

Designing disorder into crystalline materials

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Crystals are a state of matter characterised by periodic order. Yet crystalline materials can harbour disorder in many guises, such as non-repeating variations in composition, atom displacements, bonding arrangements, molecular orientations, conformations, charge states, orbital occupancies or magnetic structure. Disorder can sometimes be random, but more usually it is correlated. Frontier research into disordered crystals now seeks to control and exploit the unusual patterns that persist within these correlated disordered states in order to access functional responses inaccessible to conventional crystals. In this Review we survey the core design principles that guide targeted control over correlated disorder. We show how these principles — often informed by long-studied statistical mechanical models — can be applied across an unexpectedly broad range of materials, including organics, supramolecular assemblies, oxide ceramics and metal–organic frameworks. We conclude with a forward-looking discussion of the exciting link between disorder and function in responsive media, thermoelectrics and topological phases.

INTRODUCTION

All materials are disordered at finite temperature. Liquids, glasses and gels exhibit no long-range structural periodicity; fibres and liquid crystals are ordered in fewer than three dimensions; microporous materials such as zeolites and metal–organic frameworks (MOFs) are themselves crystalline but can nonetheless contain a fluid-like or glass-like guest phase within their pores. Many other classes of partially-ordered phases have been studied since the earliest days of structural science^{1–3}. In crystals, where the equilibrium positions of atoms are periodically ordered, disorder is nonetheless always present — most commonly in the form of thermal motion. But crystals can be disordered in other ways, particularly when some aspect of their structure has an internal degree of freedom. For example, paramagnetic MnO is a crystal even though the Mn^{2+} magnetic moments are not ordered. In plastic crystals, such as in ices, molecular centres-of-mass exhibit long-range order but molecular orientations do not. Alloys are positionally ordered yet compositionally disordered (Fig. 1a–c). Such are the disordered crystals discussed in seminal works in the field^{4,5} and those covered in this Review.

Our motivation for surveying the ways in which disorder might be incorporated intentionally within crystals and its effect on their physical properties comes from the empirical finding that many functional crystalline materials are indeed disordered in some non-trivial way. The photovoltaic hybrid lead–halide perovskites⁶, ferroelectric BaTiO_3 (Ref.^{7,8}) and magnetite⁹ (Fe_3O_4) are just some examples of recent or enduring interest (Fig. 1d–f). In each case it is clear that the disordered component — whatever its particular nature — is far from random, and the presence of specific correlations or patterns is likely important for the particular function of interest. Of course, the nature and phase behaviour of disordered crystalline states have long been studied within the statistical mechanical and crystallographic communities^{5,10,11}. So too are the physical properties of functional materials, which are the bread-and-butter of condensed matter physics and materials chemistry. Yet, the link between correlated disorder and property is an emerging, active and challenging field at the frontier of structural science. At its heart lie a number of important questions. How does one design a disordered crystal? What is the form of that disorder, and how is it controlled and characterised? And, most importantly, what properties does it impart? In the answers to these questions lie the secret of how one might design functional materials by controlling disorder.

Because correlated disorder is often a consequence of geometry, its nature can transcend the particular chemistry or physics from which it evolves. Hence, there exist unexpected parallels between ostensibly unrelated materials: magnetocaloric **[G]** $\text{Tb}(\text{HCOO})_3$ and benzenetrisamide nucleating agents, or $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ relaxors **[G]** and Prussian blue analogue cathode materials. Although each system has its own peculiarities, as we discuss in detail below, there are common aspects that influence them all. For example, each system has access to a large configurational degeneracy that in turn enables a heightened response to external stimuli¹². Likewise, the particular patterns that persist within a disordered state can couple to other properties that also depend on correlations, such as electronic states and collective vibrations⁵. Although our focus is on materials in which disorder arises from atomic-scale degrees of freedom, the underlying geometric origin of this disorder means that it can be mapped across multiple lengthscales. Hence, a design strategy for manipulating electronic band structure may be relevant to photonics when translated onto optical length scales¹³. And, reversing the argument, understanding how shape drives disordered packings of (macroscopic) polyhedra can in turn help direct molecular orientational disorder in hybrid materials¹⁴.

Here, we discuss several chemical design strategies for incorporating particular types of disorder, such as electronic instabilities, compositional complexity, directed self-assembly, molecular shape and low-energy dynamics. In each section we find ourselves drawing on a handful of statistical mechanical models that have largely been developed in the context of frustrated magnetism**[G]**. Consequently, we pre-empt our survey of design strategies by covering the fundamentals of these models, placing them as much as possible in a chemical context. We then take each design strategy in turn and illustrate its relevance to a number of examples drawn from the recent literature. Our hope is to make clear the role of geometry and the link to function where possible. We conclude this Review by offering some perspectives on this field: we attempt to anticipate areas of materials chemistry in which disordered crystals offer uniquely valuable opportunities for functional materials design and discovery.

MODELS OF CORRELATED DISORDER

The statistical mechanical models relevant to disordered crystals are based on three fundamental aspects — the relevant microscopic degrees of freedom, the interactions between those degrees of freedom, and the lattice on which these are collectively arranged⁵. Much of the corresponding literature has historically been phrased in terms of spin models, but in our discussion below we highlight the parallels between chemical and spin models, which are often straightforward and well established⁴. After introducing each aspect by itself, we then summarise the most important ways in which their various combinations can be exploited to produce complex disordered states **[Au: here do you mean that the different models can be combined to describe complex disordered states?] – No, we’re using ‘aspect’ here to refer to the three aspects introduced at the start of this paragraph, and which become the headings of the next three subsections. The combinations of (i) degrees of freedom, (ii) interactions, and (iii) lattice together produce a single model.**

Degrees of freedom

The simplest magnetic degrees of freedom are Ising spins, which can orient parallel or antiparallel to some axis¹⁵. Because the phase behaviour of Ising models is independent of the physical origin of the Ising degree of freedom, such models can be applied to any system in which the components can be in one of two distinguishable but equivalent states¹⁶. Some examples of Ising degrees of freedom of relevance to non-magnetic systems, together with some of the more complex variants discussed below, are represented in Fig. 2a. If the components of a disordered material can adopt any one of $n > 2$ equivalent states, then the behaviour is often well described by a n -state Potts model¹⁷. The three possible orientations of a dimethylammonium cation (DMA⁺) on the 12-coordinate site of the hybrid perovskite [DMA]Mn(HCOO)₃ or the orientations of Mn³⁺ Jahn–Teller distortions in LaMnO₃ are two examples that have been interpreted in terms of Potts models^{18,19}. Mathematically, all Ising and Potts degrees of freedom behave as discrete scalars.

XY models are the simplest involving continuous degrees of freedom: they involve the orientation of spin vectors of unit length lying within a plane²⁰. The spin orientation is described by a phase θ that can assume any value between 0 and 2π . Similarly, the orientation of molecules in rotator phases²¹ is a continuous degree of freedom, but there are also more subtle mappings to collective tilt distortions²², superconducting states²³ and vertical shifts in periodic columnar phases²⁴. If not all orientations θ are equally likely — perhaps as a result of the local crystal field — then the system is said to be anisotropic and the crystal free energy may include so-called ‘single-ion’ terms taken from the series expansion $D_1 \cos \theta + D_2 \cos 2\theta + \dots$. In 2D, this anisotropy is characterized by the circular harmonics. In 3D, the simplest continuous degree of freedom is the Heisenberg spin: a unit vector that can point anywhere in space²⁵. The orientation of polar molecules, such as the methylammonium ions (MA⁺) in MAPbI₃²⁶, or cation displacements, such as the off-centering of Ti atoms in BaTiO₃, can be described in this way (often with some significant anisotropy, now in 3D and hence characterised by the spherical harmonics)²⁷. Heisenberg spins are to dipolar degrees of freedom (for example, displacement or orientation) as Ising states are to monopolar degrees of freedom (for example, site occupancy or charge state).

Quadrupolar and higher-order multipolar equivalents have also been used to describe the phase behaviour of disordered crystals, in which the key multipole is determined by the shape of a relevant molecule; for example, octupoles for tetrahedral molecules such as CH₄ or hexapoles for trigonal-planar molecules such as the nitrate ion²⁸. Formally, these more complex degrees of freedom are characterised by tensors, the dimensions of which depend on the multipole order. Quadrupoles are usually the most straightforward to interpret, as they can be represented by 3×3 matrices and relate to the axial orientation of non-polar rod-like or disc-like molecules, such as CO₂ or the guanidinium cation. The corresponding model in statistical mechanics is that of nematic[G] phases, such as those that occur in some liquid crystals²⁹. There are other, less frequently encountered, degrees of freedom of relevance to disordered crystals. Examples include quaternions, which are used to describe the orientation of molecules of arbitrarily low symmetry, and axial vectors for freely-rotating objects³⁰.

Interactions

Long-range interactions tend to drive long-range order. Therefore, it is unsurprising that the key interactions between degrees of freedom in disordered crystals are usually short-range in nature (Fig. 2b). The simplest and most common short-range interaction is described by the inner (scalar) product between degrees of freedom across neighbouring sites. This product is a generic measure of the similarity of the two degrees of freedom at these sites, irrespective of the particular mathematics involved. For example, the inner product $e_i e_j$ of two Ising states $e_i, e_j = \pm 1$ is +1 if $e_i = e_j$ and −1 otherwise. For XY or Heisenberg degrees of freedom $\mathbf{S}_i, \mathbf{S}_j$, the inner product $\mathbf{S}_i \cdot \mathbf{S}_j$ is again obviously largest if $\mathbf{S}_i = \mathbf{S}_j$ and has the same functional form as the exchange interaction for magnetic spins. For this reason, the interaction is often called exchange (or ‘effective’ exchange) irrespective of its physical origin and its strength is usually expressed in terms of a coupling constant J (Ref.⁵). The sign of J determines whether neighbouring sites tend to adopt similar or dissimilar states. These cases are the equivalents of ferromagnetic or antiferromagnetic exchange, and hence the prefixes ‘ferro’ and ‘antiferro’ are used widely to indicate the sign of an interaction irrespective of the degrees of freedom involved. So, the MA⁺ cations in [MA]Mn(HCOO)₃ are said to exhibit antiferrodipolar order, because their orientation alternates between neighbouring sites³¹. By contrast, the guanidinium (Gua⁺) cations in [Gua]Cd(HCOO)₃ exhibit ferroquadrupolar order, because their plane normals align along a single common axis³².

Long-range interactions, such as those between next-nearest neighbours and beyond, may also be important, although one ordinarily expects a reduction in the magnitude of the corresponding J . Some long-range interactions can adopt the same effective form as an exchange interaction. The best known example is that of dipoles on the pyrochlore lattice. A geometric peculiarity in this structure is that the contribution to the dipolar interaction from next-nearest-neighbour and beyond effectively cancels, and the surviving nearest-neighbour term can be recast in terms of the inner product $\mathbf{S}_i \cdot \mathbf{S}_j$ (Ref.³³). Interactions of a system with an external field usually take the same form as exchange, except that the coupling constant J is in the general case a tensor, the dimensions of which depend on the natures of the relevant degree of freedom and conjugate field.

Other kinds of interactions involve higher-order exchange, as in the case of the biquadratic interaction for XY spins, which

is proportional to $(\mathbf{S}_i \cdot \mathbf{S}_j)^2$. In spin models, this interaction controls the degree of nematic order — the tendency for spins to align along a common axis, whether parallel or antiparallel³⁴. A chemical analogy is that of molecular orientations in solid CO, for which the alignment axes exhibit long-range order, but the CO dipoles exhibit a head-to-tail disorder³⁵. We will come to discuss a less obvious mapping in the mixed-metal cyanides $\text{Au}_x\text{Ag}_{1-x}(\text{CN})$ in more detail below. The simplest picture is that these interactions represent the second-order term in the general series expansion $J(\mathbf{S}_1, \mathbf{S}_2) = J_1(\mathbf{S}_1 \cdot \mathbf{S}_2) + J_2(\mathbf{S}_i \cdot \mathbf{S}_j)^2 + \dots$. Further interaction types are those involving antisymmetric exchange^{36,37}, and multi-body interactions (that is, involving more than two sites) such as the six-body terms thought to govern cation order in some rock-salt sulfides, nitrides and carbides^{38,39}.

A final interaction type we need to consider is that described by the compass models⁴⁰. These involve anisotropic interactions, by which we mean that neighbouring sites interact differently depending on their mutual orientation. Probably the most famous example is the Kitaev interaction on the honeycomb lattice⁴¹. This interaction couples a single x, y , or z component of neighbouring Heisenberg spins, with the particular component depending on the orientation of the vector joining the magnetic sites. Kitaev was primarily concerned with the properties of the quantum ($S = \frac{1}{2}$) case, and indeed his approach has been used not only to study magnetic disorder but also to describe collective orbital states in strongly-correlated oxides⁴⁰. Perhaps surprisingly, simple classical analogues emerge from sensible bonding considerations in ferroelectrics and metal–organic frameworks. An example we explore in more detail below is that of paraelectric BaTiO_3 , in which the x -component of Ti off-center displacements couples strongly only along the a crystal axis and so on.

Lattice

It is clear that lattice geometry is crucial to the phase behaviour of systems featuring anisotropic interactions, because interaction and orientation are explicitly linked. But even for isotropic interactions, one intuitively expects different phase behaviour for different lattice topologies because of the different number and connectivity of neighbours. Symmetry is understandably crucial. Because disorder is favoured by the existence of a shallow configurational landscape with many equivalent or nearly-equivalent states, most correlated disordered states involve high-symmetry lattices. A handful of the most common high-symmetry lattices is given in Fig. 2c.

Geometric frustration and competing interactions

Perhaps the key advantage of couching disordered phases in terms of their underlying statistical mechanics is that the phase behaviour of these models is almost always known from theory or computation. A textbook result is, for example, that 1D models do not order at any finite temperature, hence, any system that can be mapped onto these 1D models will fail to order⁴². Likewise, it is known that Ising models can order in 2D¹⁰, but 2D models with continuous degrees of freedom are always unstable with respect to vortex formation⁴³. Some models, such as the Heisenberg ferromagnets, exhibit straightforward order–disorder transitions; others give rise to particularly unusual states that are disordered but far from random.

