying the behavior of our Hamiltonian for nonzero values of both J_1 and J_2 . We define the parameters

$$\theta = \tan^{-1} \left(\frac{J_2}{J_1} \right), \quad (6)$$

$$J = J_1 + J_2, \quad (7)$$

such that the pure-Kitaev and pure-steric interaction models explored in the previous section correspond to the cases $\theta = 0$ and $\pi/2$, respectively.

Monte Carlo simulations carried out for the intermediate case $J_2/J_1 = 9\%$ (i.e., $\theta = \pi/35$), a value we will come to show is representative of the general case, indicate the presence of two specific-heat anomalies (Fig. 4). Inspection of the temperature dependence of the local-order parameters ϕ_K, ϕ_s shows that the higher-temperature anomaly coincides with the onset of Kitaev order, and the lower-temperature anomaly coincides with the onset of local order found in the steric interaction model described above (Fig. 4); hence we label the two transition temperatures T_K and T_s , respectively.

The key result of our study concerns the behavior of the single-particle correlation function $\langle \mathbf{e} \rangle$ across these two transitions. This correlation function is a direct measure of

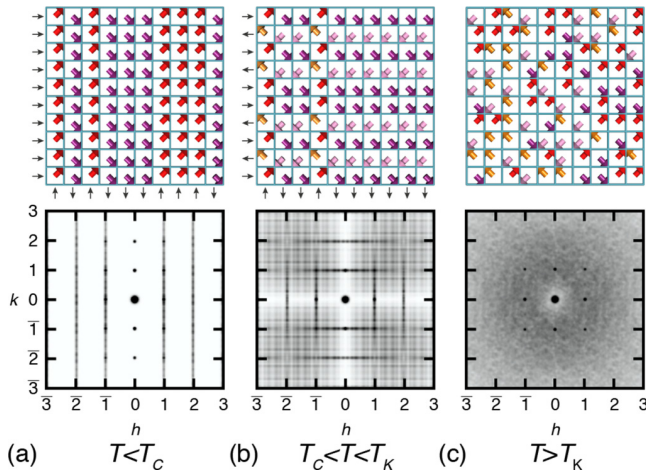


FIG. 5. Representative displacement configurations and single-crystal scattering patterns for the three temperature regimes of the intermediate case ($\theta = \pi/35$) studied in Fig. 4. (a) At low temperatures $T < T_C$ the system is polar; in the specific example shown here the bulk polarization is oriented to the right-hand side. Note the persistence of configurational disorder in the vertical component of the polarization for a given column of displacement vectors. This persistent disorder is reflected in the presence of streaks of diffuse scattering perpendicular to the $\mathbf{a}^*$ axis in reciprocal space. (b) The intermediate-temperature regime $T_C < T < T_K$ resembles the low-temperature behavior of the pure-Kitaev model. The system is nonpolar, but strongly correlated Kitaev-type local order gives rise to streaks of diffuse scattering perpendicular to both $\mathbf{a}^*$ and $\mathbf{b}^*$ axes in reciprocal space. (c) At high temperatures $T > T_K$ the system is paraelectric.

the magnitude of bulk polarization: $P = |\langle \mathbf{e} \rangle|$. As for the individual Kitaev and steric interaction models, we find no meaningful change in P across T_K (Fig. 4); hence this local-order transition is again hidden and is not associated with any long-range symmetry breaking. By contrast, the transition at T_s involves the emergence of a nonzero bulk polarization and so represents a Curie point with $T_C = T_s$. Consequently, the phase behavior for $0 < \theta < \pi/4$ involves three regimes. At low temperatures $T < T_C$ the system is polar, with local order that reflects at once the ground states of both Kitaev and steric interaction models. For intermediate temperatures $T_C < T < T_K$, the system is nonpolar and resembles the low-temperature behavior for $\theta = 0$ (Kitaev order). Finally, at temperatures above T_K local order is progressively lost, and the system approaches the paraelectric limit. Representative configurations taken from these three regimes are shown in Fig. 5, together with the corresponding diffraction patterns. As anticipated, the behavior at T_K closely resembles that observed in the pure-Kitaev limit ($\theta = 0$).

The long-range symmetry-breaking process identified by the behavior of the order parameter P at T_C is clearly evident in both real space and reciprocal space. We interpret this behavior by contrasting it with the low-temperature behavior of the pure-Kitaev model. In the Kitaev ground states each row or column has a common polarization along the row/column axis; the system is disordered because these collective axial polarizations do not themselves order [Fig. 5(a)]. This disordered

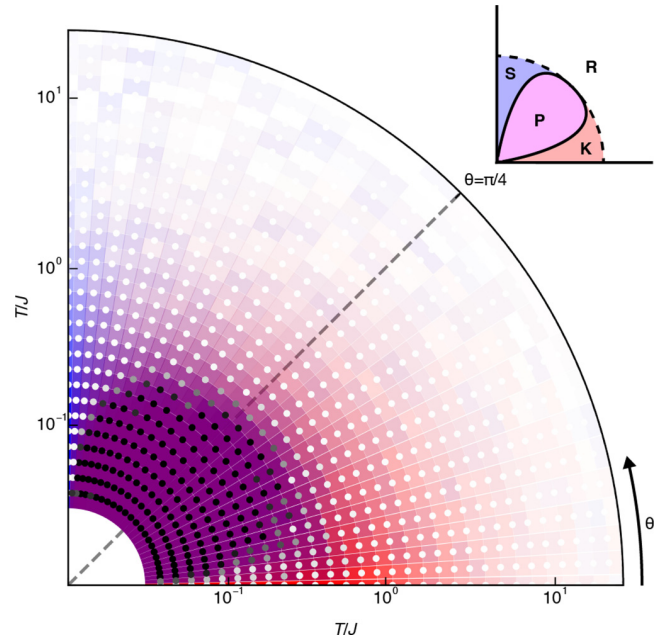


FIG. 6. Phase diagram for the model described by Eq. (2), given in terms of the polar coordinates $r = T/J$ and θ as defined in Eq. (6). For each (r, θ) value the corresponding sector is colored by the values of ϕ_K (red) and ϕ_S (blue). The corresponding polarization magnitude is illustrated by the saturation of the small circle: $|\langle \mathbf{e} \rangle| = 0$ (white) to >0.5 (black). Our key result is that polar states (black points) emerge from the combination of Kitaev- and steric-type local order (purple shading). Inset: local-order phase diagram, with Kitaev (K), steric (S), polar (P), and “random” (R) states indicated.

state supports next-nearest-neighbor displacements that act in direct opposition, which is evident in the value of $\phi_s < 1$ for the Kitaev ground state (Fig. 3). For finite values of θ , these opposing displacements are penalized by the Hamiltonian (2), and the polar ground state emerges as the mechanism by which the displacements are removed. As in the Kitaev ground state each row/column maintains a common polarization, but collective polarizations are now ordered along one crystal axis [Fig. 5(b)]. This order distinguishes one axis from the other and reduces the (average) plane group symmetry from $p4m$ to pm . From an average-structure perspective it is as if a polar distortion has condensed from a paraelectric parent phase. Yet, as we have seen, the state at temperatures just above T_C supports strong correlations and is not truly paraelectric. Moreover, even the polar ground state remains disordered: the diffraction pattern contains continuous streaks of diffuse scattering parallel to the polar axis [Fig. 5(b)].

