

Investigation of Structure and Electrical Hysteresis in Functional Materials



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A thesis submitted for the degree of
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Abstract

This thesis addresses issues regarding structure and electrical hysteresis in two functional materials; the semiconductor $\text{CH}_3\text{NH}_3\text{PbI}_3$, which is the prototypical material used in lead-halide perovskite solar cells, and the magnetic multiferroic CuFeO_2 .

Thin film $\text{CH}_3\text{NH}_3\text{PbI}_3$ is characterised by electrical hysteresis loop measurements which show that the current-voltage hysteresis observed in lead-halide perovskite solar cells cannot be attributed to a ferroelectric nature of the material but instead indicate a conductive hysteretic mechanism. This is further investigated through dielectric spectroscopy of crystals of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$, which reveal dispersive, thermally activated hopping conduction due to ionic vacancy conduction. The low activation energies reveal that ionic vacancy migration is the likely underlying mechanism of current-voltage hysteresis.

The structural details of $\text{CH}_3\text{NH}_3\text{PbI}_3$ are investigated by X-ray and neutron scattering. X-ray diffraction gives no indication of a polar crystal structure at room temperature and the extent of symmetry twinning is characterised. Quasielastic neutron scattering on crystals of $\text{CH}_3\text{NH}_3\text{PbI}_3$ is used to study the rotational dynamics of the CH_3NH_3 molecule, resolved in $\mathbf{q}$ -space. This reveals the highly isotropic nature of CH_3NH_3 molecular reorientation throughout the tetragonal phase.

In the multiferroic material CuFeO_2 , a ferroelectric polarisation memory effect is characterised through history-dependent pyrocurrent measurements. Uniaxial strain is applied to control the magneto-structural domain population, however the polarisation memory is found to only depend on the magnetic history of the material. Simulations of the magnetic domain wall spin structures by Monte Carlo methods predict the existence of helical domain walls in the magnetic ground state. It is proposed that these helical domain walls can act to store information on the helical state of the ferroelectric phase, thus accounting for the observed memory effects.

for my family, with love

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Definitions of initialisms and acronyms

- PCE : Power Conversion Efficiency
- MA : Methylammonium (CH_3NH_3)
- FA : Formamidinium ($\text{CH}(\text{NH}_2)_2$)
- DWM : Double Wave Method
- FTO : Fluorine-doped tin oxide
- DC : Direct Current
- RC : Resistance $\times$ Capacitance, the time constant of a simple circuit
- DMM : Digital Multi-Meter
- LFD : Low Frequency Dispersion
- DFT : Density-Functional Theory
- PPMS : Physical Property Measurement System
- AH2700 : Andeen-Hagerling 2700A high-accuracy capacitance bridge
- DM effect : Dzyaloshinskii-Moriya effect
- RAM/ROM : Random Access Memory/ Read Only Memory
- FWHM : Full-Width at Half-Maximum
- HWHM : Half-Width at Half-Maximum
- SDW : Spin-Density Wave
- HTM : Hole-Transporting Material
- CCR : Closed-Cycle Refrigerator
- CTC : Charge-Transfer Complex
- NMR : Nuclear Magnetic Resonance
- FEIC : Ferroelectric-Incommensurate
- 3SL : Three-Sublattice
- 4SL : Four-Sublattice
- 5SL : Five-Sublattice
- IT : Isosceles Triangle

Chapter 1

Introduction

Condensed matter physics is arguably the branch of physics that has caused the largest technological transformation to the world over the past century. From the development of the semiconductor transistor and the integrated circuit that underpins modern computational technology, to the use of powerful superconducting magnets in magnetic resonance imaging machines and particle accelerators, research into the fundamental quantum properties of materials has driven technological advancement in a wide variety of industries. Yet the scope for further technological advancement arising from condensed matter physics research is perhaps greater still. Recent discoveries such as the remarkable electronic properties of graphene [1], the existence of topological insulators [2–4] and the development of lead-halide perovskites for photovoltaics [5, 6] have generated intensive research activity, while the potential for scalable quantum computation, enhanced information storage in magnetic materials and high temperature superconductivity are but a few of the exciting areas of research also being pursued.