Triangular Ising antiferromagnets (TIA) are common examples of systems which support strongly-correlated disordered states. The TIA ground state features all the configurations for which individual triangles contain two ‘up’ and one ‘down’ Ising state, or vice versa (Fig. 3a)⁴⁴. The system is said to be geometrically frustrated because of the incompatibility between its degrees of freedom and the lattice on which they sit. In physical realisations of a TIA, longer-range interactions, however weak, can break crystal symmetry and remove this frustration at some sufficiently low temperature T_c . In the temperature range $T_c \leq T \lesssim |J|$, the system is disordered but strongly correlated. The ratio $f = |J|/T_c$ is a crude measure of the degree of frustration ($f > 10$ is typically considered strong). Geometric frustration plays a key role in stabilising the states of many disordered functional materials^{12,45}.

Systems containing competing interactions can exhibit a similar kind of structural complexity to that seen in geometrically frustrated phases. Probably the best known example of this type of systems are those described by the 1D axial next-nearest neighbour Ising (ANNNI) model (Fig. 3b)⁴⁶. This model accounts for two kinds of interactions: J_1 that acts between neighbouring sites, and J_2 between next-nearest neighbours. For certain choices of J_1, J_2 the two interactions are irreconcilable. Consider, for example, the case in which J_1 favours like Ising states at neighbouring sites, but J_2 favours state inversion. Any triplet of three successive sites must violate at least one or other interaction. The phase behaviour that arises for different J_1/J_2 ratios is (in)famously complex. As we explore in more detail below, ANNNI models have been used to rationalise the structural complexity of various families of layered materials^{47,48}.

Correlated disorder, hidden order and emergence

There is, in principle, a very large number of different disordered states accessible through the various degrees of freedom, interactions and lattice types enumerated above. In practice, however, certain states recur more frequently than others. We

have already flagged the TIA and ANNNI models as examples and Fig. 3c–e highlights a handful of others. A particularly well known example in the chemical literature is the family of ices, all members of which are related to the pyrochlore Ising antiferromagnet^{2,49}. As for the TIA, the ground state of this model is not unique but is characterised by a famous local rule — namely, that each tetrahedron of the pyrochlore lattice connects two sites in one Ising state and two in the other (Fig. 3c). In water ice itself, the Ising states represent the directions of hydrogen bonds between neighbouring H₂O molecules. As this local rule propagates across the pyrochlore lattice, the pairs of neighbouring sites in a common Ising state form a dense set of non-intersecting 1D paths. This is a specific example of a broader family of so-called loop or spaghetti phases (Fig. 3d)^{50,51}. Each site is a member of exactly one spaghetti because it shares its Ising state with exactly two neighbours — one in each of the two tetrahedral units of which it is a member. Dimer states are a related family, for which each site is associated a single neighbour (Fig. 3e)⁵². These various unconventional states are different examples of ‘procrystals’ that can be identified on the basis of their highly-structured diffuse scattering patterns^{53,54}.

From a conventional crystallographic viewpoint, there is no distinction between the symmetries of correlated disordered states and that of their random counterparts since their configurational averages are characterised by the same crystallographic space-group. Indeed the transition from random to strongly-correlated disorder is often accompanied by a broad specific heat anomaly rather than the sharp maximum in specific heat associated with conventional phase changes. In some cases the transition is said to involve ‘hidden order’^{4,55}. The entropy change associated with formation of the correlated state can of course be measured. Historically, there has been great interest in relating entropy changes to the microscopic degrees of freedom at play (Fig. 3f). Pauling’s early rationalisation of the residual entropy of ice is a particularly successful example². Nevertheless, we now know that, at least in some cases (most famously the ices), the correlated state is characterised by a very different type of symmetry — that of an emergent gauge field, an abstract description of the family of configurations obeying strict local rules — that is reflected in highly-structured diffuse scattering^{54,56,57}.

A final introductory point we need to make is that many of the disordered states we consider are known to support emergent phenomena operating on a different length-scale from that of the fundamental degrees of freedom from which they arise. We have already alluded to the existence of vortex states in some 2D models. These vortices and their 3D equivalents (such as magnetic skyrmions **[G]**) are topological objects that can carry a quantised effective charge and, in turn, can be used to store information (Fig. 3g)⁵⁸. Likewise, violations of the ‘2-in-2-out’ ice state behave as emergent monopoles that interact with one another according to an effective electrostatics⁵⁶. More generally, the excitations that transform any one specific disordered configuration into another correspond to collective degrees of freedom, which are intermediate between the localised excitations of isolated molecules and the lattice vibrations of conventional crystals⁵⁹. The key conclusion is that correlated disordered states are known a priori to support a variety of unusual physical properties, many of which can be anticipated by understanding the statistical mechanics of the corresponding microscopic model. By inverting this link into a design strategy we can, in principle, hope to engineer materials with a specific emergent property by controlling the underlying degrees of freedom, interactions and crystal lattice.

DESIGN STRATEGIES

In this section we review the key approaches by which the materials chemist can control and design disorder in crystals. Our starting point is the exploitation of electronic instabilities, which give rise to local symmetry-lowering phenomena that couple strongly and have a profound effect on various physical properties. We then show how analogous symmetry lowering can be achieved through compositional complexity in mixed-ion systems. In supramolecular crystals, symmetry-lowering is intrinsic to the particular building blocks used, and we proceed to show how self-assembly can also be directed to give a range of complex disordered states. Molecular shape plays an analogous role in hybrid materials. In all cases, the resultant disorder can be static or dynamic, and the section concludes by showing how these same design approaches when applied to dynamic disorder can also yield crystals with anomalous — and useful — vibrational characteristics.

Electronic instabilities

The Jahn–Teller (JT) effect and its variants provide an obvious strategy for incorporating disorder in crystals and for linking that disorder to electronic properties^{60,61}. JT distortions lower local symmetry, so there is automatically a family of equivalent JT states, and their interconversion corresponds to a local degree of freedom. Because JT stabilisation involves redistribution of electrons and variation in bond lengths, there is a very natural interaction between neighbouring degrees of freedom. And, because orbital occupancies are affected, different cooperative JT states often give different electronic and/or magnetic behaviour.

The manganite perovskite LaMnO₃ is a canonical example in which JT effects give rise to a correlated disordered state with specific electronic and magnetic properties. Its $t_{2g}^3 e_g^1$ Mn³⁺ *d*-electron configuration is degenerate and so can be stabilised by coupling to a local distortion of the same E_g symmetry^{61,62}. In principle, the twofold degeneracy of the E_g configuration means that the available distortion space is itself two-dimensional — it includes any linear combination of the pair of orthogonal

distortions known by the labels Q_2 and Q_3 (Fig. 4a). But in practice the subset of six discrete distortions giving a pair each of long, short and intermediate Mn–O bonds (the Q_2 state) is favoured energetically. This distortion couples O atom positions to the occupancy of e_g orbitals. And, because each O atom connects two Mn^{3+} centres, there is a natural mechanism for generating interactions between neighbouring distortions (and, hence, e_g orbital occupancies) of the Mn^{3+} sublattice. So the choice of local distortion orientation behaves as a Potts-type degree of freedom, and the JT effect provides a direction-dependent antiferroic coupling between neighbouring states (that is, long Mn–O bonds tend to avoid meeting at the same O atom). Indeed, an anisotropic Potts model accounts well for the physical behaviour of LaMnO_3 , rationalising the existence of an orbital order–disorder transition at $T_{\text{JT}} = 750$ K that couples to a switch from anisotropic to isotropic magnetism and a hundred-fold decrease in resistivity (Fig. 4b)^{19,63,64}. On doping to form the mixed-valence series $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, the fraction of JT-active sites is decreased, the orbital disordered state stabilised and T_{JT} lowered⁶⁵. By $x \simeq \frac{1}{3}$, T_{JT} is commensurate with the magnetic ordering temperature ($\simeq 300$ K), and the system exhibits a colossal magnetoresistance (CMR) effect⁶⁶, whereby its electrical conductivity is strongly perturbed by an applied magnetic field. The study of CMR remains an active field, but it is nonetheless clear that the configurational degeneracy of orbital states and the coupling between orbital and magnetic degrees of freedom at these critical temperatures are fundamental ingredients.

Second-order Jahn–Teller (SOJT) distortions can be exploited in a conceptually similar manner. The SOJT effect removes local inversion symmetry so as to allow mixing between orbitals of different symmetries, such as the filled ns and empty np orbitals of the ‘lone-pair’ p -block cations (such as Pb^{2+} and Bi^{3+}) or the vacant $M\text{-}nd$ and filled $\text{O-}2p$ states of d^0 transition-metal-containing oxides⁶⁰. The direction and magnitude of the displacement responsible for inversion-symmetry breaking act as local degrees of freedom. As for conventional (first order) JT distortions, the SOJT effect results in the strengthening of some bonding interactions at the expense of others, which again provides a source of coupling between neighbouring sites. In the case of BaTiO_3 , for example, off-centering of the Ti^{4+} cation along a local $[111]$ diagonal (towards one face of the TiO_6 coordination polyhedron) strengthens three mutually-perpendicular Ti–O bonds and weakens the other three (Fig. 4c)^{7,27}. The tendency for each O atom to participate in one strong and one weak Ti–O bond drives an anisotropic interaction that couples local displacements into polar chains and is, in turn, implicated in the emergence of bulk polarisation and ferroelectric response^{7,8,67}. Anomalous dielectric (rather than ferroelectric) behaviour is observed in $\text{Bi}_2\text{Ti}_2\text{O}_7$, in which Bi^{3+} cations are arranged on the pyrochlore lattice⁶⁸. Collective inversion-symmetry breaking at the Bi^{3+} site now results in a geometrically frustrated state conceptually related to that of the spin-ices. It is the shallow configurational landscape of this dipole-ice state that allows an anomalously large dielectric response to applied field, observed also in many other Bi-containing pyrochlores^{69,70}.

Metal–insulator transitions (MITs) of the Peierls type, which are typical distortions of 1D crystal lattices, also arise from JT-like instabilities. The one-dimensional nature of $d^1 \text{MO}_2$ phases ($M = \text{V}$ or Nb) leads to long-range symmetry breaking at the MIT as chains form of alternating short M–M dimers and long M...M pairs^{71–73}. By contrast, the analogous transition would be hidden for $\text{Y}_2\text{Nb}_2\text{O}_7$ as there is a large configurational degeneracy of Nb–Nb dimer decorations on its pyrochlore lattice (Fig. 4d)^{74,75}. In the related d^2 system $\text{Y}_2\text{Mo}_2\text{O}_7$, the same type of orbital-ice phase results in a large variance in magnetic superexchange strengths that in turn stabilises an unusual spin-glass ground state^{76,77}. These systems are specific examples of disordered ‘orbital molecule’ phases — semiconducting states in which the unpaired electrons of transition-metal cations are either shared to form metal–metal bonds or delocalised across a handful of neighbouring sites (for example, in the trimerons **[G]** of Fe_3O_4)^{73,78}. It increasingly seems that many orbital-molecule phases exhibit n -mer order–disorder transitions, such as that involving trimer–tetramer arrangements in AlV_2O_4 ⁷⁹, fluctuating dimers in CuIr_2S_4 ⁸⁰, and the formation of a trimeron liquid in Fe_3O_4 ⁹. Just as JT disordering in LaMnO_3 has a profound effect on electronic properties of the system, one might anticipate similarly important electronic anomalies associated with orbital-molecule disorder. Indeed there are strong conceptual parallels to complex ordering in zintl or intermetallic phases⁸¹ and also to the resonance valence bond model originally proposed by Anderson in the context of high-temperature superconductivity⁵².

So, from a design perspective, transition-metals and/or p -block cations with particular electronic configurations can be chosen to favour very specific types of local degrees of freedom. JT-active first-row transition-metal cations will exhibit collective JT phases with antiferro-type nearest-neighbour interactions. SOJT-active cations will give XY or Heisenberg degrees of freedom that will couple through ferroic compass-type interactions (although dipolar contributions may also be important). $4d$ and $5d$ transition metals with open shell configurations may form ‘hidden’ gapped phases in which cations have displaced in an antiferrodistortive sense. In each case, the nature of the underlying lattice is crucial in stabilising the relevant disordered state.

Compositional complexity

From a chemistry perspective, a straightforward approach by which disorder might be introduced into a crystal structure is to employ different components that can occupy the same crystallographic site. Alloys are an obvious example. So too are the many solid solutions routinely studied in materials chemistry. In many cases, compositional disorder is essentially random — such is the basis of Vegard’s law and the tuning of ‘chemical pressure’, for example^{82,83}. The less trivial cases are those in which compositional disorder is strongly correlated, such as occurs whenever local rules are important and/or geometric frustration plays a role⁸⁴. In the discussion that follows, we include vacancies as a kind of compositional variable, although there will be

cases (precisely as discussed in Ref. 4) in which the distinction between vacancy and displacive (dis)order is semantic rather than physical.