The phase behavior driven by the Hamiltonian (2) for other values of θ is conceptually very similar. When $\theta > \pi/4$ ($J_2 > J_1$) the transition temperatures T_K, T_s swap their order, and the Curie temperature is now associated with T_K rather than T_s . For $\theta = \pi/4$ the three transition temperatures coincide. For all values of θ between (but not equal to) the limits of zero and $\pi/2$, the ground state is the polar disordered state identified above. A representation of the general phase behavior is given in Fig. 6 as a radial function of θ and T/J . What is clear is that bulk polarization emerges as the intersection of the

locally ordered low-temperature states of the Kitaev and steric interaction models.

For completeness we note that the use of periodic boundary conditions will necessarily introduce finite-size effects into our MC simulations. For example, the 1D order in the Kitaev state cannot be truly long range at any finite temperature; instead, any physical realization must contain domain walls associated with Ising spin flips of this component. In terms of the polar phase that we find to emerge from combined Kitaev- and steric-type orders, the implication is that “bulk” polarization will persist for a given $\mathbf{e}$ only over a domain of finite (but arbitrarily large) size. The direction of $\mathbf{e}$ will vary from domain to domain, with domain size inversely proportional to temperature. This picture is, of course, entirely consistent with the presence of domains within the polar (ferroelectric) state in the absence of an external field.

E. Extension to three dimensions

Entirely analogous behavior occurs in a three-dimensional variant of this same interaction model. The underlying lattice is now cubic rather than square, and the states representative of local polarizations are parallel to one of the cube diagonals. Hence $\mathbf{e}_r \in \langle 111 \rangle$ can adopt one of eight vector values. The modified Hamiltonian is

$$\mathcal{H} = -J_1 \sum_{\mathbf{r}} (e_{\mathbf{r}}^x e_{\mathbf{r}+\mathbf{a}}^x + e_{\mathbf{r}}^y e_{\mathbf{r}+\mathbf{b}}^y + e_{\mathbf{r}}^z e_{\mathbf{r}+\mathbf{c}}^z) + J_2 \sum_{\mathbf{r}, \mathbf{r}'} \delta[\mathbf{e}_{\mathbf{r}}^{\parallel} - \mathbf{e}_{\mathbf{r}'}^{\parallel} - 2(\mathbf{r}' - \mathbf{r})], \quad (8)$$

with $\mathbf{a}, \mathbf{b}, \mathbf{c}$ being the lattice vectors. The steric interaction sum is taken over pairs of next-nearest neighbors $\mathbf{r}, \mathbf{r}'$, with the terms $\mathbf{e}_{\mathbf{r}}^{\parallel}, \mathbf{e}_{\mathbf{r}'}^{\parallel}$ corresponding to the components of $\mathbf{e}_{\mathbf{r}}, \mathbf{e}_{\mathbf{r}'}$ along the axis connecting $\mathbf{r}$ and $\mathbf{r}'$:

$$\mathbf{e}_{\mathbf{r}}^{\parallel} = \frac{\mathbf{e}_{\mathbf{r}} \cdot (\mathbf{r}' - \mathbf{r})}{|\mathbf{r}' - \mathbf{r}|^2} (\mathbf{r}' - \mathbf{r}). \quad (9)$$

We carried out a series of 3D MC simulations driven by this Hamiltonian using the same protocol as described above. The only two meaningful differences were the MC simulation size (we used a configuration corresponding to a $10 \times 10 \times 10$ supercell of the perovskite structure) and the possible states at each lattice point: $\mathbf{e}_{\mathbf{r}}$ were assigned one of eight vector values $\in \langle 111 \rangle$. Again, we found that the individual Kitaev and steric interaction terms of Eq. (8) each give rise to specific heat anomalies with no corresponding changes in macroscopic symmetry.

As a representative example of the intermediate behavior, we consider the case $J_1/J_2 = 25$. The temperature dependence of the specific heat, shown in Fig. 7, again reveals two phase transitions and hence identifies three phase fields. The nature of these phases is entirely analogous to that in the various two-dimensional models described above. The highest-temperature phase is paraelectric; the intermediate phase is nonpolar and supports strong one-dimensional order of the Kitaev type. Both of these phases have $Pm\bar{3}m$ crystal symmetry. By contrast, the lower-temperature transition involves global symmetry breaking and leads to a ground-state polar phase with $P4mm$ symmetry. Again, this state is heavily disordered, with collective axial degrees of freedom present along two of the

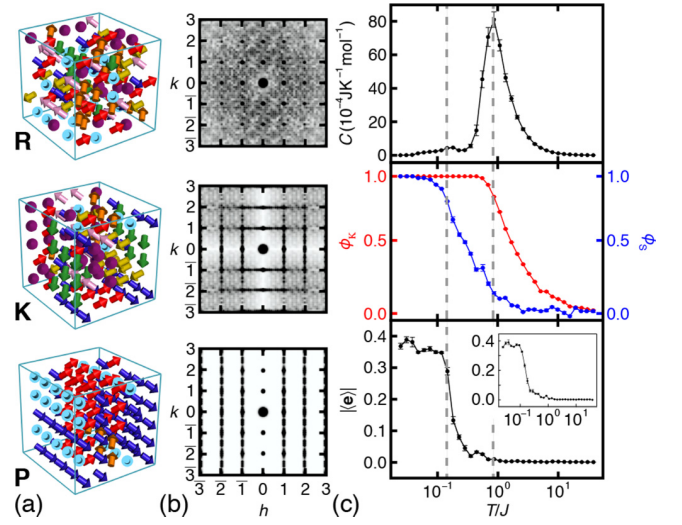


FIG. 7. Phase behavior of a representative example of the interaction model described by Eq. (8). (a) Displacement configurations within the high-temperature random (R) state, the intermediate-regime Kitaev (K) state, and the low-temperature polar (P) state. (b) The corresponding single-crystal scattering patterns show the emergence of increasingly structured diffuse scattering patterns as local order is increased. Note the reduced long-range symmetry of the P state. (c) Temperature dependence of the (top-bottom) specific heat, local-order parameters, and bulk polarization as determined by MC simulations. The inset shows the order parameter variation determined using a parallel MC simulation carried out for a smaller supercell ($8 \times 8 \times 8$ unit cells); again, the same behavior is observed.

three crystal axes. This transition is equivalent to the highest-temperature (cubic/tetragonal) transition reported in the MC study of BaTiO_3 in Ref. [14].

We note for completeness that the Kitaev-like interaction term in Eq. (8) gives rise to a conceptually interesting manifold of “icelike” low-temperature states. Whereas conventional Ising spin ices are based on a topology of connected tetrahedra and obey the well-known “two-in-two-out” rules [32], the simple-cubic ices that emerge from the Kitaev model are assembled from connected octahedra that obey a local “three-in-three-out” rule (Fig. 8). In cross section these configurations correspond to the square ice model [24,33]; moreover, the states are related to the “ C_3F ” procrySTALLINE phase described in Ref. [29] and the distribution of O and N atoms in magnetoresistive $\text{EuWO}_{1.5}\text{N}_{1.5}$ [31,34]. This is a model to which we expect to return in future studies.