The development of devices utilising the unique properties of functional materials is underpinned by an intensive effort to understand the fundamental properties of these materials originating in the theories of quantum mechanics,

statistical mechanics and electromagnetism. A detailed fundamental understanding of the physics of condensed matter systems has enabled advancement of the field through the comprehensive characterisation of experimental results, while the predictive power of theory offers real scope for predicting material properties. Notable examples include the prediction of topological phases of matter [7], the prediction of the Josephson effect [8] and the prediction of the magnetoelectric effect [9, 10].

Understanding the relationships between the crystal structure and electronic properties of a material is critical to the development of functional materials. The atomic electron configurations plus the arrangement and separation of the atoms in a crystal structure determines the nature and extent of the Heisenberg exchange interactions between electrons in the material. This in turn determines the electronic band structure of the crystal, which gives rise to its electronic and optical properties, such as the band gap and electrical conductivity of a semiconductor. Furthermore, for atoms with magnetic moments due to their electron configurations, the exchange interaction and geometry of the magnetic lattice determines the collective magnetic ordering of the crystal. This can lead to a range of magnetic orderings, from ferromagnetism and antiferromagnetism to more complex spin ordering such as helical ordering or spin liquid states. Underpinning these relationships between crystal structure and electromagnetic properties is the symmetry of the crystal structure. The symmetry of a crystal directly determines the allowed macroscopic order parameters such as a ferroelectric polarisation, as well as imposing symmetry constraints on physical properties such as the electronic band structure.

In order to characterise materials for potential device applications, one must also understand how the state of a system changes under external forces, in particular the response of the system under electric and magnetic fields. One effect that must

be taken into account is the potential for hysteresis, when the state of a system depends on its history. Hysteresis is characteristic of ferroic materials, where the state of the macroscopic ferroic order parameter depends on the history of the material. This makes ferroic materials desirable for information storage devices, as hysteresis enables switching between two or more ground states of the system. However, a more general type of hysteresis, where the history of the system has indirectly affected other functional properties, may pose challenges. Such an effect is observed in perovskite photovoltaic devices, where hysteresis in the current-voltage characteristics are observed [11].

In the remainder of this chapter I shall introduce the concept of symmetry and the formalism of group theory, and discuss its application to condensed matter systems relevant to the work presented in the thesis. I will then briefly discuss the physics of two groups of functional materials; multiferroics and semiconductors, before giving an outline of the thesis.

1.1 Symmetry in condensed matter physics

A fundamental concept that underpins the physics of ordered solids is the concept of symmetry. In crystalline materials, the periodic nature of the crystal lattice gives translational symmetry to the material, while many phase transitions are characterised by the breaking of particular symmetries. The application of group theory is a powerful theoretical framework that can be used to describe the symmetries of a material and to determine the effect of these symmetries on the material's physical properties. In this section I shall introduce the concept of groups and irreducible representations and describe the application of group theory to the physical properties of a system. A more extensive coverage of the theorems and applications of group theory can be found in many texts [12, 13].

1.1.1 Definition of a group

A group is defined as a collection of elements $a, b, c, \dots$ that satisfy four conditions;

- One must first define a binary operation for the group, also referred to as a composition, and denoted by $\circ$. The composition of two elements of the group must also be an element of the group. For example, one can write relations such as

$$a \circ b = c. \quad (1.1)$$

- The composition of elements must be associative;

$$(a \circ b) \circ c = a \circ (b \circ c). \quad (1.2)$$

- There must exist an identity element, e , within the group;

$$a \circ e = e \circ a = a. \quad (1.3)$$

- For every element a , there exists an inverse element a^{-1} ;

$$a \circ a^{-1} = a^{-1} \circ a = e \quad (1.4)$$

Group theory is powerful for the symmetry analysis of crystals as the symmetry operations of a crystal can be shown to form a group, known as the space group of the crystal. Space groups consist of point group symmetry operations and translational symmetry operations (and combinations thereof). The fact that the symmetry operations of a crystal form a group means that one can form *representations* of the group that act on a linear vector space. This provides a mathematical formalism to determine how the symmetry of a system affects its physical properties.