A clear example of nontrivial compositional disorder occurs in oxynitride perovskites such as SrMO_2N ($\text{M} = \text{Nb}, \text{Ta}$)^{85–87}. The octahedral coordination environment of each M^{5+} cation consists exclusively of four O and two N atoms, with the two nitride ligands arranged *cis* to one another in order to allow π -donation into orthogonal t_{2g} orbitals. Despite this prescribed coordination environment, the system can maximise its configurational entropy by adopting a disordered arrangement of zig-zag M–N–M linkages (Fig. 4e). Depending on the precise chemistry and synthesis temperature, it is possible to navigate different phases in which this zig-zag disorder extends in either two or three dimensions⁸⁸. In all cases, the point symmetry of the MO_4N_2 octahedron is effectively C_{2v} . This allows the central M cation to displace towards the edge spanned by both nitrides (that is, the local C_2 axis), giving rise to a local dipole. Hence, this compositional decoration drives a collective off-centering that is conceptually related to that arising from SOJT effects as described above (Fig. 4f). As for the SOJT systems, the off-centre displacements are correlated by an anisotropic interaction of the form:

$$\mathcal{H} = J \sum_{\mathbf{r}} (e_{\mathbf{r}}^x e_{\mathbf{r}+\mathbf{a}}^x + e_{\mathbf{r}}^y e_{\mathbf{r}+\mathbf{b}}^y + e_{\mathbf{r}}^z e_{\mathbf{r}+\mathbf{c}}^z), \quad (1)$$

where superscript x, y, z denote the Cartesian components of the displacement vector $\mathbf{e}_{\mathbf{r}} \in \{110\}$ at lattice site \mathbf{r} , and $\mathbf{a}, \mathbf{b}, \mathbf{c}$ are the lattice vectors⁶⁷. What differs between the oxynitrides and SOJT systems is the sign of the coupling constant J and hence the type of local order that emerges. In the oxynitrides, $J > 0$ and displacements tend to alternate in direction from site to site, whereas collective polarisation emerges in the SOJT systems because $J < 0$. Moreover, the off-centre displacements are effectively fixed during synthesis for the former, but may be driven between equivalent states in the latter. An ongoing challenge in this area is to establish a clear link between this very prescribed type of compositional disorder and the various attractive physical properties of oxynitrides, such as their high dielectric constants, photocatalysis and CMR behaviour⁸⁹.

Entirely analogous correlated compositional disorder may be expected in many other important mixed-anion phases, not least the oxyfluorides and oxyhydrides^{90,91}. In all cases, bonding considerations provide a strong set of local rules that, depending on the exact chemistry, synthesis conditions and lattice geometry, do not necessarily drive long-range order.

When a single crystallographic site can be occupied by two different components, composition behaves as an Ising variable. Therefore, any complex disordered state based on Ising degrees of freedom might in principle be realised through judicious choice of the composition and underlying crystal geometry. For example, the two-in-two-out ice states of the Ising pyrochlore antiferromagnet are realised through the distribution of Cr^{3+} and (non-magnetic) Sb^{5+} in $\text{RE}_2\text{CrSbO}_7$ pyrochlores ($\text{RE} = \text{Y}, \text{Yb}, \text{Dy}, \text{Er}$)⁹². Here, the ambient-temperature magnetic behaviour is dominated by ferromagnetic interactions between Cr^{3+} ions, which are frustrated despite the geometrically-frustrated cation ordering. Not so for the defect pyrochlore CsNiCrF_6 , where there is strong interplay between the ice-like arrangement of Ni^{2+} and Cr^{3+} and the now-frustrated Heisenberg antiferromagnetic interactions between those ions (Fig. 4g)⁹³. Similar effects are seen in RbFe_2F_6 , where $\text{Fe}^{2+}/\text{Fe}^{3+}$ charge order provides the underlying compositional complexity⁹⁴. These systems are rare examples of multiple Coulomb phases because they each support two emergent gauge fields: one involving composition (or charge) and the other magnetism. The same concept extends naturally beyond the pyrochlore lattice. YbMgGaO_4 is a classical spin liquid stabilised by compositional disorder of Yb and Mg on the triangular lattice⁹⁵. The use of correlated disorder to drive unconventional magnetism — for example, in the stabilisation of quantum spin liquids^{45,96} and disorder-induced magnetic patterning in intermetallics⁹⁷ — is an emerging frontier of condensed-matter physics.

In a more obviously chemical context, non-random cation disorder in rock-salt oxides is increasingly viewed as a design parameter in the application of these systems as cathode materials^{98–101}. Taking as the general case the composition LiMO_2 , where M is a trivalent transition-metal cation (or mix of cations with average charge $3+$), the tendency to distribute the more highly charged M^{3+} species so as to avoid M...M neighbours gives rise to an effective antiferroic interaction between compositional Ising states. These are frustrated on the fcc cation sublattice of the rock-salt structure, which no doubt accounts the complexity of this family of materials. Hence, Li^+ -ion arrangements are driven by longer-range interactions, which may or may not enforce long-range order. Order facilitates structural characterisation, but it also results in anisotropy — such as in layered LiCoO_2 — that increases strain during charge–discharge cycles and, hence, can reduce battery lifetimes¹⁰². There is now great interest in the manipulation of short-range order within isotropic disordered systems to optimise battery performance¹⁰¹.

An incompatibility between composition and lattice geometry can be exploited to favour disordered states. For example, antiferroic interactions are not frustrated on the simple cubic lattice. This accounts for the well-known family of double-perovskites ($\text{A}_2\text{BB}'\text{O}_6$), in which the B-site cations of one type (B or B') are connected exclusively to those of the other type. However, complexity can be introduced by varying the ratio of substituents B and B' from 1:1 to 1:2. This is precisely the composition that optimises the complexity of domain structure in relaxor ferroelectrics (such as $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$) and relaxor ferromagnets (such as $\text{LaNi}_{2/3}\text{Sb}_{1/3}\text{O}_3$)^{103,104}. The tendency for like B-site cations to avoid occupying neighbouring sites automatically partitions the underlying cubic lattice into its two constituent interpenetrating fcc lattices: one which is occupied exclusively by the majority B-site cation, and the other occupied by both types in a 1:2 ratio (again frustrated)¹⁰⁵. Hence, Prussian blue analogues of general formula $\text{M}^{\text{II}}[\text{M}^{\text{III}}(\text{CN})_6]_{2/3}\square_{1/3}$ (\square = vacancy) are also of this same structure type and show a similar degree of

structural complexity that now affects the distribution and connectivity of vacancies¹⁰⁶. In this particular family, as in the disordered rocksalt cathode materials discussed above, there are signs that the type of local order in the disordered state might be tuned rationally by varying chemical composition and/or synthesis approach — an appealing kind of defect engineering^{99,100,106}. Similar approaches have been used to optimise superconducting transition temperatures in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ crystals¹⁰⁷, and are currently being explored in the field of MOFs¹⁰⁸, in which the concentration — if not yet arrangement — of vacancy clusters (for example, in UiO-66 and its derivatives) can be used to tune mechanical, sorption and catalytic behaviour^{109,110}.

For each of the examples discussed above, compositional disorder is imprinted during synthesis and hence is presumed static. But in certain systems with large vacancy concentrations and/or suitably polarisable ions, it is possible for compositionally disordered states to respond dynamically to external stimuli. A number of well known classes of disordered crystals fall into this category. One is that of the fast-ion conductors. To take the paradigmatic example of $\alpha\text{-AgI}$, the Ag^+ cations are distributed on a multi-site sublattice that is dominated by vacancies¹¹¹. The hopping barrier is sufficiently low that at readily-accessible temperatures the Ag^+ sublattice behaves as if liquid. In the oxide-ion analogues, such as Bi_2O_3 and yttria-stabilised zirconia, this ionic mobility is widely exploited in fuel cell technology¹¹². A second example of responsive occupational disorder is given by the many proton-based ferroelectrics, such as KH_2PO_4 (KDP)¹¹³. In these systems, H^+ ions can occupy one of two equivalent (or nearly equivalent) sites, and the application of an external field can induce flipping from one site to the other with a concomitant change in bulk polarisation. In proton or lithium-ion conductors, the available sites for H^+/Li^+ ions form connected paths to allow bulk transport in the presence of an ion gradient; the same design rules of site degeneracy and low inter-site barrier heights apply¹¹⁴.

Directed self-assembly

The nature of proton disorder in water ice, although couchable in terms of hydrogen-bond (Ising) degrees of freedom, arises spontaneously from the shape and charge distribution of the H_2O molecule itself. In this sense, one might speak of its 2-in-2-out disorder as ‘encoded’ within the molecule, and the emergence of a strongly-correlated disordered state as a process of directed self-assembly^{2,115}. Because the four hydrogen bonds made by each H_2O molecule are tetrahedrally disposed, the vast majority of solid ice phases are based on tetrahedral nets¹¹⁶. For most of these, the number of different decorations by H_2O molecules satisfying sensible hydrogen-bonding rules is so large that there is a non-vanishing (‘extensive’) configurational entropy associated with orientational disorder, which in turn stabilises the disordered state above some characteristic temperature⁴. The dielectric properties of ordered and disordered ices are fundamentally different and, indeed, many ordered phases are polar¹¹⁷. But perhaps the most important physical implication of orientational disorder in water ice is its effect on volume: disorder expands the hydrogen-bonded network to the extent that ordered ice would sink rather than float in water¹¹⁶.

The concept that molecular components of appropriate design might encode for complex disordered states is illustrated neatly by a number of 2D (or quasi-2D) supramolecular assemblies. The approach taken in Ref. 118 develops from the observation that trimesic acid self-assembles into a hydrogen-bonded honeycomb when deposited onto an appropriate surface¹¹⁹. The larger molecule *p*-terphenyl-3,5,3',5'-tetracarboxylic acid (TPTC) is a steric and functional mimic of a trimesic acid dimer pair, in which the intra-dimer hydrogen bonds are replaced by covalent bonds. TPTC also self-assembles into a honeycomb, but with one third of the links — exactly one associated with each node of the underlying net — now covalent (Fig. 5a)¹¹⁸. The presence of correlated disorder leads to an unexpectedly dynamic assembly, in which defects behave as emergent topological charges¹²⁰. A conceptually similar mesoscopic analogue forms spontaneously from the aggregation of dumbbells (connected circular pairs): the aggregate resembles a triangular packing of circles, but each is a member of exactly one dimer^{121,122}. Both examples reflect a common design strategy of engineering dimer decorations of ordered lattices¹²³. Because the problem of distributing dimers on the honeycomb lattice maps onto the TIA, TPTC assemblies have the same configurational entropy and excitations as that model system⁵³. In this case, the corresponding Ising degree of freedom, effective antiferroic interactions, and underlying triangular lattice are emergent properties of the TPTC assembly. Such mappings allow indirect routes for the design of specific phases.

TIA assemblies can also be generated through self-assembly in a much more direct way. By way of example, substituted 1,3,5-benzenetrisamides (BTAs) are known to assemble spontaneously into columnar phases^{124,125}. The approximately-planar molecules stack through π - π interactions into columns, that are further stabilised by helical strands of amide hydrogen bonds on their edges. This hydrogen bonding is strongly directional and gives each molecular stack an electric dipole moment oriented parallel or antiparallel to the stacking axis. The up or down sense of this dipole is an Ising degree of freedom¹²⁶. In the solid, columns form a dense packing to give a triangular arrangement of Ising states. Dipole-dipole interactions between neighbouring columns provide the final ingredient of antiferroic coupling, such that the TIA phase emerges spontaneously (Fig. 5b)^{126,127}. The configurational degeneracy of this phase renders the system especially sensitive to weak longer-range interactions, which can be tuned by varying substituents on the trisamide core¹²⁷. In this way the system can be optimised to stabilise polar nanodomains, a motif that is thought to enhance their functional role as crystallisation nucleation agents¹²⁸.

In two dimensions, XY models tend to offer a richer physics than do their Ising analogues. A well-known example is the instability of XY models to the formation of vortex-antivortex pairs. In these cases, the XY orientations rotate continuously around a point — either in the same (vortex) or in the opposite (antivortex) sense relative to path around that point (Fig. 3g).

Vortices and antivortices can be assigned effective charges (+1 and -1, say), have their own phase behaviour, and have potential application in data storage^{43,129}. Assemblies of periodic chains can adopt the same phase behaviour as 2D XY models because the vertical position z of periodic chains acts as an effective XY degree of freedom through the simple mapping $\theta = 2\pi z$. Probably the best understood example is that of the linear cyanide polymers $\text{Ag}_{1-x}\text{Au}_x\text{CN}$, all of which involve triangular packings of periodic chains²⁴. The effective pairwise interactions are governed by a balance of metallophilic and electrostatic contributions, which varies as a function of composition. For AgCN, electrostatics win out. Chain neighbours are best stabilised by relative shifts $\Delta z = \frac{1}{2}$ that place the CN^- anions of one chain next to the Ag^+ cations of the other. Therefore, the interaction between effective XY degrees of freedom is antiferroic. The situation reverses for AuCN, in which aurophilic interactions more strongly favour coalignment of neighbouring chains and the effective XY interaction is ferroic. For the intermediate composition $\text{Ag}_{1/2}\text{Au}_{1/2}\text{CN}$, the energetics are extremely finely balanced, and higher-order (biquadratic) interactions stabilise a frustrated nematic phase that contains a high density of vortex-antivortex pairs (Fig. 5c)¹³⁰. So the family of linear cyanide polymers provides an attractive example in which composition can be used to navigate phase space to target specific states of particular interest. In principle, the phase behaviour of the diverse families of urea and thiourea clathrates may yet be interpretable (and manipulable) in this same context¹³¹.

Just as 2D physics can be realised in columnar phases, so is it that 1D physics emerges in layered systems. Here, as ever, Ising models are the best studied⁴⁷. The canonical example is that of close-packed structures, in which successive layers can be in one of two equivalent arrangements, and cubic and hexagonal close packing arise from effective ferroic and antiferroic interactions, respectively, between next-neighbour layers. The structures of stacking-faulted ices — disordered ice phases containing a mixture of cubic- and hexagonal-type packing arrangements — have been rationalised in this context by establishing that effective interaction energy governing successive layer orientations is comparable to the available thermal energy at ice formation¹³². A similar effect is likely responsible for stacking disorder in $\text{Ni}(\text{CN})_2$, despite the difference in layer geometry¹³³. By contrast, the complex polymorphism of silicon carbides is understood in terms of competing interactions between successive layers that map their phase behaviour onto the ANNNI model⁴⁷. One of the key targets of this area is to use complex layering motifs to reduce thermal conductivity, for example, in layered chalcogenides¹³⁴. As in the columnar cyanides, layer composition appears to be the most straightforward, if still empirical, design variable for navigating the effective 1D phase space spanned by these systems.