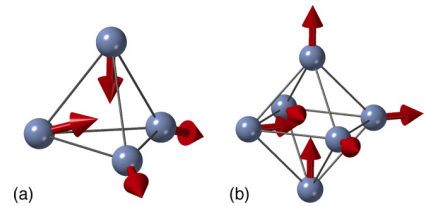


FIG. 8. Icelike states for simple polyhedra. (a) The two-in-two-out configuration of pyrochlore spin ices, and (b) the three-in-three-out configuration of the cubic Kitaev model.

III. CONCLUDING REMARKS

Returning to the context of inversion symmetry breaking in ferroelectrics, we suggest that the Hamiltonian (8) is likely relevant to the emergence of polarization in well-studied systems such as BaTiO_3 and KNbO_3 . Both single-crystal diffuse scattering [15,16] and powder pair distribution function [14] measurements indicate that the “paraelectric” state of these systems just above T_C is far from random and resembles instead the low-temperature behavior of the Kitaev model. Hence we are in the $J_1 > J_2$ regime of (8), which is sensible given the strong directional coupling between SOJT distortions expected for these systems (see Fig. 2). We have shown that the instability that drives the $Pm\bar{3}m/P4mm$ transition, and hence the emergence of a spontaneous polarization, in these two compounds need not involve ferroelectric coupling of the Ti/Nb displacements *per se* but may instead take the form of a local instability associated with steric or screened electrostatic interactions mediated by the A-site cations. Our goal here is not so much to explain the ferroelectric response of these systems, but rather to demonstrate that the combination of two judiciously chosen local-order instabilities may, in principle, couple to a bulk polar distortion in a manner that is conceptually similar to the HIF mechanism.

One of the clear challenges that emerges from our study is the need for a much fuller understanding of the interplay be-

tween global and local symmetry-breaking mechanisms. The conventional Landau description breaks down in attempting to describe local-order transitions (e.g., at T_K and T_S in our study) but provides a very natural and appealing explanation of the global symmetry-breaking process that occurs at T_C . In other systems, local-structure transitions have been described in terms of Higgs transitions of an emergent gauge theory in an approach that is inherently non-Landau [28]. Consequently, we suggest that the rationalization of these two viewpoints is an appealing area for future theoretical study. In the context of materials design, the central question raised by our study is, what particular types of local-order mechanisms might, when combined, necessarily couple to polarization (or ferromagnetization or ferroelasticity and so on)? The ability to answer this question then informs the targeting of specific bonding motifs or components with specific local instabilities as an entirely new approach to functional materials discovery.

ACKNOWLEDGMENTS

The authors gratefully acknowledge valuable discussions with N. A. Benedek (Cornell) and financial support from the ERC (Grant No. 279705), the Royal Society (to M.S.S.), the Leverhulme Trust (Grant No. RPG-2015-292), and Hertford College Oxford to E.H.W.

-
- [1] F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon, Oxford, 1962).
 - [2] J. F. Scott, *Ferroelectrics Rev.* **1**, 1 (1998).
 - [3] G. Shirane, J. D. Axe, J. Harada, and J. P. Remeika, *Phys. Rev. B* **2**, 155 (1970).
 - [4] A. P. Levanyuk and D. G. Sannikov, *Sov. Phys. Usp.* **17**, 199 (1974).
 - [5] B. B. Van Aken, T. T. M. Palstra, A. Filippetti, and N. A. Spaldin, *Nat. Mater.* **3**, 164 (2004).
 - [6] C. J. Fennie and K. M. Rabe, *Phys. Rev. B* **72**, 100103(R) (2005).
 - [7] E. Bousquet, M. Dawber, N. Stucki, C. Lichtensteiger, P. Hermet, S. Gariglio, J.-M. Triscone, and P. Ghosez, *Nature (London)* **452**, 732 (2008).
 - [8] N. A. Benedek and C. J. Fennie, *Phys. Rev. Lett.* **106**, 107204 (2011).
 - [9] Y. S. Oh, X. Luo, F.-T. Huang, Y. Wang, and S.-W. Cheong, *Nat. Mater.* **14**, 407 (2015).
 - [10] B. Xu, D. Wang, H. J. Zhao, J. Íñiguez, X. M. Chen, and L. Bellaiche, *Adv. Funct. Mater.* **25**, 3626 (2015).
 - [11] N. A. Hill, *J. Phys. Chem. B* **104**, 6694 (2000).
 - [12] M. J. Pitcher, P. Mandal, M. S. Dyer, J. Alaria, P. Borisov, H. Niu, J. B. Claridge, and M. J. Rosseinsky, *Science* **347**, 420 (2015).
 - [13] W. Cochran, *Adv. Phys.* **9**, 387 (1960).
 - [14] M. S. Senn, D. A. Keen, T. C. A. Lucas, J. A. Hriljac, and A. L. Goodwin, *Phys. Rev. Lett.* **116**, 207602 (2016).
 - [15] R. Comès, M. Lambert, and A. Guinier, *Solid State Commun.* **6**, 715 (1968).
 - [16] R. Comès, M. Lambert, and A. Guinier, *Acta Crystallogr., Sect. A* **26**, 244 (1970).
 - [17] A. Kitaev, *Ann. Phys. (NY)* **321**, 2 (2006).
 - [18] K. Ran, J. Wang, W. Wang, Z.-Y. Dong, X. Ren, S. Bao, S. Li, Z. Ma, Y. Gan, Y. Zhang, J. T. Park, G. Deng, S. Danilkin, S.-L. Yu, J.-X. Li, and J. Wen, *Phys. Rev. Lett.* **118**, 107203 (2017).
 - [19] S. K. Choi, R. Coldea, A. N. Kolmogorov, T. Lancaster, I. I. Mazin, S. J. Blundell, P. G. Radaelli, Y. Singh, P. Gegenwart, K. R. Choi, S.-W. Cheong, P. J. Baker, C. Stock, and J. Taylor, *Phys. Rev. Lett.* **108**, 127204 (2012).
 - [20] Z. Nussinov and J. van den Brink, *Rev. Mod. Phys.* **87**, 1 (2015).
 - [21] A. Mishra, M. Ma, F.-C. Zhang, S. Guertler, L.-H. Tang, and S. Wan, *Phys. Rev. Lett.* **93**, 207201 (2004).
 - [22] J. A. M. Paddison, H. Jacobsen, O. A. Petrenko, M. T. Fernández-Díaz, P. P. Deen, and A. L. Goodwin, *Science* **350**, 179 (2015).
 - [23] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, and A. H. Teller, *J. Chem. Phys.* **21**, 1087 (1953).
 - [24] D. A. Keen and A. L. Goodwin, *Nature (London)* **521**, 303 (2015).
 - [25] R. Okazaki, T. Shibauchi, H. J. Shi, Y. Haga, T. D. Matsuda, E. Yamamoto, Y. Onuki, H. Ikeda, and Y. Matsuda, *Science* **331**, 439 (2011).
 - [26] C. Castelnovo, R. Moessner, and S. L. Sondhi, *Nature (London)* **451**, 42 (2008).
 - [27] B. Toudic, P. Garcia, C. Odin, P. Rabiller, C. Ecolivet, E. Collet, P. Bourges, G. J. McIntyre, M. D. Hollingsworth, and T. Breczewski, *Science* **319**, 69 (2008).
 - [28] S. Powell, *Phys. Rev. B* **84**, 094437 (2011).
 - [29] A. R. Overy, A. B. Cairns, M. J. Cliffe, A. Simonov, M. G. Tucker, and A. L. Goodwin, *Nat. Commun.* **7**, 10445 (2016).