1.1.2 Point groups and representations

Point groups consist of symmetry operations that leave at least one point invariant. For example, consider the symmetry operations of a water molecule. There exists a twofold rotation axis 2_z through the oxygen atom, as well as two orthogonal mirror planes m_y , m_x , that intersect at the oxygen atom. The molecule is also symmetric under the identity operation E . It is easy to verify that these operations form a group by creating a multiplication table, as shown in Table 1.1.2, which shows how the composition of any two operators forms a third operator in the group. This also displays how each element has an inverse that results in an identity operation (in this case each element is its own inverse), as well as allowing verification of the associative nature of the composition. In total, there are 32 crystallographic point groups, composed of proper and improper rotations that leave at least one point of a crystal fixed, which are also capable of maintaining the three-dimensional translational symmetry of a crystal.

As the symmetry elements form a group, one can form *representations* of the group. A representation of a group is defined as the mapping of the group elements onto linear operators which act on a linear vector space. A common example would be representing the symmetry operators as three-dimensional matrices that act on a three-dimensional vector space, such as a cartesian basis set (x, y, z) . In this case, the composition operation is represented by matrix multiplication. In the example of

a \ b				
	E	2_z	m_y	m_x
E	E	2_z	m_y	m_x
2_z	2_z	E	m_x	m_y
m_y	m_y	m_x	E	2_z
m_x	m_x	m_y	2_z	E

Table 1.1: Multiplication table for the point group $mm2$. The element on the top row is applied first, followed by the element in the first column i.e. the table entry gives the result of the composition $a \circ b = c$.

the point group $mm2$, one three-dimensional matrix representation of the elements is

$$E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, 2_z = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, m_y = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, m_x = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

which act on the cartesian basis vectors (x, y, z) .

A representation is said to be reducible if one can choose a basis set such that the matrices representing all members of the group can be written in the same block diagonal form. If this is the case, then the linear space is broken down into a set of subspaces. Each block then forms a representation of the group onto a subspace. If a representation cannot be further broken down into a block diagonal form then it is said to be irreducible. For example, the 3D representation of $mm2$ shown above is reducible into three 1D irreducible representations. In the example, all matrices are already in block diagonal form of three 1×1 blocks due to the choice of basis being eigenfunctions of the group. A key part of symmetry analysis is transforming the representation of symmetry operators on a large vector space to a sum of irreducible representations that describe how the symmetry operators act on a set of subspaces. In general, each irreducible representation describes the transformation of a set of eigenfunctions with the same eigenvalue, hence representation theory can be used to determine how the symmetry of a physical problem determines energy degeneracies and eigenfunctions of the system. The use of irreducible representations will be employed in Chapter 4, where irreducible representations are used to describe the rotational modes of a molecule in a crystal environment.

1.1.3 Space groups

In a crystal, the periodic nature of the structure means that translational symmetry operations must be taken into account to describe the symmetry of the system. A space group is defined as the set of translation operations and point group operations that transform the crystal into itself. The space groups can be formed by

1.1. Symmetry in condensed matter physics

combining the 32 point groups with translation symmetry operations of the 14 Bravais lattices, giving a total of 230 space groups [13]. The symmetry elements of a space group include point operations (the identity operation, rotations, mirror reflections, inversion and roto-inversion operations), pure translations operations of the Bravais lattice, as well as compound operations that include both point and translation operations. The compound operations include glide planes, which are defined by reflection in a plane followed by a translation parallel with that plane, and screw axes, which are defined by rotation about an axis followed by a translation along the direction of the axis.

If a space group does not contain compound operations, then the point operations of the group leave at least one point of the crystal invariant. In this case the space group is called a symmorphic group, and the point group of the crystal can be obtained from the point symmetry operations about this invariant point. If compound operations are contained within the space group, then the point operations obtained by removing all translations do not leave any point within the crystal invariant. In this case the space group is called a nonsymmorphic group, and the point group of the crystal is formed by removing the translational operations from of the compound operations. For example, the point group of space group $I4/mcm$ (long symbol $I4/m2/c2/m$) is determined by removing the translation of the c -glide, giving $4/m2/m2/m$, or $4/mmm$ in short notation. The consideration of the crystal point group is important as many physical properties are determined by the point group symmetry operations of a crystal, as opposed to the full space group, as explained in the following section.