Molecular shape as a symmetry lowering mechanism

An important theme of soft-matter science is that shape alone can drive extraordinary phase complexity. This complexity arises from two effects: a shaped object has additional orientational degrees of freedom that a spherical particle does not; and the interactions between shaped particles are inherently anisotropic. In a survey of the dense packings of 145 high-symmetry convex polyhedra, only 24 were found to form ordered crystalline phases (including the remarkable quasicrystalline packing of tetrahedra)^{14,135}. In general, polyhedra exhibiting large anisotropy favour liquid crystalline states, whereas those exhibiting low anisotropy tend to form plastic crystals. The inverse relationships have long been used by chemists as design principles. For example, hexahydroxytriphenylene derivatives make good discotic liquid crystals¹³⁶, in which the orientational order dominates over the positional order. In contrast, C_{60} is easily stabilised in a plastic phase, in which the molecular centres of mass order but orientations do not^{137,138}. In soft matter, one relies on supramolecular interactions to determine the geometry of the lattice, which makes it especially challenging to predict their phase behaviour. Nevertheless a number of important paradigmatic systems — from simple solids such as $\text{CO}_{(\text{s})}$ through to the many industrially-important families of liquid crystals^{139,140} — fall into precisely this category. Because of the absence of direct control over the underlying lattice in soft matter systems, we do not discuss them here. However, the link between disorder and function is as important for many soft materials as it is for the systems we discuss here. A clear example is the role of orientational disorder in promoting ionic conductivity in both organic ionic plastic crystals^{141–144} and ‘melting’ coordination polymers^{145,146}.

Ref. 4 distinguishes between the role of molecular shape in molecular crystals and its role in salts containing both atomic and molecular ions. In the latter case, electrostatic interactions help organise molecular units onto a specific lattice, and the interactions between molecules are no longer direct but are longer-range and/or mediated by the atomic component. Hence, there is now scope for control over all three fundamental ingredients — degrees of freedom, interactions, and lattice — so as to allow engineering disordered systems of a specific type. The difference in point symmetry between the molecule (local) and its crystallographic site (average) determines the molecular orientational degrees of freedom. The underlying lattice is of course constrained by the crystal structure. And the effective interactions between neighbouring molecules are often dominated by dipolar terms and/or coupling to strain. From a statistical mechanical viewpoint, the alkali cyanides (such as KCN) and molecular ferroelectrics such as NaNO_2 are probably the best known examples^{147–149}.

Our focus here is on systems of particular recent interest, in which molecules are contained within the cavities of a host framework. The examples of greatest currency are certainly the organic-inorganic hybrid perovskites¹⁵⁰, but metal-organic frameworks and clathrates are also related. From a design perspective, the key attraction is that the geometry of the host strictly determines the geometry of the lattice on which the molecular components are arranged. The strategy of exploiting differences in local and crystallographic symmetry to control microscopic degrees of freedom applies equally well; orientational coupling

between neighbouring molecules is often dominated by dipolar and/or higher-order multipolar interactions. Moreover, there is particular scope for interplay between orientational disorder and materials properties through coupling to the host framework.

A simple example of order–disorder transitions in hybrid perovskites is given by the imidazolium cyanoelpasolites¹⁵¹, analogues of the $A_2BB'O_6$ double-perovskites discussed above. The point symmetry of the imidazolium cation (C_{2v}) is incompatible with that of the A-site (T_d) in the double-perovskite structure. There are four equivalent ways of lowering the local symmetry appropriately that correspond to alignment of the imidazolium plane normal to the four $\langle 111 \rangle$ cube diagonals (Fig. 6a). (At lower temperatures, further symmetry breaking allows alignment of the imidazolium orientations within these planes.) Hence, at high temperatures, imidazolium orientations behave as 4-state Potts degrees of freedom. In these particular materials, coupling to strain gives effective ferroquadrupolar interactions ($|J| \simeq 100$ K), the strength of which can be tuned through chemical pressure of the surrounding lattice: increasing lattice size acts to decrease $|J|$. A quadrupolar order–disorder transition occurs at $T_c \simeq 4.7J$ that follows closely the simple 4-state Potts ferroquadrupolar model on the simple cubic lattice. This scale of T_c , which is representative of orientational order–disorder transitions in molecular perovskites, is clearly attractive for device applications. Many of the closely-related formate perovskites show equivalent transitions involving ordering of polar A-site cations^{152,153}. The existence of magnetic ordering transitions in this same family then provides an attractive avenue for developing multiferroics^{152,154,155}. The ferroelectric–paraelectric transitions in the topical all-organic perovskites [MDABCO][NH₄]X₃ (MDABCO = N-methyldabconium; X = Cl, Br, I) are an additional high-profile example¹⁵⁶. Simple Ising or Potts-type models seem to account well for the experimental phase behaviour of those hybrid perovskites to which they have been applied^{18,151,157}.

The entropy change associated with orientational order–disorder transitions can be exploited in the design of barocalorics [G] for solid-state cooling (Fig. 6b)¹⁵⁸. The key example in this context is [TPrA][Mn(dca)₃] (TPrA⁺ = tetrapropylammonium; dca[−] = dicyanamide)¹⁵⁹. At ambient pressure, the system exhibits an order–disorder transition at $T_c = 330$ K, which involves internal conformational degrees of freedom of the TPrA⁺ cation. The entropy change involved in this transition $\Delta S = 18.7 \text{ J K}^{-1} \text{ mol}^{-1}$ is amplified by the coupling between TPrA⁺ conformations and orientations of the dca[−] framework linkers. On application of hydrostatic pressure, T_c increases rapidly ($\partial T_c / \partial p = 23.1 \text{ K kbar}^{-1}$), forming the basis of a barocaloric cooling strategy (Fig. 6b). A similar transition is observed in magnetocalorics, in which ordering is driven by an external magnetic field rather than hydrostatic pressure. Frustrated magnets such as Gd₃Ga₅O₁₂ and Tb(HCOO)₃ tend to form particularly good magnetocalorics^{160–162}. Their shallow configurational landscape imparts a heightened susceptibility to external field that in turn reduces the critical field B_c at which ordering occurs. The same strategy of exploiting geometric frustration might in principle allow optimisation of barocaloric response in analogues of [TPrA][Mn(dca)₃].

Orientational disorder of the MA⁺ cations is thought to play an important role in preventing exciton recombination in the photovoltaic MAPbI₃^{163,164}. MA⁺ reorientations provide a strongly varying dipolar field at the perovskite A-site, which in turn helps screen the Coulombic electron–hole interaction. At the same time, molecular degrees of freedom couple to large-scale distortions of the surrounding [PbI₃][−] lattice that help localise electronic states. The distortions are amplified by the susceptibility of the Pb²⁺ cation to SOJT effects, which may couple in a manner related to that discussed above for ferroelectric BaTiO₃/KNbO₃¹⁶⁵. Hence, the lead halide perovskites has a large number of entangled degrees of freedom such that the timescales associated with various ordinarily-separate processes are now linked: electron localisation, dipolar field fluctuations, cation off-centering, lattice distortions and MA⁺ molecular reorientations. In terms of design rules, the role of shape is to break A-site symmetry over timescales longer than that of uninhibited exciton recombination, and the role of disorder to avoid collective structural and electronic relaxation.

Polarisability is a kind of incipient shape. CsPbI₃ is an effective analogue of MAPbI₃ because the spherical electron density of the large and polarisable Cs⁺ ion is easily perturbed by surrounding fields¹⁶⁶. So the low-energy distortions of the anionic PbI₃[−] framework can easily couple to charge redistribution at the Cs⁺ site in the same way they might couple to MA⁺ reorientations in MAPbI₃.

Low energy dynamics and incipient disorder

In dynamically disordered systems, the configurational landscape of related states is sufficiently shallow as to be navigated thermally. Hence, the same design strategies that drive correlated (static) disorder can also give dynamically disordered systems with unusual thermal properties — so long as the barrier height for interconverting between equivalent states is reduced below the available thermal energy.

A good example is that of the rock-salt thermoelectrics such as PbTe^{167,168}. The susceptibility of the Pb²⁺ $6s^2 6p^0$ configuration to a SOJT distortion favours local symmetry lowering that couples through the same anisotropic interactions operating in BaTiO₃. Here, the distortion involves off-centering of Pb²⁺ in order to form a set of stronger Pb–chalcogenide interactions at the expense of others. The barrier height for interconverting between equivalent off-centering directions is determined by the relative energies of the Pb and chalcogenide orbitals^{169–171}. In the case of PbO, for example, the distortion is static. But in PbTe, the off-centering displacements are dynamic and result in a particularly soft optic branch in the phonon dispersion (Fig. 6c,d)¹⁶⁷. Indeed the branch is so soft it mixes with — and hence flattens — the acoustic branches and the corresponding phonon–phonon coupling amplifies anharmonic scattering, in turn slowing thermal transport¹⁶⁷. Because the Pb–Te interactions responsible for

off-centering are correlated strongly only along the $\langle 100 \rangle$ directions, there is weak localisation in reciprocal space and the contribution to thermal scattering is proportionately large^{167,172}. PbTe is one of the few known materials in which the optic phonons are sufficiently low in energy and involve sufficiently extreme displacements that their contribution can be seen directly in the experimental pair distribution function¹⁷³. This has led to some confusion in interpretation^{174–176}, which now appears mostly to have been resolved^{172,173}. In more general terms, Ref. 177 discusses the key distortions responsible for low thermal conductivity in the language of resonant bonding, which reflects the importance of configurational degeneracy for driving phonon softening and maximising anharmonicity in many thermoelectrics.

An entirely analogous mechanism drives the anomalously large dielectric response of many bismuth pyrochlores (such as $\text{Bi}_2\text{Ti}_2\text{O}_7$), for which dynamic off-centering of Bi^{3+} ($5s^25p^0$) is key^{70,178}. In zeolites, there are so many different mechanisms by which correlated rotations and translations of Si– AlO_4 tetrahedra can occur and the barriers between different displacement patterns so low that dispersionless bands of rigid-unit mode [G] (RUM) excitations are dragged into the low-energy phonon spectrum¹⁷⁹. An important implication of the density of these RUMs in k -space is the ability of zeolites to support localised distortions with very low energy penalties¹⁸⁰. This kind of local flexibility mimics the conformational flexibility of enzyme active sites and is thought to favour catalytic efficiency and ion transport in zeolites¹⁸¹.

An interesting balance between static and dynamic correlated disorder occurs in the cubic negative thermal expansion (NTE) material ZrW_2O_8 ¹⁸². The dominant incipient structural distortion in this system involves concerted translations and rotations of WO_4 tetrahedra that act to connect neighbouring tetrahedra into one-dimensional chains ('spaghetti'), at once both increasing the W coordination number from four to five and reducing the system volume^{51,183}. The crystal symmetry is such that there is no unique way of forming these chains, and a simple Pauling-type calculation suggests a configurational entropy of about $R \ln(9/8)$ if the spaghetti-forming distortions were static⁵¹. Because this configurational entropy is extensive, the corresponding dynamic fluctuations must be dense in k -space, which is why there are so many volume-reducing phonon modes and hence why ZrW_2O_8 shows NTE. Under applied pressure or (somewhat bizarrely) on hydration, the same set of distortions are activated in a static sense (that is, the interconversion barrier height raised). This results in pressure-induced amorphisation (PIA) in the former case and negative hydration expansion (NHE) in the latter. Hence, a single common landscape of correlated disordered states is responsible for each of the unusual phenomena of NTE¹⁸², NHE¹⁸⁴ and PIA¹⁸⁵ in this one material.

FUTURE DIRECTIONS

Where might the field be heading, in more general terms? In this final section we identify a handful of directions for future study and articulate the central challenges faced in controlling, characterising, and exploiting disordered crystals.

Adaptive materials from disordered states

A common theme amongst the many applications of disordered crystals is the importance of configurational degeneracy and the heightened susceptibility of disordered states to perturbation by external stimuli¹². In these respects there is a strong conceptual parallel to the axioms of dynamic combinatorial chemistry¹⁸⁶. A combinatorial system is highly degenerate because one library samples a large collection of discrete molecular entities. It is susceptible because host–guest interactions readily perturb the system to bias the configurational landscape towards a smaller subset of now-favoured states. Dynamic combinatorial chemistry exploits the configurational flexibility of a suitable library to identify optimised receptors for a given guest. Might not we apply similar concepts in the context of disordered crystals? The ability for suitably-designed disordered crystals to navigate reversibly their relevant configurational space (for example, through molecular reorientations, spin flips and hydrogen-bond inversion. . .) would reflect a combinatorial flexibility distinct from the conventional mechanical flexibility of, for example, wine-rack frameworks¹⁸⁷. By this mechanism, a single disordered crystal might adapt in different ways to optimise its interactions with a variety of different adsorbates¹⁸⁸, for example, or to accommodate the deformations induced by a variety of different strains¹⁸⁷, or even to self-heal as spontaneous reorganisation annihilates defects¹⁸⁹.

Correlated disorder engineering

The implications of the unusual gauge field symmetries of many disordered crystals also warrant further investigation. It is clear already that these symmetries can be exploited in the design of hybrid improper ferroelectrics, for example, to avoid reliance on lone-pair-active cations such as Pb^{2+} ⁶⁷. Alternatively, the coexistence of short-range and long-range correlations (as exemplified by the 'pinch-point' magnetic scattering features of spin-ices¹⁹⁰) may allow tuning of the electronic and vibrational structure of disordered crystals⁵³. To some extent, these relationships are already being used empirically to link, for example, displacive and/or compositional disorder to phonon anomalies in thermoelectrics and ferroelectrics^{167,191}, or to the spin-liquid behaviour of frustrated magnets⁹⁵. Yet, there is much still to be understood regarding these disorder–property relationships in

more general terms. A common theme is the intermediacy of collective behaviour — states that are neither entirely localised nor extensive. In the domain of photonic materials, such states result in a variety of fascinating optical properties^{192,193}, and the long-term goal in this respect has to be exploitation of gauge field symmetries to engineer materials with equally anomalous electronic or phononic properties. Moreover, the gauge field excitations are themselves important. Although these have been studied extensively in the context of the spin-ice monopoles¹⁹⁴, the analogous topological defects, their interactions and their emergent dynamics in non-magnetic disordered crystals remain largely unexplored.