- [30] M. Yang, J. Oró-Solé, J. A. Rodgers, A. B. Jorge, A. Fuertes, and J. P. Attfield, [Nat. Chem.](#) **3**, 47 (2011).
- [31] P. J. Camp, A. Fuertes, and J. P. Attfield, [J. Am. Chem. Soc.](#) **134**, 6762 (2012).
- [32] S. T. Bramwell and M. J. Harris, [J. Phys.: Condens. Matter](#) **10**, L215 (1998).
- [33] J. M. Ziman, *Models of Disorder: The Theoretical Physics of Homogeneously Disordered Systems* (Cambridge University Press, Cambridge, 1979).
- [34] M. Yang, J. Oró Solé, A. Kusmartseva, A. Fuertes, and J. P. Attfield, [J. Am. Chem. Soc.](#) **132**, 4822 (2010).

Extreme cooperative swelling in topologically disordered fibre entanglements

Alistair R. Overy,^{1,2} Raj Pandya,¹ Phillip M. Maffettone,¹ Philip A. Chater,² Arkadiy Simonov¹ & Andrew L. Goodwin^{1,*}

¹*Department of Chemistry, University of Oxford, Inorganic Chemistry Laboratory, South Parks Road, OX1 3QR, Oxford, UK*

²*Diamond Light Source, Chilton, Oxfordshire, OX11 0DE, UK*

Entangled states are ubiquitous amongst fibrous materials, whether naturally occurring (keratin, collagen, DNA) or synthetic (nanotube assemblies, elastane). A key mechanical characteristic of these systems is their ability to reorganise in response to external stimuli, as implicated in *e.g.* hydration-induced swelling of keratin fibrils in human skin. During swelling, the curvature of individual fibres changes to give a cooperative and reversible structural reorganisation that opens up a pore network. The phenomenon is known to be highly dependent on topology, even if the nature of this dependence is not well understood: certain ordered entanglements (‘weavings’) can swell to many times their original volume while others are entirely incapable of swelling at all. Given this sensitivity to topology, it is puzzling how the disordered entanglements of many real materials manage to support cooperative dilation mechanisms. Here we use a combination of geometric and lattice-dynamical modelling to study the effect of disorder on swelling behaviour. The model system we devise spans a continuum of disordered topologies and is bounded by ordered states whose swelling behaviour is already known to be either vanishingly small or extreme. We find that while topological disorder often quenches swelling behaviour, certain disordered states possess a surprisingly large swelling capacity. Crucially, we show that the extreme swelling response previously observed only for certain specific weavings can be matched—and even superseded—by that of disordered entanglements. Our results establish a counterintuitive link between topological disorder and mechanical flexibility that has implications not only for polymer science but

also for our broader understanding of collective phenomena in disordered systems.

The packing of one-dimensional objects in three-dimensional space is a non-trivial geometric problem of relevance to the phase behaviour of synthetic polymers,¹ carbohydrate fibres,² carbon nanotubes,^{3,4} biomaterials,^{5–7} liquid crystals,^{8–10} lipid assemblies,¹¹ superconductors,^{12,13} skyrmion magnets,¹⁴ and hybrid inorganic–organic frameworks.¹⁵ The simplest possible arrangements are the rod packings,^{16,17} where packing symmetry relates the position and orientation of each rod to those of its neighbours [Fig. 1(a)–(c)]. Rods have no curvature, but fibres may; curvature allows for denser assemblies and its introduction into the rod packings transforms them into periodic ‘weavings’ with the same underlying topology yet different packing density.^{18–20} This transformation reflects the mechanism by which physical processes that affect curvature—such as hydration⁷ or thermal treatment¹—can in turn control the volume of fibre assemblies without requiring changes in topology. The ability of a particular weaving to swell as curvature varies is quantified by the ratio $\tau = V_{\max}/V_{\min}$ between the unit cell volumes of the extended (‘max’) and dense (‘min’) geometries. The magnitude of τ is a function of weaving topology.¹⁸ For the ubiquitous hexagonal fibre packing, $\tau = 1$; it cannot swell. This is true also for the simple cubic packing Π^* (itself related to the crystal structure of elemental W).¹⁶ By contrast, the Σ^* packing—which describes the arrangement of channels in gyroid membrane structures—admits an extreme swelling ratio $\tau = 5.429$ that is comparable to the effect observed experimentally in key biopolymers [Fig. 1(c),(d)].⁷ In other words, whereas the process of varying fibre curvature can result in a five-fold volume increase for weavings with the Σ^* topology, the same mechanism has no effect on other fibre arrangements, such as those related to the hexagonal or Π^* rod packings.

An inevitable corollary of this specificity is that the swelling ability of any fibre assembly must be sensitive to the presence of topological disorder. This argument is entirely consistent with intuition: one expects the cooperative unwinding mechanism responsible for dilation to be locked as disorder introduces knots—perhaps even at extremely low concentrations.¹⁸ Optical microscopy clearly reveals the presence of varying degrees of topological disorder within a variety of synthetic and natural fibre packings for which swelling is considered important [Fig. 1(e)]. By convention,

such systems (we use the term ‘entanglements’ hereafter) are generally modelled in terms of two independent components: an ordered weaving whose topology reflects structural motifs present locally within the fibre assembly, and a separate random-coil fraction.²¹ Hence there is a fundamental disconnect between our understanding that mechanical response is so strongly topology dependent, on the one hand, and the approximation of real systems in terms of a non-interacting two-phase model, on the other hand. Moreover the recent discovery of reversible dilatancy in ‘random’ coils²² together with the longer-established identification of negative Poisson ratios in amorphous foams²³ collectively illustrate the propensity for topologically disordered networks to exhibit mechanical responses that are difficult to anticipate based on the consideration of ordered states alone. So the relationship between topological disorder in fibre entanglements and cooperative mechanical responses such as swelling is an open, interesting, and important question.

Here we study this relationship using a combination of geometric and lattice-dynamical approaches. A key challenge is to devise a methodology that allows topological disorder to be controlled systematically such that disorder might be correlated directly with mechanical response. We identify a common topological parent of both Π^* and Σ^* weavings which allows us to generate intermediate entanglements of essentially arbitrary (but quantifiable) degrees of topological disorder. Moreover, because the swelling capabilities of the bounding topologies are so very different—*i.e.* vanishingly small in the case of Π^* and extreme in the case of Σ^* —we can anticipate that τ must vary with degree of topological disorder. We use lattice-dynamical calculations to measure τ as a function of entanglement topology, benchmarking our results against the exact values of the limiting cases Π^* and Σ^* .¹⁸ We show that the swelling capacity of the Σ^* weaving is indeed sensitive to disorder, but that certain disordered topologies allow recovery of extreme swelling behaviour. Indeed our key result is the discovery of disordered entanglements that are capable of swelling to even greater extents than the Σ^* weaving itself (*i.e.* $\tau \gtrsim 6$). Hence we show definitively that topological order is not prerequisite for the large swelling behaviour observed in some fibrous materials, with disordered entanglements capable of supporting the collective rearrangements required for extreme and counterintuitive mechanical response.