1.1.4 Neumann's principle

The relationship between symmetry and physical properties is succinctly expressed by Neumann's principle. Neumann's principle states that the physical properties of a

crystal must be invariant under the point group symmetry operations of the crystal. This has important consequences for many different types of functional materials, including multiferroics and semiconductors.

Multiferroic materials are defined as materials that exhibit more than one ferroic order parameter, including ferroelectricity, ferromagnetism and ferroelasticity. These orders are characterised by spontaneous electrical polarisation (a polar vector), spontaneous magnetisation (an axial vector) and spontaneous strain (a symmetric rank-2 tensor). Neumann's principle places restrictions on whether a material can exhibit multiferroic properties, based on its crystal/magnetic point group (in the case of ferroelectric/magnetic materials), or on the relationship between the point groups across a phase transition (in the case of ferroelastic materials). For a crystal to support a macroscopic electrical polarisation, all elements of the crystal point group must leave at least one component of a general polar vector invariant. In the formalism of representations, this means that at least one component of the vector (x, y, z) must transform according to the totally symmetric representation of the point group. This requirement is satisfied for the 10 polar point groups; $1, 2, m, mm2, 3, 3m, 4, 4mm, 6, 6mm$. With the exception of the trivial point group 1, the symmetry operations of each polar group place restrictions on the direction of the allowed macroscopic polar vectors. An additional symmetry that must be considered for magnetic materials is the symmetry under the time reversal operator, which transforms $t \rightarrow -t$. In general, spin angular momentum can be written as the cross product of position and momentum, and therefore the time reversal operator inverts the direction of a spin $\mathbf{S}$. Thus in a magnetic material, the point/space group symmetry operations of the crystal can be combined with the time reversal operator to define a magnetic point/space group. A macroscopic axial vector, such as a magnetisation, can then only exist in magnetic point groups which leave such an axial vector invariant.

While the discussion so far has considered polar and axial vectors, which are rank-1 tensors, the principles are also applicable to higher rank tensors representing physical properties, such as the rank-2 dielectric permittivity tensor. In general, one must consider the transformation properties of the tensor based on the tensor product of the underlying vector spaces. As any non-zero tensor component must be invariant under all symmetry operations, one must consider if the totally symmetric irreducible representation is contained within the tensor product of the vector spaces. For example, the number of unique elements of the dielectric permittivity tensor ϵ_{ij} in the $4/mmm$ point group can be determined by considering the reduction of the tensor product of two vector spaces $\Gamma = (x, y, z)$. In terms of representations, $\Gamma = \Gamma_2^- + \Gamma_5^-$, and one finds that

$$\Gamma \otimes \Gamma = 2\Gamma_1^+ + \Gamma_2^+ + \Gamma_3^+ + \Gamma_4^+ + 2\Gamma_5^+. \quad (1.5)$$

As the product representation contains two copies of the totally symmetric representation Γ_1^+ , it follows that there are two unique (non-zero) elements of ϵ_{ij} (these can be shown to be $\epsilon_{11} = \epsilon_{22}$ and ϵ_{33}).

The principles of symmetry invariance also have profound implications for the quantum mechanical properties of a crystal, such as the symmetry of electron wavefunctions in a semiconductor. If the Hamiltonian $\hat{\mathcal{H}}$ of a system has invariance under a set of symmetry operators, and these operators commute with $\hat{\mathcal{H}}$, then it can be shown that the wavefunctions formed by applying the symmetry operators to eigenfunctions of $\hat{\mathcal{H}}$ are also eigenfunctions with the same eigenvalue [12]. In a semiconductor, one can consider the energies of electrons moving in a periodic potential $V(\mathbf{r})$, which has the translational and point symmetry of the crystal. While the full Hamiltonian for a crystal includes electron-electron interactions, in the mean-field approximation the assumption is made that each electron experiences the same periodic potential $U(\mathbf{r})$ due to the ions and other electrons. In this case,