Disorder as a synthesis strategy

The variation in bond strengths within compositionally disordered materials can be exploited to render specific parts of a crystal structure more susceptible to subsequent reaction than others. For example, in some layered MOFs, linker vacancies accumulate between — rather than within — layers, allowing selective delamination and the targeted synthesis of 2D systems¹⁹⁵. The assembly–disassembly–organization–reassembly (‘ADOR’) process for generating unconventional zeolite topologies is conceptually related because it exploits the difference in germanate and silicate hydrolysis susceptibilities to allow selective bond-breaking^{196,197}. An obvious direction for development is to apply this strategy to complex compositionally-disordered states so as to synthesise isotropic open structures through entangled delamination. For example, selective bond-breaking within spaghetti phases (Fig. 3d) may generate a new class of high-surface-area crystalline ‘gels’, connected chemically only within individual spaghetti strands, yet mechanically stable because of the topologically entanglement of neighbouring strands.

Unconventional data storage

It was Schrödinger who suggested that aperiodic crystals might be used to store information¹⁹⁸, and — in this spirit — Mackay highlighted that DNA can be considered a disordered 1D crystal with each unit (base) in one of four possible states³. Most conventional approaches to data storage follow variants on this same idea: each of N bits is arranged in a periodic array and encodes information by adopting one of n degenerate states, giving a total of n^N possible configurations. The information stored in each bit is independent of that in the others such that, if any one state is erased, the information is lost. For disordered systems with extensive configurational entropies, the configurational landscape also grows as n^N , but n is now usually non-integral. This reflects a classical entanglement of local degrees of freedom across arbitrarily large distances within the crystal (related to the intermediacy of collective states discussed above). A remarkable consequence is that the information contained within a single bit is now recoverable on erasure because of this inbuilt degeneracy (Fig. 7). Hence, disordered crystals may provide a unique opportunity for high-density data storage and manipulation with intrinsic error-correcting capabilities.

Central challenges

Whatever direction the field takes, we anticipate that four central challenges will play a crucially important role in developing new families of functional disordered crystals. The first is the task of establishing the underlying theory: what states are possible? How they depend on degrees of freedom, interactions and lattice geometries? What are their entropies, symmetries and excitations? Much is already known in this respect, but even ostensibly well-understood systems continue to surprise.

The second challenge is the more chemical: how do we, as materials chemists, controllably introduce or manipulate a specific type of disorder within a crystalline material? Indeed the focus of this Review has been on key strategies for achieving precisely this type of control, but of course our limited exposition is by no means the whole story.

Third, there is the difficult experimental challenge of characterising the disorder within any such crystal^{11,54,199}. The historical emphasis has been on entropy and spectroscopic measurements. More recently this emphasis has shifted to the application of scattering techniques, including pair distribution function and single-crystal diffuse scattering studies. In all cases, the difficulty lies not only in measurement but in interpretation.

Finally, there is the challenge of establishing a robust link between physical properties and the type of disorder. Sometimes this link will be obvious (plastic crystals are soft, for example), but we expect such cases are in the minority. Instead, solving this problem will more frequently rely on the application of computational methods, which for disordered systems presents its own particular challenge.

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TOC SUMMARY

Correlated disorder drives a variety of important and useful physical properties in crystalline materials. This Review explores the link between disorder and function, and surveys the core design principles that allow targeted control over correlated disorder in crystals.

GRAPHICAL ABSTRACT

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FIG. 1. Canonical disordered crystals. (a) In a paramagnet, the positions of magnetic ions (red spheres) are periodic, but the arrangements of the corresponding spins (blue vectors) are not²⁰⁰. (b) Plastic crystals are similar, with the disorder now involving molecular orientations¹³⁷. (c) Disordered alloys contain a superposition of positional order and compositional disorder⁴. (d) The photovoltaic lead–halide perovskites support a variety of disorder types, including orientational disorder of methylammonium cations (in the central site) and distortions of the anionic lead–halide framework (connected polyhedra)¹⁶⁶. (e) In ferroelectric BaTiO₃, polarisation emerges from correlated disorder of Ti⁴⁺ off-centering along local $\langle 111 \rangle$ axes (coloured arrows)⁸. (f) And the emergence of ferrimagnetism in Fe₃O₄ couples to local Fe²⁺–Fe³⁺ charge order in a dynamically-disordered ‘trimeron liquid’ phase⁹.

FIG. 2. Common local degrees of freedom, interactions, and lattice types. (a) Degrees of freedom may be discrete, such as the binary Ising (left) and n -state Potts (top right) models. Examples of the former include, from top to bottom, up/down spin orientation, composition, spin-state, charge-state, cyanide-ion orientation, hydrogen-bond direction, linker orientation, or supramolecular polarisation direction^{2,15,127,201–203}. Examples of the latter include orbital orientations and A-site cation orientations in molecular perovskites^{18,19}. Commonly-encountered continuous degrees of freedom include XY states (middle) and Heisenberg (bottom left) or quadrupolar spins (bottom right). The examples of XY states shown here are planar spin orientation (left), molecular orientation in rotator phases (middle), and deformation phase angle selected during symmetry lowering (right). Heisenberg and quadrupolar degrees of freedom are shown as directional or axial orientations of freely-rotating molecules⁴. (b) Representations of some key interactions of relevance to disordered states^{4,67,151,201}. (c) High-symmetry lattices in one, two and three dimensions. All these lattices are both uninodal and edge-transitive. In other words, each site in a given lattice is related to all other sites by crystal symmetry; so too for the lattice edges (interaction pathways)^{204,205}.

FIG. 3. Models of disorder and competing interactions. (a) The ground state of the triangular Ising antiferromagnet: note no triangle has at its vertices three Ising states of the same type⁴⁴. (b) Competing nearest-neighbour (J_1) and next-nearest neighbour (J_2) interactions in the 1D axial next-nearest neighbour Ising (ANNNI) model give a series of complex phases (shaded region of phase diagram, right) of relevance to stacking sequences in layered materials^{48,206}. In this representation the Ising state (white or black circle) maps to the slip direction of neighbouring layers (diagonal lines in stacking diagram, middle)⁴⁸. (c) Ice-like states map to the ground states of the pyrochlore Ising antiferromagnet. Here, the vertices of each tetrahedron partition into two Ising states of one type, and two of the other: (left–right) hydrogen-bond direction², spin orientation⁴⁹, composition⁹², and orbital phase⁷⁷. (d) Spaghetti phases are characterised by dense Ising lattice decorations in which like Ising states form connected one-dimensional paths, meaning that each site is associated with two of its neighbours^{50,51}. (e) Dimer states occur when each site is associated with a single neighbour^{53,201,207}. (f) Transitions to correlated disordered states are usually characterised by a broad maximum in the the function C/T , where C is the specific heat and T the temperature (red line). The corresponding entropy change S is characteristic of a given disordered state. For example, that of the spin-ice $\text{Dy}_2\text{Ti}_2\text{O}_7$ ²⁰⁸ (black line) does not approach the Ising limit $R \ln 2$ (upper dashed line) expected if its ground state were fully ordered. Instead, its limit (lower dashed line) is reduced by the Pauling configurational degeneracy of the spin-ice ground state. (g) 2D continuous models are susceptible to the formation of topological defects, such as vortex–antivortex pairs⁴³.

FIG. 4. Correlated disorder from electronic instabilities and compositional complexity. (a) The E_g distortion space of an octahedrally-coordinated transition-metal ion is spanned by the Q_2 and Q_3 distortions. The Q_2 distortion occurs in Jahn–Teller active LaMnO_3 (Mn^{3+} , d^4), giving one pair of long Mn–O bonds, one short pair and one intermediate pair. There are six equivalent distortions (red lines)⁶¹. (b) The orbital order–disorder transition in LaMnO_3 involves a progression from alternating $Q_{2,xy}$ distortions at $T < T_{JT}$ to a correlated disordered population of all six Q_2 states at $T > T_{JT}$ ²⁰⁹. (c) Correlated off-centering of Ti^{4+} ions in BaTiO_3 driven by second-order Jahn–Teller effects. The distortions strengthen some Ti–O bonds at the expense of others. That each O atom is bound strongly by just one Ti drives Kitaev-like interactions (Eq. (1)) responsible for complex disorder in BaTiO_3 ^{7,8}. (d) Peierls-type distortions in the hypothetical pyrochlore $\text{Y}_2\text{Nb}_2\text{O}_7$ would result in the formation of dimers covering the pyrochlore lattice.⁷⁴ (e) The zig–zag path of M–N–M linkages (black lines) in oxynitride perovskites SrMO_2N gives a disordered covering of the underlying perovskite lattice. The nodes of this lattice (red circle) are occupied by MO_4N_2 coordination octahedra of varying orientation^{85,87}. (f) Local anion order in $\text{EuWO}_{1.5}\text{N}_{1.5}$ couples W-atom displacements through the same interaction described by Eq. (1) and observed in the case of BaTiO_3 as (c) but with the sign of the interaction parameter J inverted^{8,67,89}. (g) One possible arrangement of Ni and Cr atoms in CsNiCrF_6 ⁹³, chosen to emphasise the mapping to the dimer state in (d). Note, each dimer in the latter is replaced by a pair of cations of the same type in the former.

FIG. 5. Correlated disorder by self-assembly. (a) *p*-terphenyl-3,5,3',5'-tetracarboxylic acid (TPTC) molecules assemble in 2D through formation of hydrogen-bonded carboxylate dimers to give a disordered network describable in terms of a dimer decoration of the hexagonal lattice¹¹⁸. (b) Directional hydrogen-bonding interactions (green arrow) give a bulk polarisation to columns of 1,3,5-benzenetrisamides (BTA) molecules. Dense assemblies of these columns involve triangular packing, with adjacent stacks tending to adopt inverse polarisations (black and white, here). The corresponding state relates to the triangular Ising antiferromagnet^{126,127}. (c) Self-assembly of the columnar cyanides $\text{Au}_{1-x}\text{Ag}_x\text{CN}$ is driven by inter-chain interactions, which vary periodically with relative chain displacement Δz , and hence effective phase $\theta = 2\pi z$. These interactions take the form $E = J_1 \cos(\Delta\theta) + J_2 \cos^2(\Delta\theta)$, which relates the phase behaviour of the family of columnar cyanides to that of the triangular bilinear–biquadratic XY magnets. Phases stabilised for different J_1, J_2 include chiral disordered states (green shaded region) and a nematic phase (orange region) relevant to $\text{AuAg}(\text{CN})_2$. Topological charges (vortices–antivortices) in these magnets are mapped onto screw dislocations in the cyanides²⁴. Part b is adapted with permission from ref.¹²⁶. Part c is adapted with permission from ref.²⁴.

FIG. 6. Molecular shape and low-energy dynamics. (a) The orientation of the planar imidazolium cation, H_2Im^+ , is characterised by first order by a quadrupole (red arrows, left). Order–disorder transitions in imidazolium cyanoelpasolites (for example, $(\text{H}_2\text{Im})_2\text{Rb}[\text{Co}(\text{CN})_6]$) are well characterised by the four-state Potts model, with each Potts state corresponding to a single imidazolium orientation¹⁵¹. (b) The hybrid perovskite $[\text{TPrA}][\text{Mn}(\text{dca})_3]$ exhibits a conformational order–disorder transition on cooling below 331 K. The ordered state (left) can be stabilised by applying pressure, which provides a mechanism for barocaloric cooling¹⁵⁹. (c) A representation of the valence charge distribution in PbTe upon activation of the low-energy optic phonons; note the emergence of a lone-pair on the Pb^{2+} cation¹⁷³. (d) The incipient second-order Jahn–Teller (SOJT) distortion in PbTe results in an anomalously low energy of the zone-centre optic branch (red circle) and softening of the transverse acoustic (TA) branch of the phonon dispersion. Both features are implicated in the favourable thermoelectric behaviour of PbTe ¹⁷³. Part b is adapted with permissions from ref.¹⁷³.

FIG. 7. Data storage in disordered states.(a) Information stored in a conventional array of bits (here 1–6) is irrecoverable if a single bit is erased (black square). (b) Mapping tiles to bit states. Each tile has two black edges and two white edges (see the square-ice model of Ref. 210). That this model has an extensive entropy ensures that the number of tilings satisfying matching rules grows with system size, in turn allowing information storage. (c) The information encoded within each bit is no longer independent of its neighbours, such that the loss of one tile does not imply information loss. Here, the missing tile must correspond to state ‘5’.