We begin by describing our methodology for generating microscopic models of entangled states. These models will later form the input for lattice-dynamical calculations to determine swelling behaviour. Our model generation approach consists of two steps: first we obtain a topological representation of each entanglement with a quantifiable degree of disorder, and second we embed this topological state as an atomistic configuration, the geometry of which is then optimised using a set of simple pairwise interaction potentials.

In Fig. 2(a) we illustrate a single unit cell (space group symmetry $Ia\bar{3}d$) of the parent network from which our various entanglements are derived. The nodes of this network occupy the $48g$ Wyckoff sites and are connected by two symmetry-inequivalent types of linker [shown in red and teal in Fig. 2(a)]. Four linkers meet at each node: two of each type. Entanglements are obtained by partitioning the linkers into equal sets such that each set contains exactly two linkers meeting at every node (see SI for further details). Consequently a given linker set describes a family of self-avoiding one-dimensional paths embedded on the network, which is dense with respect to coverage of the nodes; we associate with each set its constituent fraction x of teal linkers. The trivial partitioning is the single possibility that completely respects linker type, giving entanglements with the Π^* ($x = 0$; *i.e.* all red linkers) and Σ^* ($x = 1$; *i.e.* all teal linkers) topologies [Fig. 2(b),(c)]. Entanglements corresponding to intermediate values of x represent approximants to disordered states, consistent by design with the periodic boundary conditions imposed by the underlying network unit cell [Fig. 2(d)]. The use of larger supercells gives increasingly realistic approximants but at considerable computational cost. The topologies generated using this approach are related both to the ‘spaghetti states’ of Coulomb phases such as the spin ices^{24,25} and also to the procrySTALLINE networks of Ref. 26 as realised in *e.g.* transition-metal oxyfluorides.^{27,28}

Having generated an entanglement for a given value of x , the corresponding linker set is decorated by atoms to give a crude atomistic representation of a fibre structure with the same topology (see SI). Finally, the atom positions are relaxed subject to a combination of harmonic bond potentials and electrostatic repulsion between fibres. The harmonic potential acts to maintain fibre connectivity while the electrostatic term maximises fibre separation; both terms—full details of

which are given as SI—are implemented so as to respect the topology imprinted during set partitioning. An illustration of the result of this process is given in Fig. 2(e), with further representative relaxed configurations shown in the SI.

We proceeded to use lattice-dynamical calculations to identify the swelling behaviour for our various entanglements, our eventual goal having been to characterise the function $\tau(x)$, $0 \leq x \leq 1$. Before presenting our results we describe first the basic approach we have taken together with our benchmarking checks for the (well understood) Π^* and Σ^* topologies. For a given value of x we generated a range of topologically-distinct entanglements as described above. Then, for each entanglement, we used the General Utility Lattice Program (GULP)²⁹ to perform a structural relaxation, which was in turn repeated for a variety of different nominal cell lengths d . The motivation for varying cell length was to access different states of the same topology with different degrees of swelling. Each of these relaxed configurations can be compared to one another as entanglements of unit-diameter fibres after rescaling by the closest inter-fibre separation r . This gives a final simulation cell of length $L = d/r$. By repeating our calculations while incrementally varying d , we can determine what particular range of L values is accessible to a given entanglement without deforming the fibres themselves (*i.e.* changes in curvature are allowed, but stretching is not). For each of these allowed L -states of a given entanglement, fibres are in direct contact; at the minimum value $L = L_{\min}$ the fibres have their greatest curvature and the entanglement is most densely packed, while at the maximum value $L = L_{\max}$ the system is at its most swollen with an open pore network (*i.e.* low fibre curvature). The swelling ratio is simply a measure of the relative volumes of the dense and open states:

$$\tau = \left(\frac{L_{\max}}{L_{\min}} \right)^3. \quad (1)$$

For the Π^* weaving at $x = 0$ we can access only a small range of L -states with $L \simeq 4$ [Fig. 3(a)]. Hence $L_{\min} \simeq L_{\max}$ and $\tau(0) = 1.04 \simeq 1$, as expected. By contrast, for the Σ^* weaving at $x = 1$ our GULP relaxations give L -states with $4.20 \leq L \leq 6.67$, and hence our approach estimates $\tau(1) = 4.0$ [Fig. 3(b)]. An illustration of the GULP configurations across this range of L -states is given in Fig. 3(e). The progression from $L_{\min}$ to $L_{\max}$ clearly identifies the

same cooperative swelling mechanism already established in Ref. 18. For context, we note that the swelling ratio determined using our new approach is about as close to the exact result ($\tau = 5.429 \dots$) as that obtained in the earlier simulations of Ref. 30 ($\tau = 3.9$). The level of agreement we find here corresponds to a *ca* 10% uncertainty in the value of L , which we will come to show is sufficient for qualitative comparison of the swelling capabilities of different entanglements. In each of these calculations—as in representative examples of the disordered entanglements described below—we verified reversibility through repeated cycling of d trajectories (see SI). Moreover, perturbations in the numerical parameters employed in our GULP simulations (*e.g.*, harmonic potential strength, effective fibre charge density) had no meaningful effect on the critical ratio $L_{\max}/L_{\min}$, and hence on τ (see SI).

The motivation for developing this approach is that it is sufficiently general to allow estimation of $\tau(x)$ for entanglements corresponding to intermediate values $0 < x < 1$. A survey of our results for these intermediate disordered states is given in Fig. 4(a), which reveals a highly non-trivial relationship between topological disorder and capacity for swelling. There appear to be two competing trends at play. On the one hand, there is the anticipated continuum of states between Σ^* and Π^* for which disorder quickly favours the limit $\tau \rightarrow 1$. So, for example, low levels of topological disorder within the Σ^* topology appear to quench swelling in most cases. On the other hand, there is a broad distribution of a small fraction of entanglements for which surprisingly large values of τ are realised. Taken together, these two effects mean that at intermediate values of x some entanglements show very small swelling effects while others show very large effects; we illustrate this point in Fig. 3(c),(d) by plotting the allowed L -states for two entanglements at $x = 0.5$ with contrasting swelling abilities. Importantly, our results identify the existence of disordered entanglements with swelling ratios even larger than that of the ordered Σ^* topology. In Fig. 3(f) we show the swelling mechanism for one such entanglement. The mechanism is clearly strongly cooperative, even if its nature is very different to that for the Σ^* weaving (by way of example).

Just as the relationship between topology and swelling capability remains poorly understood even for ordered weavings,^{18,20} so too is there no obvious rationale for the variance in τ we observe

for different disordered fibre entanglements. Our key point, of course, is simply that large values of τ are accessible to disordered states. Nevertheless we do make some further observations regarding our results. First, the variable x does not by itself guarantee disorder for intermediate values since ordered configurations with $x = 0.5$ are realisable in principle (even if statistically improbable). Nevertheless the configurations we observe to give extreme swelling responses are *not* ordered, as evidenced by their trivial $P1$ symmetry. And, second, our approach for generating disordered configurations remains based on a specific geometric model and necessarily allows us to explore only a small and finite subset of the family of allowed disordered entanglements. Consequently we have established only a lower bound on the maximum swelling behaviour of this broader family. In other words, disordered entanglements of suitable topologies may in fact show superior swelling responses to ordered weavings. In terms of the implications for engineering materials with dilatant properties, our results suggest that control over the extent and type of topological disorder may be as effective a design strategy as one of targeting specific ordered motifs.