the Hamiltonian can be written as a one electron Hamiltonian

$$\left[-\frac{\hbar^2 \nabla^2}{2m} + U(\mathbf{r}) \right] \phi_n(\mathbf{r}) = E_n \phi_n(\mathbf{r}), \quad (1.6)$$

where $U(\mathbf{r})$ has the translational and point symmetry of the crystal. The translational symmetry of $\hat{\mathcal{H}}$ means that one can form eigenstates in the Bloch form;

$$\phi_{\mathbf{k}}(\mathbf{r}) = \mathbf{e}^{i\mathbf{k} \cdot \mathbf{r}} \mathbf{u}_{\mathbf{k}}(\mathbf{r}), \quad (1.7)$$

where $u_{\mathbf{k}}(\mathbf{r})$ has the same translational symmetry as the crystal. The wavefunctions are therefore labelled by the quantum number $\mathbf{k}$, which is the wavevector of the electron state defined in the reciprocal space of the crystal. As the first term of Equation 1.6 is spherically symmetric and $U(\mathbf{r})$ has the point symmetry of the crystal, it follows that the eigenstates $\phi_{\mathbf{k}}$ and $\phi_{\mathbf{k}'} = R\phi_{\mathbf{k}}$ have the same energy, for all elements R of the point group of the crystal. Additionally, $\phi_{\mathbf{k}}^\dagger(\mathbf{r}) = \mathbf{e}^{-i\mathbf{k} \cdot \mathbf{r}} \mathbf{u}_{\mathbf{k}}^\dagger(\mathbf{r})$ is also an eigenfunction with eigenvalue $E_{-\mathbf{k}} = E_{\mathbf{k}}$, giving inversion symmetry to the energy surface in $\mathbf{k}$ -space. Thus, electron eigenstates of a crystal are labelled by the wavevectors $\mathbf{k}$, which can be restricted to the first Brillouin zone in reciprocal space due to the translational symmetry of the crystal, while the first Brillouin zone has the point symmetry of the crystal in addition to inversion symmetry. An important consequence of these considerations is that the electron wavefunctions can be symmetrised, that is they can be written in a form that has definite transformation properties under the crystal symmetry operations. Therefore the wavefunctions transform as representations of the crystal point group, and representation theory allows the determination of the energy level degeneracies and eigenstate symmetries at a given $\mathbf{k}$ -point. Additionally, at high symmetry and zone boundary $\mathbf{k}$ -points, restrictions are placed on physical properties such as the group velocity, which transforms as a polar vector. One can also use representation theory to determine

whether certain optical transitions are allowed between given states in the electronic band structure [12].

Clearly there is a fundamental relationship between the crystal symmetry and physical properties, and knowledge of the crystal symmetry of a material is essential to understand its physical properties.

1.1.5 Domain formation at phase transitions

In many physical systems, phase transitions are characterised by the breaking of symmetries from a high symmetry to a low symmetry phase. A natural consequence of symmetry breaking is the formation of domains. In order to break a symmetry element of a higher symmetry phase, a distortion of the crystal structure must occur, however there will always be degeneracy between different distortions, with the degenerate distortions being related by the broken symmetry elements of the higher symmetry phase. In the nucleation and growth model of phase transitions, the low symmetry phase will nucleate and grow from many locations in a macroscopic crystal, with each nucleation domain characterised by one of the degenerate distortions from the high symmetry phase. Over the whole crystal, this will create a statistical sample of the different degenerate distortions, resulting in the formation of symmetry equivalent domains. For example, in a phase transition from a structure with point group $2/m$ to a structure with point group 2, the mirror symmetry can be broken by a distortion parallel or anti-parallel to the twofold axis ($\pm z$), hence within the material two domain types will form with distortions along $\pm z$ relative to the higher symmetry structure. These two domain types can be transformed into each other by the broken mirror symmetry operation of $2/m$. However, the size of each domain will be dependent on the details of the microscopic interactions, such as the energy cost of domain walls, the ease of domain wall motion and pinning by defects.