REFERENCES

- ¹ Warren, B. E. The diffraction of X-rays in glass. *Phys. Rev.* **45**, 657–661 (1934).
- ² 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).
- ³ Cartwright, J. H. E. & Mackay, A. L. Beyond crystals: the dialectic of materials and information. *Phil. Trans. R. Soc. Lond. A* **370**, 2807–2822 (2012).
- ⁴ Parsonage, N. G. & Staveley, L. A. K. *Disorder in Crystals* (Clarendon Press, Oxford, 1978).
- ⁵ Ziman, J. M. *Models of disorder. The theoretical physics of homogeneously disordered systems* (Cambridge University Press, Cambridge, 1979).
- ⁶ Weller, M. T., Weber, O. J., Henry, P. F., Di Pumpo, A. M. & Hansen, T. C. Complete structure and cation orientation in the perovskite photovoltaic methylammonium lead iodide between 100 and 352 K. *Chem. Comm.* **51**, 418–4183 (2015).
- ⁷ 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).
- ⁸ Senn, M. S., Keen, D. A., Lucas, T. C. A., Hriljac, J. A. & Goodwin, A. L. Emergence of long-range order in BaTiO₃ from local symmetry-breaking distortions. *Phys. Rev. Lett.* **116**, 207602 (2016).
- ⁹ Perversi, G. *et al.* Co-emergence of magnetic order and structural fluctuations in magnetite. *Nature Commun.* **10**, 2857 (2019).
- ¹⁰ Onsager, L. Crystal statistics. I. A two-dimensional model with an order-disorder transition. *Phys. Rev.* **65**, 117–149 (1944).
- ¹¹ Welberry, T. R. Diffuse x-ray scattering and models of disorder. *Rep. Prog. Phys.* **48**, 1543–1593 (1985).
- ¹² Moessner, R. & Ramirez, A. P. Geometrical frustration. *Physics Today* **59**, 24–29 (2006).
- ¹³ Froufe-Pérez, L. S. *et al.* Role of short-range order and hyperuniformity in the formation of band gaps in disordered photonic materials. *Phys. Rev. Lett.* **117**, 053902 (2016).
- ¹⁴ Damasceno, P. F., Engel, M. & Glotzer, S. C. Predictive self-assembly of polyhedra into complex structures. *Science* **337**, 453–457 (2012).
- ¹⁵ Ising, E. Beitrag zur Theorie des Ferromagnetismus. *Z. Physik* **31**, 253–258 (1925).
- ¹⁶ Brush, S. G. History of the Lenz-Ising model. *Rev. Mod. Phys.* **39**, 883–893 (1967).
- ¹⁷ Potts, R. B. Some generalized order-disorder transformations. *Math. Proc. Camb. Phil. Soc.* **48**, 106–109 (1952).
- ¹⁸ Šimenas, M., Balčiūnas, S., Maczka, M., Banyš, J. & Tornau, E. E. Structural phase transition in perovskite metal–formate frameworks: a Potts-type model with dipolar interactions. *Phys. Chem. Chem. Phys.* **18**, 18528–18535 (2016).
- ¹⁹ Ahmed, M. R. & Gehring, G. A. Potts model for the distortion transition in LaMnO₆. *Phys. Rev. B* **74**, 014420 (2006).
- ²⁰ Vaks, V. G. & Larkin, A. I. On phase transitions of second order. *Sov. Phys. JETP* **22**, 678–687 (1966).
- ²¹ Sirota, E. B. The rotator phases of neat and hydrated 1-alcohols. *J. Chem. Phys.* **105**, 7763–7773 (1996).
- ²² Meier, Q. N. *et al.* Global formation of topological defects in the multiferroic hexagonal manganites. *Phys. Rev. X* **7**, 041014 (2017).
- ²³ Abrikosov, A. A. The magnetic properties of superconducting alloys. *J. Phys. Chem. Solids* **2**, 199–208 (1957).
- ²⁴ Cairns, A. B. *et al.* Encoding complexity within supramolecular analogues of frustrated magnets. *Nature Chem.* **8**, 442–447 (2016).
- ²⁵ Joyce, G. S. Classical Heisenberg model. *Phys. Rev.* **155**, 478–491 (1967).
- ²⁶ Leguy, A. M. A. *et al.* The dynamics of methylammonium ions in hybrid organic–inorganic perovskite solar cells. *Nature Commun.* **6**, 7124 (2015).
- ²⁷ Zhong, W., Vanderbilt, D. & Rabe, K. M. First-principles theory of ferroelectric phase transitions for perovskites: The case of BaTiO₃. *Phys. Rev. B* **52**, 6301–6312 (1995).
- ²⁸ James, H. M. & Keenan, T. A. Theory of phase transitions in solid heavy methane. *J. Chem. Phys.* **31**, 12–41 (1959).
- ²⁹ Frenkel, D. *Statistical mechanics of liquid crystals*, chap. 9, 689–762. Les Houches, Session LI, 1989, Liquids, Crystallisation et Transition Vitreuse (Elsevier Science Publishers B. V., 1997).
- ³⁰ Karney, C. F. F. Quaternions in molecular modeling. *J. Mol. Graph. Model.* **25**, 595–604 (2007).
- ³¹ Pato-Doldán, B. *et al.* Magnetic transitions and isotropic versus anisotropic magnetic behaviour of [CH₃NH₃][M(HCOO)₃] M = Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺ metal–organic perovskites. *J. Mater. Chem. C* **4**, 11164–11172 (2016).
- ³² Evans, N. L. *et al.* Control of multipolar and orbital order in perovskite-like [C(NH₂)₃]Cu_xCd_{1–x}(HCOO)₃ metal–organic frameworks. *J. Am. Chem. Soc.* **138**, 9393–9396 (2016).
- ³³ den Hertog, B. C. & Gingras, M. J. P. Dipolar interactions and origin of spin ice in Ising pyrochlore magnets. *Phys. Rev. Lett.* **84**, 3430–3433 (2000).
- ³⁴ Läuchli, A., Mila, F. & Penc, K. Quadrupolar phases of the $S = 1$ bilinear-biquadratic Heisenberg model on the triangular lattice. *Phys. Rev. Lett.* **97**, 087205 (2006).
- ³⁵ Lipscomb, W. N. Comment on crystal structures of α -CO and α -N₂. *J. Chem. Phys.* **60**, 5138 (1974).
- ³⁶ Dzyaloshinsky, I. A thermodynamic theory of “weak” ferromagnetism of antiferromagnets. *J. Phys. Chem. Solids* **4**, 241–255 (1958).
- ³⁷ Moriya, T. Anisotropic superexchange interaction and weak ferromagnetism. *Phys. Rev.* **120** (1960).
- ³⁸ Sauvage, M. & Parthé, E. Vacancy short-range order in substoichiometric transition metal carbides and nitrides with the NaCl structure. II. Numerical calculation of vacancy arrangement. *Acta Cryst.* **28**, 607–616 (1972).
- ³⁹ Urones-Garrote, E., Gómez-Herrero, A., Landa-Cánovas, Á. R., Withers, R. L. & Otero-Díaz, L. C. Order and disorder in rocksalt and spinel structures in the MgS–Yb₂S₃ system. *Chem. Mater.* **17**, 3524–3531 (2005).
- ⁴⁰ Nussinov, Z. & van den Brink, J. Compass models: Theory and physical motivations. *Rev. Mod. Phys.* **87**, 1–59 (2015).

- ⁴¹ Kitaev, A. Anyons in an exactly solved model and beyond. *Ann. Phys.* **321**, 2–111 (2006).
- ⁴² Lieb, E. & Mattis, D. C. *Mathematical Physics in One Dimension* (Academic Press, New York, 1966).
- ⁴³ Kosterlitz, J. M. & Thouless, D. J. Ordering, metastability and phase transitions in two-dimensional systems. *J. Phys. C: Solid State Phys.* **6**, 1181–1203 (1973).
- ⁴⁴ Wannier, G. H. Antiferromagnetism. The triangular Ising net. *Phys. Rev.* **79**, 357–364 (1950).
- ⁴⁵ Balents, L. Spin liquids in frustrated magnets. *Nature* **464**, 199–208 (2010).
- ⁴⁶ Bak, P. Commensurate phases, incommensurate phases and the devil’s staircase. *Rep. Prog. Phys.* **45**, 587–629 (1982).
- ⁴⁷ Yeomans, J. The theory and application of axial Ising models. *Solid State Phys.* **41**, 151–200 (1988).
- ⁴⁸ Cheng, C., Needs, R. J. & Heine, V. Inter-layer interactions and the ordering of SiC polytypes. *J. Phys. C: Solid State Phys.* **21**, 1049–1063 (1988).
- ⁴⁹ Bramwell, S. T. & Harris, M. J. Frustration in Ising-type spin models on the pyrochlore lattice. *J. Phys.: Cond. Matt.* **10**, L215–L220 (1998).
- ⁵⁰ Jaubert, L. D. C., Haque, M. & Moessner, R. Analysis of a fully packed loop model arising in a magnetic Coulomb phase. *Phys. Rev. Lett.* **107**, 177202 (2011).
- ⁵¹ Baise, M. *et al.* Negative hydration expansion in ZrW_2O_8 : Microscopic mechanism, spaghetti dynamics, and negative thermal expansion. *Phys. Rev. Lett.* **120**, 265501 (2018).
- ⁵² Anderson, P. W. Resonating valence bonds: a new kind of insulator? *Mater. Res. Bull.* **8**, 153–160 (1973).
- ⁵³ Overy, A. R. *et al.* Design of crystal-like aperiodic solids with selective disorder–phonon couplings. *Nature Commun.* **7**, 10445 (2016).
- ⁵⁴ Keen, D. A. & Goodwin, A. L. The crystallography of correlated disorder. *Nature* **521**, 303–309 (2015).
- ⁵⁵ Mydosh, J. A. & Oppeneer, P. M. Hidden order, superconductivity, and magnetism: The unsolved case of URu_2Si_2 . *Rev. Mod. Phys.* **83**, 1301–1322 (2011).
- ⁵⁶ Henley, C. L. The “Coulomb phase” in frustrated systems. *Annu. Rev. Condens. Matter Phys.* **1**, 179–210 (2010).
- ⁵⁷ Castelnovo, C., Moessner, R. & Sondhi, S. L. Spin ice, fractionalization, and topological order. *Annu. Rev. Condens. Matter Phys.* **3**, 35–55 (2012).
- ⁵⁸ Mühlbauer, S. *et al.* Skyrmion lattice in a chiral magnet. *Science* **323**, 915–919 (2009).
- ⁵⁹ Oakes, T., Garrahan, J. P. & Powell, S. Emergence of cooperative dynamics in fully packed classical dimers. *Phys. Rev. E* **93**, 032129 (2106).
- ⁶⁰ Pearson, R. G. Concerning Jahn–Teller effects. *Proc. Natl. Acad. Sci., U.S.A.* **72**, 2104–2106 (1975).
- ⁶¹ Goodenough, J. B. Jahn–Teller phenomena in solids. *Annu. Rev. Mater. Sci.* **28**, 1–27 (1998).
- ⁶² Goodenough, J. B. Theory of the role of covalence in the perovskite-type manganites $[\text{La}, M(\text{II})]\text{MnO}_3$. *Phys. Rev.* **100**, 564–573 (1955).
- ⁶³ Qiu, X., Proffen, T., Mitchell, J. F. & Billinge, S. J. L. Orbital correlations in the pseudocubic O and rhombohedral R phases of LaMnO_3 . *Phys. Rev. Lett.* **94**, 177203 (2005).
- ⁶⁴ Sartbaeva, A., Wells, S. A., Thorpe, M. F., Božin, E. S. & Billinge, S. J. L. Quadrupolar ordering in LaMnO_3 revealed from scattering data and geometric modelling. *Phys. Rev. Lett.* **99**, 155503 (2007).
- ⁶⁵ Pissas, M., Margiolaki, I., Papavassiliou, G., Stamopoulos, D. & Argyriou, D. N. Crystal and magnetic structure of the $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ compound ($0.11 \leq x \leq 0.175$). *Phys. Rev. B* **72**, 064425 (2005).
- ⁶⁶ Rao, C. N. R. & Cheetham, A. K. Giant magnetoresistance in transition metal oxides. *Science* **272**, 369–370 (1996).
- ⁶⁷ Wolpert, E. H. *et al.* Hybrid local-order mechanism for inversion symmetry breaking. *Phys. Rev. B* **97**, 134106 (2018).
- ⁶⁸ Melot, B. C. *et al.* Large low-temperature specific heat in pyrochlore $\text{Bi}_2\text{Ti}_2\text{O}_7$. *Phys. Rev. B* **79**, 224111 (2009).
- ⁶⁹ Du, H., Yao, X. & Wang, H. Relaxor-like behavior of bismuth-based pyrochlores containing sn. *J. Electroceramics* **21**, 222–225 (2007).
- ⁷⁰ Liu, Y. *et al.* Displacive disorder and dielectric relaxation in the stoichiometric bismuth-containing pyrochlores $\text{Bi}_2M^{\text{III}}\text{NbO}_7$ ($M=\text{In}$ and Sc). *J. Solid State Chem.* **182**, 2748–2755 (2009).
- ⁷¹ Morin, F. J. Oxides which show a metal-to-insulator transition at the Neel temperature. *Phys. Rev. Lett.* **3**, 34–36 (1959).
- ⁷² Corr, S. A., Shoemaker, D. P., Melot, B. C. & Seshadri, R. Real-space investigation of the structural changes at the metal-insulator transition in VO_2 . *Phys. Rev. Lett.* **105**, 056404 (2010).
- ⁷³ Attfield, J. P. Orbital molecules in electronic materials. *APL Mater.* **3**, 041510 (2015).
- ⁷⁴ Blaha, P., Singh, D. J. & Schwarz, K. Geometric frustration, electronic instabilities, and charge singlets in $\text{Y}_2\text{Nb}_2\text{O}_7$. *Phys. Rev. Lett.* **93**, 216403 (2004).
- ⁷⁵ McQueen, T. M. *et al.* Frustrated ferroelectricity in niobate pyrochlores. *J. Phys.: Condens. Matter* **20**, 235210 (2008).
- ⁷⁶ Shinaoka, H., Motome, Y., Miyake, T. & Ishibashi, S. Spin-orbital frustration in molybdenum pyrochlores $A_2\text{Mo}_2\text{O}_7$ (A = rare earth). *Phys. Rev. B* **88**, 174422 (2013).
- ⁷⁷ Thygesen, P. M. M. *et al.* Orbital dimer model for the spin-glass state in $\text{Y}_2\text{Mo}_2\text{O}_7$. *Phys. Rev. Lett.* **118** (2017).
- ⁷⁸ Senn, M. S., Wright, J. P. & Attfield, J. P. Charge order and three-site distortions in the Verwey structure of magnetite. *Nature* **481**, 173–176 (2012).
- ⁷⁹ Browne, A. J., Kimber, S. A. J. & Attfield, J. P. Persistent three- and four-atom orbital molecules in the spinel AlV_2O_4 . *Phys. Rev. Mater.* **1**, 052003(R) (2017).
- ⁸⁰ Božin, E. S. *et al.* Local orbital degeneracy lifting as a precursor to an orbital-selective Peierls transition. *Nature Commun.* **10**, 3638 (2019).
- ⁸¹ Folkers, L. C., Simonov, A., Wang, F. & Lidin, S. The mystery of the AuIn 1: 1 phase and its incommensurate structural variations. *Inorg. Chem.* **57**, 2791–2796 (2018).
- ⁸² Vegard, L. Die konstitution der mischkristalle und die raumfüllung der atome. *Z. Physik* **5**, 17–26 (1921).
- ⁸³ Pauling, L. The sizes of ions and the structure of ionic crystals. *J. Am. Chem. Soc.* **49**, 765–790 (1927).
- ⁸⁴ Castellanos, M. & West, A. R. Deviations from vegard’s law in oxide solid solutions. *J. Chem. Soc., Faraday Trans. 1* **76**, 2159–2169. (1980).