The inverse progression—from open to dense packings—bears a conceptual similarity to the ‘tension’ mechanism for negative thermal expansion (NTE),^{31,32} whereby a material contracts on heating. In this picture, the low-energy vibrational modes of a NTE material involve flexing of initially-linear bonding arrangements such that the system folds in on itself as the magnitude of vibration increases at high temperatures. Consequently, whether or not a material exhibits NTE largely relies on the existence of a collective mechanism of bond flexing that allows this concerted densification; this is the case, for example, in ZrW_2O_8 and $\text{Zn}(\text{CN})_2$.^{31,33} As for swelling, the existence of such a mechanism is known to be a non-trivial function of network topology.³⁴ It is for precisely this reason that the question as to how amorphous materials (*e.g.* silica³⁵ and some liquids³⁶) show NTE has remained one of the most important and challenging problems in the field. Our geometric model for swelling behaviour is extremely similar in that it effectively links fibre curvature with changes in cell volume. Drawing analogies to NTE, the dense packing at $L_{\min}$ would reflect the high-temperature state (bent linkages, low volume) and the open packing at $L_{\max}$ the low-temperature state (linear linkages, high volume) [Fig. 4(b)]. So our finding that disordered fibre arrangements can reduce their volume by increasing fibre curvature also estab-

lishes a heuristic explanation as to why NTE might be observed in ostensibly unrelated families of disordered materials. The extension to negative Poisson’s ratios^{37,38}—as known for some amorphous foams²³—may also follow similar arguments. Whether this mapping proves robust or not, what emerges in all cases is the obvious importance of collective degrees of freedom in driving counterintuitive physical properties of topologically disordered systems.

1. Baughman, R. H. Negative thermal expansion in crystalline linear polymers. *J. Chem. Phys.* **58**, 2976–2983 (1973).
2. Kong, L. & Ziegler, G. R. Role of molecular entanglements in starch fiber formation by electrospinning. *Biomacromolecules* **13**, 2247–2253 (2012).
3. Hall, L. J. *et al.* Sign change of poisson’s ratio for carbon nanotube sheets. *Science* **320**, 504–507 (2008).
4. Hu, R. *et al.* Harvesting waste thermal energy using a carbon-nanotube-based thermoelectrochemical cell. *Nano Lett.* **10**, 838–846 (2010).
5. Brody, I. The ultrastructure of the tonofibrils in the keratinization process of normal human epidermis. *J. Ultrastruct. Res.* **4**, 264–297 (1960).
6. Stokes, D. L. & DeRosier, D. J. Growth conditions control the size and order of actin bundles in vitro. *Biophys. J.* **59**, 456–465 (1991).
7. Norlén, L. & Al-Amoudi, A. Stratum corneum keratin structure, function and formation: the cubic rod packing and membrane templating model. *J. Invest. Dermatol.* **123**, 715–732 (2004).
8. Spicer, P. T., Hayden, L. K., Lynch, M. L., Ofori-Boateng, A. & Burns, J. L. Novel process for producing cubic liquid crystalline nanoparticles (cubosomes). *Langmuir* **17**, 5748–5756 (2001).
9. Mol, G. N., Harris, K. D., Bastiaansen, C. W. M. & Broer, D. J. Thermo-mechanical responses of liquid-crystal networks with a splayed molecular organization. *Adv. Funct. Mater.* **15**, 1155–1159 (2005).

10. Zeng, X. *et al.* Complex multicolor tilings and critical phenomena in tetraphilic liquid crystals. *Science* **331**, 1302–1306 (2011).
11. Saludjian, P. & Reiss-Husson, F. Structure of the body-centered cubic phase of lipid systems. *Proc. Natl. Acad. Sci., U.S.A.* **77**, 6991–6995 (1980).
12. Abrikosov, A. A. The magnetic properties of superconducting alloys. *J. Phys. Chem. Solids* **2**, 199–208 (1957).
13. Auslaender, O. M. *et al.* Mechanics of individual isolated vortices in a cuprate superconductor. *Nat. Phys.* **5**, 35–39 (2009).
14. Mühlbauer, S. *et al.* Skyrmion lattice in a chiral magnet. *Science* **323**, 915–919 (2009).
15. Rosi, N. L. *et al.* Rod packings and metal–organic frameworks constructed from rod-shaped secondary building units. *J. Am. Chem. Soc.* **127**, 1504–1518 (2005).
16. O’Keeffe, M. & Andersson, S. Rod packings and crystal chemistry. *Acta Cryst. A* **33**, 914–923 (1977).
17. O’Keeffe, M., Plevart, J., Teshima, Y., Watanabe, Y. & Ogama, T. The invariant cubic rod (cylinder) packings: symmetries and coordinates. *Acta Cryst. A* **57**, 110–111 (2001).
18. Evans, M. E. & Hyde, S. T. From three-dimensional weavings to swollen corneocytes. *J. R. Soc. Interface* **8**, 1274–1280 (2011).
19. Evans, M. E., Robins, V. & Hyde, S. T. Periodic entanglements II: weavings from hyperbolic line patterns. *Acta Cryst. A* **69**, 262–275 (2013).
20. Evans, M. E., Robins, V. & Hyde, S. T. Ideal geometry of periodic entanglements. *Proc. Roy. Soc. A* **471**, 20150254 (2015).
21. Segerman, E. & Stern, P. G. Two-phase model for structure of polymers. *Nature* **210**, 1258–1259 (1966).

22. Rodney, D., Gadot, B., Martinez, O. R., du Roscoat, S. R. & Orgeas, L. Reversible dilatancy in entangled single-wire materials. *Nat. Mater.* **15**, 72–77 (2016).
23. Alderson, A., Rasburn, J. & Evans, K. E. Mass transport properties of auxetic (negative poisson’s ratio) foams. *Phys. Status Solidi B* **244**, 817–827 (2007).
24. Henley, C. L. The “coulomb phase” in frustrated systems. *Ann. Rev. Cond. Matt. Phys.* **1**, 179–210 (2010).
25. Moessner, R. & Ramirez, A. P. Geometrical frustration. *Physics Today* **59**, 24–29 (2006).
26. Overy, A. R. *et al.* Design of crystal-like aperiodic solids with selective disorder-phonon coupling. *Nat. Commun.* **7**, 10445 (2016).
27. Yang, M. *et al.* Anion order in perovskite oxynitrides. *Nat. Chem.* **3**, 47–52 (2011).
28. Camp, P. J., Fuertes, A. & Attfield, J. P. Sub-extensive entropies and open order in perovskite oxynitrides. *J. Am. Chem. Soc.* **134**, 6762–6766 (2012).
29. Gale, J. D. GULP: A computer program for the symmetry-adapted simulation of solids. *J. Chem. Soc., Faraday Trans.* **93**, 629–637 (1997).
30. Evans, M. E. & Roth, R. Shaping the skin: The interplay of mesoscale geometry and corneocyte swelling. *Phys. Rev. Lett.* **112**, 038102 (2014).
31. Mary, T. A., Evans, J. S. O., Vogt, T. & Sleight, A. W. Negative thermal expansion from 0.3 to 1050 Kelvin in ZrW_2O_8 . *Science* **272**, 90–92 (1996).
32. Barron, T. H. K. & Rogers, K. J. Thermal expansion of ideal polymer crystals: Application to polyethylene. *J. Mol. Simul.* **4**, 27–35 (1989).
33. Goodwin, A. L. & Kepert, C. J. Negative thermal expansion and low-frequency modes in cyanide-bridged framework materials. *Phys. Rev. B* **71**, 140301 (2005).