The formation of domains is an important aspect of phase transitions as the

domain-averaged properties of a material can differ greatly from the intrinsic properties of each domain. For example, in a ferroelectric phase transition from point group $2/m \rightarrow 2$, in the absence of external forces one expects an equal population of $\pm P_z$ ferroelectric domains to form, which will give on average a net zero polarisation of the whole crystal. This effect can be overcome by biasing the crystal with an external electric field through the phase transition, in order to favour the nucleation and growth of one ferroelectric domain type over the other, thus creating a net macroscopic polarisation. Furthermore, the physical properties of domain walls can differ significantly from the properties of the domains. For example, ferroelectric domain walls can have a net charge, causing an increase in conductivity [14, 15], while ferromagnetic domain walls have helical or cycloidal spin arrangements as opposed to the parallel spin alignment of the ferromagnetic domains.

The issues of symmetry and domain effects are an important consideration for the materials investigated in this thesis. The first material, the semiconductor $\text{CH}_3\text{NH}_3\text{PbI}_3$, is known to exhibit current-voltage hysteresis when used in photovoltaic thin films, which has been suggested to arise due to ferroelectricity [11]. In addition to electrical measurements, the symmetry of the crystal structure will be investigated to see if there is evidence for a polar symmetry, while the effect of symmetry twin domains in the tetragonal and orthorhombic phases must also be taken into account. In the second material, the multiferroic CuFeO_2 , the effect of magnetoelastic domains on a ferroelectric memory effect is investigated, and the spin structure of the magnetic domain walls are also considered. In addition to the interesting physical phenomena displayed in these materials, the study of these systems is motivated by the potential for application in functional devices, which I shall now briefly discuss.

1.2 Multiferroic materials

While there are several primary ferroic orders, including ferroelectricity, ferromagnetism and ferroelasticity, the multiferroics that have received most attention in the literature are magnetoelectric multiferroics; materials with spontaneous magnetic and electric ordering. The coexistence of magnetic and electric ordering allows a material to exhibit magnetoelectric effects, where an electric/magnetic polarisation can be induced or manipulated with an applied magnetic/electric field, offering routes for functional behaviour in magnetoelectronic devices such as magnetic memory devices or spintronic devices. The definition of magnetoelectric multiferroics is usually extended to include all types of magnetic ordering which break time reversal symmetry, as strong magnetoelectric coupling is not limited to ferromagnetic ferroelectrics [16]. Many ferroelectrics are transition metal oxide compounds, where the predominant exchange interactions between magnetic atoms are mediated by an oxygen ligand. This tends to cause antiferromagnetic interactions between spins and can lead to a range of collinear or non-collinear magnetic orderings depending on the details of the microscopic interactions and geometry of the magnetic structure. Many types of magnetic structures, such as cycloidal or helical spin ordering, can break inversion symmetry and give rise to a ferroelectric polarisation, leading to strong coupling between the magnetic and ferroelectric order.

Magnetoelectric multiferroics can be further classified as either type-I or type-II multiferroics [17] (from herein the term multiferroic shall be used to refer exclusively to magnetoelectric multiferroics). In type-I multiferroics, the spontaneous ferroelectric and magnetic ordering arise at separate phase transitions and the coupling between the two orders is typically weak, whereas in type-II multiferroics, spontaneous magnetic ordering breaks inversion symmetry, causing a ferroelectric polarisation to develop which is strongly coupled to the magnetic order. However,

type-II multiferroic phases typically occur at much lower temperatures than type-I multiferroic phases, and the magnetically-induced polarisation is typically around three or more orders of magnitude smaller than in type-I ferroelectrics, thus currently limiting the applications in functional devices. An example of a type-I multiferroic is BiFeO_3 , which has a spontaneous polarisation $P \sim 90 \mu\text{C cm}^{-2}$ below $T_C \sim 1100 \text{ K}$ and antiferromagnetic ordering at $T_N = 643 \text{ K}$ [17]. One of the first compounds shown to display type-II multiferroicity was TbMnO_3 , which undergoes a magnetic transition at $T_N = 28 \text{ K}$ to a state with cycloidal magnetic ordering that induces a spontaneous polarisation of $800 \mu\text{C m}^{-2}$ [18].