- ⁸⁵ Page, K. *et al.* Local atomic ordering in BaTaO₂N studied by neutron pair distribution function analysis and density functional theory. *Chem. Mater.* **19**, 4037–4042 (2007).
- ⁸⁶ Yang, M. *et al.* Anion order in perovskite oxynitrides. *Nat. Chem.* **3**, 47–52 (2011).
- ⁸⁷ 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).
- ⁸⁸ Johnston, H. *et al.* Dimensional crossover of correlated anion disorder in oxynitride perovskites. *Chem. Commun.* **54**, 5245–5247 (2018).
- ⁸⁹ Yang, M., Oró-Solé, J., Kusmartseva, A., Fuentès, A. & Attfield, J. P. Electronic tuning of two metals and colossal magnetoresistances in EuWO_{1+x}N_{2-x} perovskites. *J. Am. Chem. Soc.* **132**, 4822–4829 (2010).
- ⁹⁰ Goto, Y. *et al.* Pressure-stabilized cubic perovskite oxyhydride BaScO₂H. *Inorg. Chem.* **56**, 4840–4845 (2017).
- ⁹¹ Kageyama, H. *et al.* Expanding frontiers in materials chemistry and physics with multiple anions. *Nature Commun.* **9**, 772 (2018).
- ⁹² Whitaker, M. J. & Greaves, C. Magnetic ordering in the pyrochlore Ho₂CrSbO₇ determined from neutron diffraction, and the magnetic properties of other RE₂CrSbO₇ phases (RE = Y, Tb, Dy, Er). *J. Solid State Chem.* **215**, 171–175 (2014).
- ⁹³ Fennell, T. *et al.* Multiple Coulomb phase in the fluoride pyrochlore CsNiCrF₆. *Nature Phys.* **15**, 60–66 (2019).
- ⁹⁴ Kim, S. W. *et al.* RbFe²⁺Fe³⁺F₆: Synthesis, structure, and characterization of a new charge-ordered magnetically frustrated pyrochlore-related mixed-metal fluoride. *Chem. Sci.* **3**, 741–751 (2012).
- ⁹⁵ Zhang, X. *et al.* Hierarchy of exchange interactions in the triangular-lattice spin liquid YbMgGaO₄. *Phys. Rev. X* **8**, 031001 (2018).
- ⁹⁶ Wen, J.-J. *et al.* Disordered route to the Coulomb quantum spin liquid: Random transverse fields on spin ice in Pr₂Zr₂O₇. *Phys. Rev. Lett.* **118**, 107206 (2017).
- ⁹⁷ Menéndez, E. *et al.* Direct magnetic patterning due to the generation of ferromagnetism by selective ion irradiation of paramagnetic FeAl alloys. *Small* **5**, 229–234 (2009).
- ⁹⁸ Lee, J. *et al.* Unlocking the potential of cation-disordered oxides for rechargeable lithium batteries. *Science* **343**, 519–522 (2014).
- ⁹⁹ Ji, H. *et al.* Hidden structural and chemical order controls lithium transport in cation-disordered oxides for rechargeable batteries. *Nature Commun.* **10**, 592 (2019).
- ¹⁰⁰ Jones, M. A. *et al.* Short-range ordering in a battery electrode, the ‘cation-disordered’ rocksalt Li_{1.25}Nb_{0.25}Mn_{0.5}O₂. *Chem. Commun.* **55**, 9027–9030 (2019).
- ¹⁰¹ Clément, R. J., Lun, Z. & Ceder, G. Cation-disordered rocksalt transition metal oxides and oxyfluorides for high energy lithium-ion cathodes. *Energy Environ. Sci.* **13**, 345–373 (2020).
- ¹⁰² Yabuuchi, N. *et al.* Origin of stabilization and destabilization in solid-state redox reaction of oxide ions for lithium-ion batteries. *Nature Commun.* **7**, 13814 (2016).
- ¹⁰³ Paściak, M., Welberry, T. R., Kulda, J., Kempa, M. & Hlinka, J. Polar nanoregions and diffuse scattering in the relaxor ferroelectric PbMg_{1/3}Nb_{1/3}O₃. *Phys. Rev. B* **85**, 224109 (2012).
- ¹⁰⁴ Battle, P. D., Evers, S. I., Hunter, E. C. & Westwood, M. La₃Ni₂SbO₉: A relaxor ferromagnet. *Inorg. Chem.* **52**, 6648–6653 (2013).
- ¹⁰⁵ Boström, H. L. B., Bruckmoser, J. & Goodwin, A. L. Ordered B-site vacancies in an ABX₃ formate perovskite. *J. Am. Chem. Soc.* **141**, 17978–17982 (2019).
- ¹⁰⁶ Simonov, A. *et al.* Hidden diversity of vacancy networks in Prussian blue analogues. *Nature* **578**, 256–260 (2020).
- ¹⁰⁷ Veal, B. W. *et al.* Time-dependent superconducting behavior of oxygen-deficient YBa₂Cu₃O_x: Possible annealing of oxygen vacancies at 300 K. *Phys. Rev. B* **42**, 4770–4773 (1990).
- ¹⁰⁸ Fang, Z., Bueken, B., De Vos, D. E. & Fischer, R. A. Defect-engineered metal–organic frameworks. *Angew. Chem. Int. Ed.* **54**, 7234–7254 (2015).
- ¹⁰⁹ Shearer, G. C. *et al.* Defect engineering: Tuning the porosity and composition of the metal–organic framework UiO-66 via modulated synthesis. *Chem. Mater.* **28**, 3749–3761 (2016).
- ¹¹⁰ Cliffe, M. J., Hill, J. A., Murray, C. A., Coudert, F.-X. & Goodwin, A. L. Defect-dependent colossal negative thermal expansion in UiO-66(Hf) metal–organic framework. *Phys. Chem. Chem. Phys.* **17**, 11586–11592 (2015).
- ¹¹¹ Nield, V. M., Keen, D. A., Hayes, W. & McGreevy, R. L. Structure and fast-ion conduction in α-AgI. *Solid State Ionics* **66**, 247–258 (1993).
- ¹¹² Wachsmann, E. D. & Lee, K. T. Lowering the temperature of solid oxide fuel cells. *Science* **334**, 935–939 (2011).
- ¹¹³ Grindlay, J. & Ter Haar, D. On the ferroelectric behaviour of potassium dihydrogen phosphate. *Proc. R. Soc. A* **250**, 266–285 (1959).
- ¹¹⁴ Di Stefano, D. *et al.* Superionic diffusion through frustrated energy landscape. *Chem.* **5**, 2450–2460 (2019).
- ¹¹⁵ Bernal, J. D. & Fowler, R. H. A theory of water and ionic solution, with particular reference to hydrogen and hydroxyl ions. *J. Chem. Phys.* **1**, 515–548 (1933).
- ¹¹⁶ Salzmann, C. G., Radaelli, P. G., Slater, B. & Finney, J. L. The polymorphism of ice: five unresolved questions. *Phys. Chem. Chem. Phys.* **13**, 18468–18480 (2011).
- ¹¹⁷ Bramwell, S. T. Ferroelectric ice. *Nature* **397**, 212–213 (1999).
- ¹¹⁸ Blunt, M. O. *et al.* Random tiling and topological defects in a two-dimensional molecular network. *Science* **322**, 1077–1081 (2008).
- ¹¹⁹ Barth, J. V., Costantini, G. & Kern, K. Engineering atomic and molecular nanostructures at surfaces. *Nature* **437**, 671–679 (2005).
- ¹²⁰ Stannard, A. *et al.* Broken symmetry and the variation of critical properties in the phase behaviour of supramolecular rhombus tilings. *Nature Chem.* **4**, 112–117 (2012).
- ¹²¹ Gerbode, S. J. *et al.* Glassy dislocation dynamics in 2D colloidal dimer crystals. *Phys. Rev. Lett.* **105**, 078301 (2010).
- ¹²² Muangnapoh, K., Avendaño, F. A., C. an Escobedo & Liddell Watson, C. M. Degenerate crystals from colloidal dimers under confinement. *Soft Matter* **10**, 9729–9738 (2014).
- ¹²³ Haji-Akbari, A., Haji-Akbari, N. & Ziff, R. M. Dimer covering and percolation frustration. *Phys. Rev. E* **92**, 032134 (2015).
- ¹²⁴ Miyajima, D. *et al.* Ferroelectric columnar liquid crystal featuring confined polar groups within core-shell architecture. *Science* **336**, 209–213 (2012).

- ¹²⁵ Fitić, C. F. C., Roelofs, W. S. C., Kemerink, M. & Sijbesma, R. P. Remnant polarization in thin films from a columnar liquid crystal. *J. Am. Chem. Soc.* **132**, 6892–6893 (2010).
- ¹²⁶ Simonov, A., Weber, T. & Steurer, W. Experimental uncertainties of three-dimensional pair distribution function investigations exemplified on the diffuse scattering from a tris-*tert*-butyl-1,3,5-benzene tricarboxamide single crystal. *J. Appl. Cryst.* **47**, 2011–2018 (2014).
- ¹²⁷ Zehe, C. S. *et al.* Mesoscale polarization by geometric frustration in columnar supramolecular crystals. *Angew. Chem. Int. Ed.* **56**, 4432–4437 (2017).
- ¹²⁸ Blomenhofer, M. *et al.* “Designer” nucleating agents for polypropylene. *Macromolecules* **38**, 3688–3695 (2005).
- ¹²⁹ Mermin, N. D. & Wagner, H. Absence of ferromagnetism or antiferromagnetism in one- or two-dimensional isotropic Heisenberg models. *Phys. Rev. Lett.* **17**, 1133–1136 (1966).
- ¹³⁰ Žukovič, M. & Idogaki, T. Low-temperature long-range ordering of a classical XY spin system with bilinear-biquadratic exchange Hamiltonian. *Physica B* **329–333**, 1055–1056 (2003).
- ¹³¹ Schlenk, H. & Holman, R. T. The urea complexes of unsaturated fatty acids. *Science* **112**, 19–20 (1950).
- ¹³² Playford, H. Y., Whale, T. F., Murray, B., Tucker, M. G. & Salzmann, C. G. Analysis of stacking disorder in ice I using pair distribution functions. *J. Appl. Cryst.* **51**, 1211–1220 (2018).
- ¹³³ Goodwin, A. L. *et al.* Aperiodicity, structure, and dynamics in Ni(CN)₂. *Phys. Rev. B* **80**, 054101 (2009).
- ¹³⁴ Jood, P. & Ohta, M. Hierarchical architecturing for layered thermoelectric sulfides and chalcogenides. *Materials* **8**, 1124–1149 (2015).
- ¹³⁵ Engel, M., Damasceno, P. F., Phillips, C. L. & Glotzer, S. C. Computational self-assembly of a one-component icosahedral quasicrystal. *Nature Mater.* **14**, 109–116 (2016).
- ¹³⁶ Kumar, S., Manickam, M., Varshney, S. K. & Shankar Rao, D. S. Novel heptasubstituted triphenylene discotic liquid crystals. *J. Mater. Chem.* **10**, 2483–2489 (2000).
- ¹³⁷ Sherwood, J. N. (ed.) *The Plastically Crystalline State: orientationally disordered crystals* (John Wiley & Sons, New York, 1979).
- ¹³⁸ David, W. I. F., Ibberson, R. M. & Matsuo, T. High resolution neutron powder diffraction: a case study of the structure of C₆₀. *Proc. R. Soc. Lond. A* **442**, 129–146 (1993).
- ¹³⁹ Clayton, J. O. & Giauque, W. F. The heat capacity and entropy of carbon monoxide. Heat of vaporization. Vapor pressures of solid and liquid. Free energy to 5000°K. From spectroscopic data. *J. Am. Chem. Soc.* **54**, 2610–2626 (1932).
- ¹⁴⁰ de Gennes, P. G. & Prost, J. *The Physics of Liquid Crystals* (Clarendon Press, Oxford, 1993).
- ¹⁴¹ MacFarlane, D. R., Huang, J. & Forsyth, M. Lithium-doped plastic crystal electrolytes exhibiting fast ion conduction for secondary batteries. *Nature* **402**, 792–794 (1999).
- ¹⁴² MacFarlane, D. R. & Forsyth, M. Plastic crystal electrolyte materials: New perspectives on solid state ionics. *Adv. Mater.* **13**, 957–966 (2001).
- ¹⁴³ Pringle, J. M., Howlett, P. C., MacFarlane, D. R. & Forsyth, M. Organic ionic plastic crystals: recent advances. *J. Mater. Chem.* **20**, 2056–2062 (2010).
- ¹⁴⁴ Pringle, J. M. Recent progress in the development and use of organic ionic plastic crystal electrolytes. *Phys. Chem. Chem. Phys.* **15**, 1339–1351 (2013).
- ¹⁴⁵ Horike, S. *et al.* Order-to-disorder structural transformation of a coordination polymer and its influence on proton conduction. *Chem. Commun.* **50**, 10241–10243 (2014).
- ¹⁴⁶ Nagarkar, S. S. *et al.* Enhanced and optically switchable proton conductivity in a melting coordination polymer crystal. *Angew. Chem. Int. Ed.* **56**, 4976–4981 (2017).
- ¹⁴⁷ Pauling, L. The rotational motion of molecules in crystals. *Phys. Rev.* **36**, 430–443 (1930).
- ¹⁴⁸ Lewis, L. J. & Klein, M. L. Random strains and the structure of (KBr)_{1-x}(KCN)_x mixed crystals. *Phys. Rev. Lett.* **57**, 2698–2701 (1986).
- ¹⁴⁹ Yamada, Y., Shibuya, I. & Hoshino, S. Phase transition in NaNO₂. *J. Phys. Soc. Jpn.* **18**, 1594–1603 (1963).
- ¹⁵⁰ Li, W. *et al.* Chemically diverse and multifunctional hybrid organic–inorganic perovskites. *Nature Rev. Mater.* **2**, 16099 (2017).
- ¹⁵¹ Coates, C. S. *et al.* Ferroic multipolar order and disorder in cyanoelpasolite molecular perovskites. *Phil. Trans. R. Soc. A* **377**, 20180219 (2019).
- ¹⁵² Jain, P. *et al.* Multiferroic behaviour associated with an order–disorder hydrogen bonding transition in metal–organic frameworks (MOFs) with the perovskite ABX₃ architecture. *J. Am. Chem. Soc.* **131**, 13625–13627 (2009).
- ¹⁵³ Besara, T. *et al.* Mechanism of the order–disorder phase transition, and glassy behavior in the metal-organic framework [(CH₃)₂NH₂]Zn(HCOO)₃. *Proc. Natl. Acad. Sci., U.S.A.* **108**, 6828–6832 (2011).
- ¹⁵⁴ Stroppa, A. *et al.* Electric control of magnetization and interplay between orbital ordering and ferroelectricity in a multiferroic metal–organic framework. *Angew. Chem.* **50**, 5847–5850 (2011).
- ¹⁵⁵ Stroppa, A., Barone, P., Jain, P., Perez-Mato, J. M. & Picozzi, S. Hybrid improper ferroelectricity in a multiferroic and magnetoelectric metal-organic framework. *Adv. Mater.* **25**, 2284–2290 (2013).
- ¹⁵⁶ Ye, H.-Y. *et al.* Metal-free three-dimensional perovskite ferroelectrics. *Science* **361**, 151–155 (2018).
- ¹⁵⁷ Šimėnas, M. *et al.* Simulation of structural phase transitions in perovskite methylhydrazinium metal–formate frameworks: Coupled Ising and Potts models. *J. Phys. Chem. C* **123**, 19912–19919 (2019).
- ¹⁵⁸ Lloveras, P. *et al.* Colossal barocaloric effects near room temperature in plastic crystals of neopentylglycol. *Nature Commun.* **10**, 1803 (2019).
- ¹⁵⁹ Bermúdez-García, J. M. *et al.* Giant barocaloric effect in the ferroic organic-inorganic hybrid [TPrA][Mn(dca)₃] perovskite under easily accessible pressures. *Nature Commun.* **8**, 15715 (2017).
- ¹⁶⁰ Tishin, A. M. & Spichkin, Y. I. *The Magnetocaloric Effect and its Applications* (Taylor & Francis, London, 2003).
- ¹⁶¹ Lorusso, G. *et al.* A dense metal–organic framework for enhanced magnetic refrigeration. *Adv. Mater.* **25**, 4653–4656 (2013).
- ¹⁶² Saines, P. J., Paddison, J. A. M., Thygesen, P. M. M. & Tucker, M. G. Searching beyond Gd for magnetocaloric frameworks: magnetic properties and interactions of the Ln(HCO₂)₃ series. *Mater. Horiz.* **2**, 528–535 (2015).