34. Dove, M. T., Pryde, A. K. A., Heine, V. & Hammonds, K. D. Exotic distributions of rigid unit modes in the reciprocal spaces of framework aluminosilicates. *J. Phys.: Cond. Matt.* **19**, 275209 (2007).
35. Dove, M. T. *et al.* Floppy modes in crystalline and amorphous silicates. *Phys. Rev. Lett.* **78**, 1070–1073 (1997).
36. Debenedetti, P. G. Supercooled and glassy water. *J. Phys.: Cond. Matt.* **15**, R1669–R1726 (2003).
37. Lakes, R. Foam structures with a negative poisson’s ratio. *Science* **235**, 1038–1040 (1987).
38. Greaves, G. N., Greer, A. L., Lakes, R. S. & Rouxel, T. Poisson’s ratio and modern materials. *Nat. Mater.* **10**, 823–837 (2011).
39. Larangeira de Almeida, H., Monteiro, L., Marques e Silva, R., Rocha, N. M. & Scheffer, H. Scanning electron microscopy of a blister roof in dystrophic epidermolysis bullosa. *An. Bras. Dermatol.* **88**, 966–968 (2013).
40. https://www.basf.com/press-photos/corp/en/highlights/forschung_und_entwicklung/bilderwelten_aus_der/0825_spandex_faser_55x.jpg-renditions/cq5dam.web.4-3.12.jpg.
41. Ferreira Santos, J. P., Bruna da Silva, A., Sundararaj, U. & Bretas, R. E. S. Novel electrical conductive hybrid nanostructures based on PA 6/MWCNT_{COOH} electrospun nanofibers and anchored MWCNT_{COOH}. *Polymer Eng. Sci.* **55**, 1263–1272 (2015).

Acknowledgements The authors gratefully acknowledge funding from the E.R.C. (Grant 279705), the Leverhulme Trust (Grant RPG-2015-292), the Swiss National Science Foundation to A.S, the Marshall Foundation to P.M.M., and from the Diamond Light Source to A.R.O. A.L.G. is grateful to M. Evans (TU Berlin) and M. Tucker (SNS, ORNL) for valuable discussions.

Competing Interests The authors declare that they have no competing financial interests.

Correspondence Correspondence and requests for materials should be addressed to A.L.G. (email: andrew.goodwin@chem.ox.ac.uk).

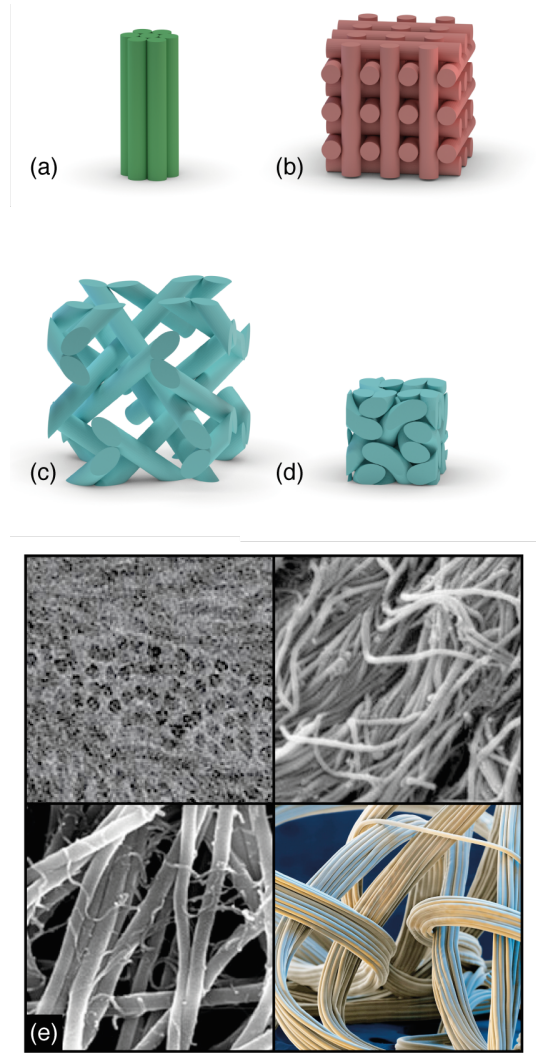


Figure 1. Rod packings and entanglements. Representations of the (a) hexagonal, (b), Π^* , and (c) Σ^* rod packings. If curvature is allowed then the Σ^* topology describes a fibre weaving with variable pore volume. A representation of this weaving in its densest state (minimal pore volume) is shown in (d). The interconversion between open (c) and closed (d) states is topologically protected and involves only a cooperative change in curvature of the individual fibres. Panel (e) gives representative microscopy images for a variety of naturally-occurring and synthetic disordered fibre entanglements: (clockwise from top-left) keratin,⁷ collagen,³⁹ elastane,⁴⁰ and carbon nanotubes.⁴¹

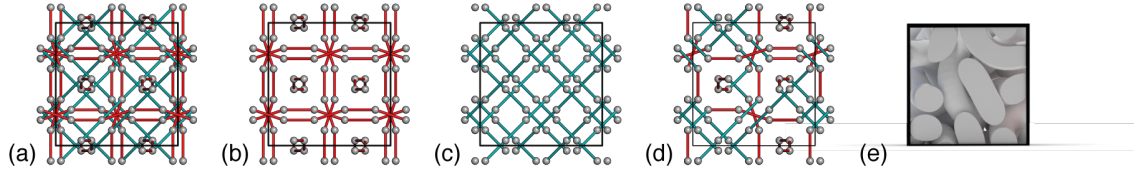


Figure 2. Generation of disordered entanglements. (a) Representation of the parent $Ia\bar{3}d$ network from which our entanglements are derived. Nodes are shown as grey spheres and occupy the $48g$ Wyckoff positions. These nodes are connected to one another by a set of two symmetry-distinct types of linkers, shown here in red and teal. Two red linkers and two teal linkers meet at each node (see SI). Entanglements are generated by partitioning this linker set into two subsets of equal size. The trivial partitioning gives the (b) Π^* and (c) Σ^* topologies, corresponding to the cases of all-red and all-teal linkers, respectively. Partitionings involving a combination of red and teal linkers are predominantly disordered, such as the example shown in (d). Subsequent geometric relaxation as described in the text and SI yields a disordered entanglement (e).