Microscopically, a magnetically induced ferroelectric polarisation can, for most materials, be explained by contributions from at least one of two mechanisms. A mechanism common to cycloidal magnetic ordering is the ‘spin-current’ mechanism, caused by the inverse Dzyaloshinskii-Moriya (DM) effect that arises from the antisymmetric magnetic exchange interaction due to spin-orbit coupling [19, 20]. This leads to a polarisation $\mathbf{P} \propto \mathbf{r}_{ij} \times \mathbf{S}_i \times \mathbf{S}_j$, which requires non-collinear spin ordering and leads to a polarisation perpendicular to the vector $\mathbf{r}_{ij}$ connecting adjacent spins. This model accounts for the magnetically induced polarisation in the cycloidal phases of materials including TbMnO_3 [18] and MnWO_4 [21, 22]. While the inverse DM effect originates in the antisymmetric magnetic exchange, the symmetric Heisenberg exchange can also give rise to a ferroelectric polarisation through a mechanism known as exchange striction [17]. This arises due to the fact that the symmetric exchange between two magnetic atoms mediated by a ligand depends on the atomic separation and bond angle and therefore the exchange energy can be minimised by atomic displacements of the bonding atoms. If the magnetic structure breaks inversion symmetry, the atomic displacements can lead to a net ferroelectric polarisation. The exchange striction mechanism is proposed as the main mechanism for ferroelectricity in the RMn_2O_5 family of compounds [23].

While these two mechanisms succeeded in explaining magnetically-induced polarisation in many multiferroic systems, one notable exception was the case of triangular lattice antiferromagnets, such as $\text{RbFe}(\text{MoO}_4)_2$ [24] and CuFeO_2 [25], where helical magnetic ordering is observed and where the ‘spin-current’ model or magnetostriction models were not considered to be applicable [26]. Instead, for CuFeO_2 , a modification of the bond charge due to variation in orbital hybridisation was proposed to account for the polarisation in the ferroelectric phase [26].

1.2.1 Device applications of multiferroics

A key challenge to overcome in the studies of multiferroic materials is to find multiferroics with functional properties close to room temperature that could be exploited for device applications. One potential application of multiferroic materials is in magnetic memory devices, which could combine the best features of existing memory technologies. Current RAM/ROM technologies typically use a combination of capacitors and transistors to store bits of data. For example, dynamic random access memory stores each bit in a capacitor in an integrated circuit, allowing high storage densities at low cost, however the volatile nature of the memory requires periodic refreshing of the memory which draws a relatively large amount of power. A multiferroic memory device could significantly improve upon the developing magnetoresistive RAM technology by incorporating electrical read/write capabilities. An example theoretical multiferroic device was described by Bibes *et al.* [27] and is shown in Figure 1.1. The device consists of a multiferroic layer where the electrical polarisation is switched by an applied voltage. Due to the multiferroic nature of the layer, this would also switch the magnetic ordering that can be coupled to a ferromagnetic material at the surface. The switching of this ferromagnetic layer then causes a change in electrical resistance across a magnetic tunnel junction that can be read electrically. In addition to memory devices,

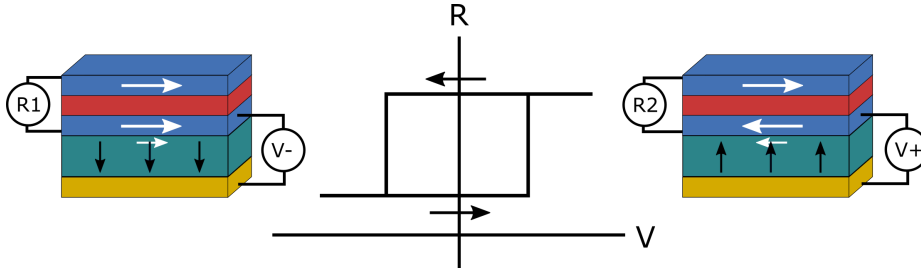


Figure 1.1: Proposed mechanism for a multiferroic memory device, based on a figure from Bibes *et al.* [27]. A voltage applied to the multiferroic layer switches a ferroelectric polarisation (black arrows) which is coupled to the magnetic order (white arrows). Exchange bias coupling between the multiferroic and a ferromagnetic layer (blue), causes a reversal of the magnetisation in ferromagnetic layer. This alters the resistance across a magnetic tunnel junction, creating a two-state magnetic memory device with an electrical read/write mechanism.

multiferroics offer the potential for novel spintronic/magnonic devices, as the magnetoelectric coupling can allow spin-waves to be controlled by applied electric fields, as has been shown for the multiferroic BiFeO_3 [28].