- ¹⁶³ Frost, J. M., Butler, K. T. & Walsh, A. Molecular ferroelectric contributions to anomalous hysteresis in hybrid perovskite solar cells. *APL Mater.* **2**, 081506 (2014).
- ¹⁶⁴ Herz, L. How lattice dynamics moderate the electronic properties of metal-halide perovskites. *J. Phys. Chem. Lett.* **9**, 6853–6863 (2018).
- ¹⁶⁵ Laurita, G., Fabini, D. H., Stoumpos, C. C., Kanatzidis, M. G. & Seshadri, R. Chemical tuning of dynamic cation off-centering in the cubic phases of hybrid tin and lead halide perovskites. *Chem. Sci.* **8**, 5628–5635 (2017).
- ¹⁶⁶ Zhu, T. & Ertekin, E. Mixed phononic and non-phononic transport in hybrid lead halide perovskites: glass-crystal duality, dynamical disorder, and anharmonicity. *Energy Environ. Sci.* **12** (2019).
- ¹⁶⁷ Delaire, O. *et al.* Giant anharmonic phonon scattering in PbTe. *Nature Mater.* **10**, 614–619 (2011).
- ¹⁶⁸ Christensen, S., Bindzus, N., Sist, M., Takata, M. & Iversen, B. B. Structural disorder, anisotropic microstrain and cation vacancies in thermoelectric lead chalcogenides. *Phys. Chem. Chem. Phys.* **18**, 15874–15883 (2016).
- ¹⁶⁹ Watson, G. W. & Parker, S. C. Origin of the lone pair of α -PbO from density functional theory calculations. *J. Phys. Chem. B* **103**, 1258–1262 (1999).
- ¹⁷⁰ Walsh, A., Payne, D. J., Egdel, R. G. & Watson, G. W. Stereochemistry of post-transition metal oxides: revision of the classical lone pair model. *Chem. Soc. Rev.* **40**, 4455–4463 (2011).
- ¹⁷¹ Skelton, J. M., Parker, S. C., Togo, A., Tanaka, I. & Walsh, A. Thermal physics of the lead chalcogenides PbS, PbSe, and PbTe from first principles. *Phys. Rev. B* **89**, 205203 (2014).
- ¹⁷² Li, C. W. *et al.* Phonon self-energy and origin of anomalous neutron scattering spectra in SnTe and PbTe thermoelectrics. *Phys. Rev. Lett.* **112**, 175501 (2014).
- ¹⁷³ Sangiorgio, B. *et al.* Correlated local dipoles in PbTe. *Phys. Rev. Mater.* **2**, 085402 (2018).
- ¹⁷⁴ Božin, E. S. *et al.* Entropically stabilized local dipole formation in chalcogenides. *Science* **330**, 1660–1663 (2010).
- ¹⁷⁵ Zhang, Y., Ke, X., Kent, P. R. C., Yang, J. & Chen, C. Anomalous lattice dynamics near the ferroelectric instability in PbTe. *Phys. Rev. Lett.* **107**, 175503 (2011).
- ¹⁷⁶ Keiber, T., Bridges, F. & Sales, B. C. Lead is not off center in PbTe: The importance of r -space phase information in extended X-ray absorption fine structure spectroscopy. *Phys. Rev. Lett.* **111**, 095504 (2013).
- ¹⁷⁷ Lee, S. *et al.* Resonant bonding leads to low lattice thermal conductivity. *Nat. Commun.* **5**, 3525 (2014).
- ¹⁷⁸ Esquivel-Elizondo, J. R., Brooks Hinojosa, B. & Nino, J. C. Bi₂Ti₂O₇: It is not what you have read. *Chem. Mater.* **23**, 4965–4974 (2011).
- ¹⁷⁹ Mukhopadhyay, A. B., Oligschleger, C. & Dolg, M. Low-frequency vibrational excitations in zeolite ZSM-5 and its partially crystalline derivatives. *Phys. Rev. B* **69**, 012202 (2004).
- ¹⁸⁰ Hammonds, K. D., Deng, H., Heine, V. & Dove, M. T. How floppy modes give rise to adsorption sites in zeolites. *Phys. Rev. Lett.* **78**, 3701–3704 (1997).
- ¹⁸¹ Sartbaeva, A. & Wells, S. A. Framework flexibility and rational design of new zeolites for catalysis. *Appl. Petrochem. Res.* **2**, 69–72 (2012).
- ¹⁸² Mary, T. A., Evans, J. S. O., Vogt, T. & Sleight, A. W. Negative thermal expansion from 0.3 to 1050 Kelvin in ZrW₂O₈. *Science* **272**, 90–92 (1996).
- ¹⁸³ Keen, D. A. *et al.* Structural description of pressure-induced amorphization in ZrW₂O₈. *Phys. Rev. Lett.* **98**, 225501 (2007).
- ¹⁸⁴ Duan, N., Kameswari, U. & Sleight, A. W. Further contraction of ZrW₂O₈. *J. Am. Chem. Soc.* **121**, 10432–10433 (1999).
- ¹⁸⁵ Perottoni, C. A. & da Jornada, J. A. H. Pressure-induced amorphization and negative thermal expansion in ZrW₂O₈. *Science* **280**, 886–889 (1998).
- ¹⁸⁶ Otto, S., Furlan, R. L. E. & Sanders, J. K. M. Selection and amplification of hosts from dynamic combinatorial libraries of macrocyclic disulfides. *Science* **297**, 590–593 (2002).
- ¹⁸⁷ Reynolds, E. M. *et al.* Function from configurational degeneracy in disordered framework materials. *Faraday Discuss.* doi:10.1039/D0FD00008F (2020).
- ¹⁸⁸ Serre, C. *et al.* Role of solvent-host interactions that lead to very large swelling of hybrid frameworks. *Science* **315**, 1828–1831 (2007).
- ¹⁸⁹ Yue, L., Wang, S., Wulf, V. & Willner, I. Stiffness-switchable DNA-based constitutional dynamic network hydrogels for self-healing and matrix-guided controlled chemical processes. *Nat. Commun.* **10**, 4774 (2019).
- ¹⁹⁰ Fennell, T. *et al.* Magnetic coulomb phase in the spin ice Ho₂Ti₂O₇. *Science* **326**, 415–417 (2009).
- ¹⁹¹ Hlinka, J. *et al.* Origin of the “waterfall” effect in phonon dispersion of relaxor perovskites. *Phys. Rev. Lett.* **91**, 107602 (2003).
- ¹⁹² Wiersma, D. S. Disordered photonics. *Nature Photon.* **7**, 188–196 (2013).
- ¹⁹³ Mittal, S. *et al.* Topologically robust transport of photons in a synthetic gauge field. *Phys. Rev. Lett.* **113**, 087403 (2014).
- ¹⁹⁴ Castelnovo, C., Moessner, R. & Sondhi, S. L. Magnetic monopoles in spin ice. *Nature* **451**, 42–45 (2008).
- ¹⁹⁵ Cliffe, M. J. *et al.* Metal–organic nanosheets formed via defect-mediated transformation of a hafnium metal–organic framework. *J. Am. Chem. Soc.* **139**, 5397–5404 (2017).
- ¹⁹⁶ Morris, R. E. & Čejka, J. Exploiting chemically selective weakness in solids as a route to new porous materials. *Nat. Chem.* **7**, 381–388 (2015).
- ¹⁹⁷ Roth, W. J. *et al.* A family of zeolites with controlled pore size prepared using a top-down method. *Nat. Chem.* **5**, 628–633 (2013).
- ¹⁹⁸ Schrödinger, E. *What is life?* (Cambridge University Press, Cambridge, 1944).
- ¹⁹⁹ Billinge, S. J. L. & Levin, I. The problem with determining atomic structure at the nanoscale. *Science* **316**, 561–565 (2007).
- ²⁰⁰ Shull, C. G., Strauser, W. A. & Wollan, E. O. Neutron diffraction by paramagnetic and antiferromagnetic substances. *Phys. Rev.* **83**, 333–345 (1951).
- ²⁰¹ Anderson, P. W. Ordering and antiferromagnetism in ferrites. *Phys. Rev.* **102**, 1008–1013 (1956).
- ²⁰² Fairbank, V. E., Thompson, A. L., Cooper, R. I. & Goodwin, A. L. Charge-ice dynamics in the negative thermal expansion material Cd(CN)₂. *Phys. Rev. B* **86**, 104113 (2012).
- ²⁰³ Cruddas, J. & Powell, B. J. Spin-state ice in elastically frustrated spin-crossover materials. *J. Am. Chem. Soc.* **141**, 19790–19799 (2019).
- ²⁰⁴ Wells, A. F. *Structural Inorganic Chemistry* (Clarendon Press, Oxford, 1984), 5th edn.

- ²⁰⁵ Delgado-Friedrichs, O., O’Keeffe, M. & Yaghi, O. M. Taxonomy of periodic nets and the design of materials. *Phys. Chem. Chem. Phys.* **9**, 1035–1043 (2007).
- ²⁰⁶ Fisher, M. E. & Selke, W. Infinitely many commensurate phases in a simple Ising model. *Phys. Rev. Lett.* **44**, 1502–1505 (1980).
- ²⁰⁷ Powell, S. & Chalker, J. T. SU(2)-invariant continuum theory for an unconventional phase transition in a three-dimensional classical dimer model. *Phys. Rev. Lett.* **101**, 155702 (2008).
- ²⁰⁸ Ramirez, A. P., Hayashi, A., Cava, R. J., Siddharthan, R. & Shastry, B. S. Zero-point entropy in ‘spin ice’. *Nature* **399**, 333–335 (1999).
- ²⁰⁹ Thygesen, P. M. M. *et al.* Local structure study of the orbital order/disorder transition in LaMnO₃. *Phys. Rev. B* **95**, 174107 (2017).
- ²¹⁰ Lieb, E. H. Residual entropy of square ice. *Phys. Rev.* **162**, 162–172 (1967).

GLOSSARY

magnetocaloric:

material that exhibits a strong reversible entropy change under applied magnetic field

relaxor:

material with strong dielectric response characterised by broad frequency dependent maximum of dielectric permittivity as a function of temperature and the absence of macroscopic symmetry breaking

frustrated magnetism:

the suppression of conventional order in magnetic materials by an incompatibility between the geometric arrangement of interacting spins and the nature of the interactions themselves

nematic:

characterised by axial order

magnetic skyrmion:

a topologically stable non-collinear ('knot') spin texture

trimeron:

a small polaron quasiparticle characterised by the delocalisation of electrons across a linear triplet of atoms

barocaloric:

material that exhibits a strong reversible entropy change under applied pressure

rigid-unit mode:

collective distortion of a network of connected polyhedra that propagates without geometric distortion of the polyhedra themselves