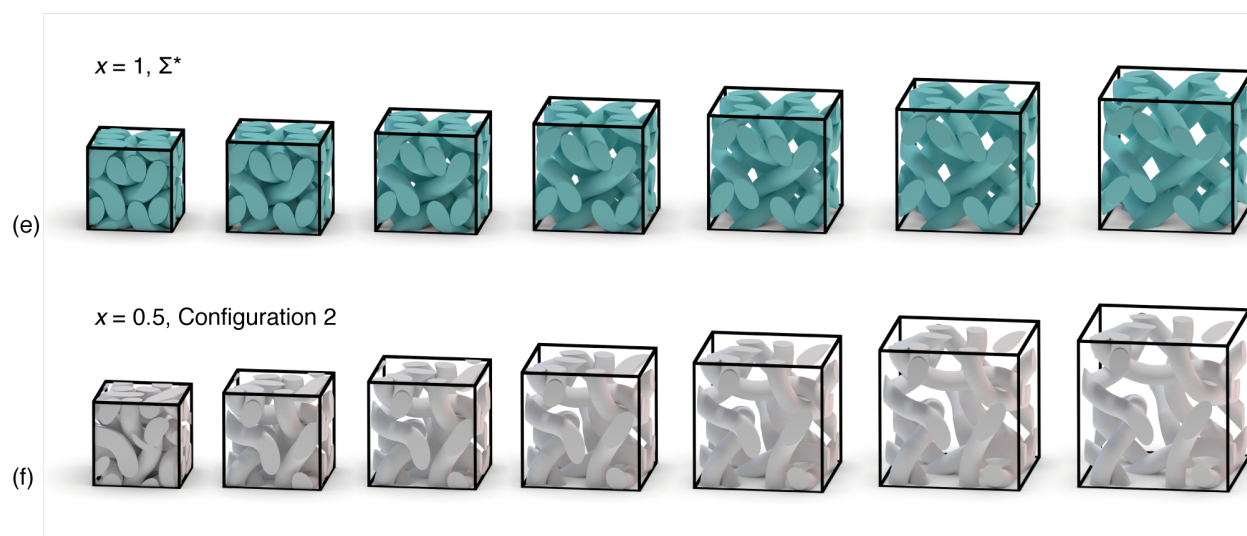
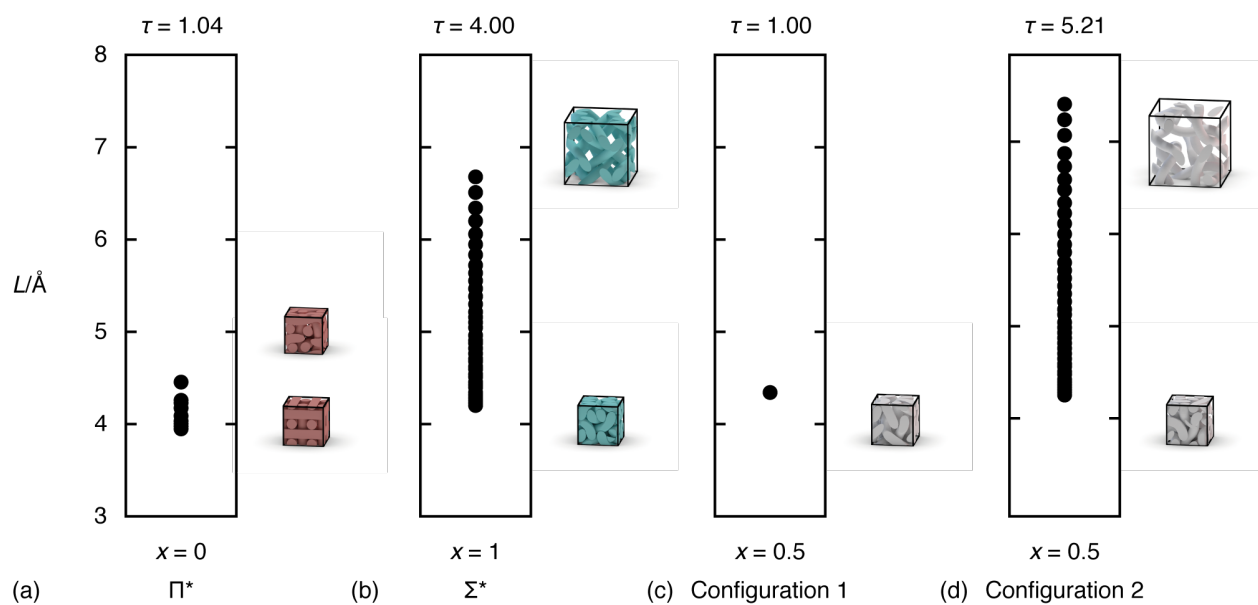


Figure 3. Swelling of ordered and disordered entanglements. Panels (a)–(d) show the range of relative unit cell dimensions accessible to entanglements with different topologies: (a) Π^* , (b) Σ^* , (c) a disordered entanglement with $x = 0.5$ and minimal swelling capacity, and (d) a disordered entanglement also with $x = 0.5$ but with an extreme swelling capacity. Representations of the collapsed and extended entanglements are shown on the right of each plot. (e) Illustration of the swelling mechanism for the Σ^* weaving, as described in Ref. 18. (f) The corresponding mechanism for the disordered entanglement of panel (d). Note that in both (e) and (f) fibres remain in contact with one another, but pore volume increases as the entanglement curvature is decreased.

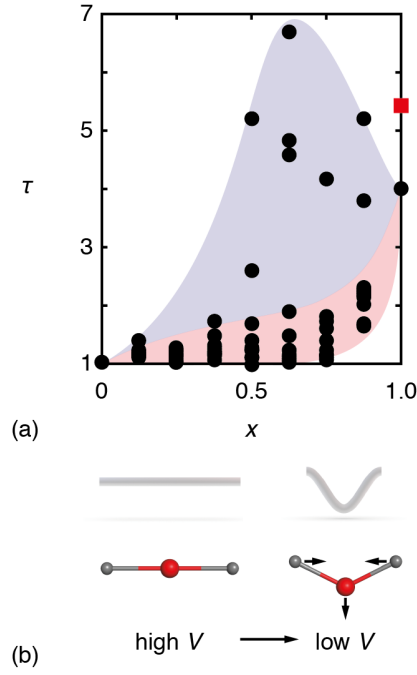


Figure 4. Disorder/swelling relationship. (a) Variation in swelling capacity τ with degree of topological disorder x . The value $\tau(1)$ is given both for the empirical calculation of our study (black circle) and for the DFT result of Ref. 20 (red square). Our data show that disorder mostly quenches swelling capacity (shaded red area) but that certain disordered topologies can show extreme capacities (shaded blue area). (b) Correspondence between variation in fibre curvature and the tension mechanism of negative thermal expansion (NTE). In NTE materials, increased transverse displacements at high temperatures act to reduce volume by increasing the effective curvature of the framework backbone.

Appendix F

Contents of the CD Appendix

- An electronic copy of this thesis.
- Fortran Monte Carlo code for the generation of procrystalline states.
- Python code for the SCLD analysis of the .eig outputs of the General Utility Lattice Program.
- Sample GULP input files (.gin) for the phononic studies of Chapters 4 and 5.
- The ABINIT input file (.in) for calculating the electronic density of states in Chapter 5.
- Sample MPB input files (.ctl) for the calculation of photonic states in Chapter 5.
- Fortran Monte Carlo code for the generation of disordered fibre entanglements.
- Initial GULP input files (.gin) for the calculation of swelling of the Π^* , Σ^* packings and a disordered entanglement of fibres.
- Animations of the swelling response of the Σ^* packing and a disordered entanglement of fibres.