As discussed previously, a barrier to the utilisation of multiferroic materials in devices is the fact that type-I multiferroics are usually multiferroic at room temperature but have weak coupling between the orders, while type-II multiferroics have strong coupling but are typically only found at temperatures significantly below room temperature. Understanding the key coupling mechanisms, demonstrating functional behaviour and finding new materials with enhanced multiferroic properties is crucial to the realisation of functional multiferroic devices.

1.3 Semiconductors for photovoltaic devices

The fundamental electronic properties of semiconductors make them suitable for utilisation in a wide variety of functional materials. One area of research that continues to see intensive research effort is the use of semiconductors as the principal component of photovoltaic devices, which utilise several key properties of

semiconductors.

As discussed previously, the translational symmetry of the crystal structure leads to electron states being labelled by the wavevector $\mathbf{k}$, while the electronic energy states as a function of $\mathbf{k}$ are known as the electronic band structure. A semiconductor is a material with an energy gap between the highest occupied energy band (valence band) and the lowest unoccupied energy band (conduction band). Thus at zero temperature there is no electrical conduction, while at elevated temperatures low levels of conduction become possible through thermal excitations from the valence band to the conduction band. Additionally, a semiconductor can be doped with an impurity atom to give electron energy states within the band gap, which can contribute to the thermal population of free carriers in the conduction or valence band. The presence of a band gap is also the defining property of an insulator, however for an insulator the band gap is typically much larger, although there is no defined cut-off. For example silicon, a typical semiconductor, has a band gap of 1.17 eV at 0 K, whereas diamond, an insulator, has a band gap of 5.4 eV at 0 K.

The size of the band gap in semiconductors allow the absorption of a significant fraction of the solar spectrum, while also producing a sizeable photovoltage under illumination. The Shockley-Queisser limit for the maximum obtainable power conversion efficiency from a solar cell in a single semiconductor device occurs for a band gap of 1.34 eV, which has an efficiency limit of 33.7% [29]. Efficiencies above $\sim 30\%$ are possible for band gaps in the range of 1.0 eV to 1.6 eV, making a range of semiconductors suitable for use in photovoltaic devices. Furthermore, multi-layered devices can exceed the efficiency of a single-layer device, by combining multiple semiconductors with different band gaps.

While the band gap places a limit on the maximum obtainable efficiency, in order to reach this limit one must be able to efficiently separate and transport photogenerated charges within the semiconductor. The absorption of a photon

excites an electron from a valence band state to a conduction band state, creating an empty ‘hole’ state in the valence band. This electron-hole pair can form a bound state known as an exciton due to coulombic attraction, and rapid dissociation of the exciton is essential to avoid recombination. In band theory, electrons occupying conduction band states can be considered as free carriers with an effective mass m^* determined by the curvature of the band;

$$m^* = \hbar^2 / \frac{d^2 E}{dk^2}. \quad (1.8)$$

Meanwhile empty states in the valence band can be considered as a positive charged carrier known as a hole, which has an analogous effective mass determined by its band curvature. The radius of an exciton state is proportional to the dielectric constant and inversely proportional to the effective masses of the electron and hole, while the dielectric constant of the material also acts to screen the coulombic interaction and reduce the exciton binding energy [30]. Therefore a high dielectric constant and low effective masses are favourable to increase the spatial separation of the electron and hole and favour thermal dissociation into a free electron and hole before recombination occurs. In order to efficiently transport and extract the free charge carriers, recombination must also be limited, which can occur due to photon emission, via impurity assisted trapping or due to higher order processes such as Auger recombination [31]. Low recombination rates result in long charge carrier lifetimes and long carrier diffusion lengths, enabling the photogenerated charges to be extracted at the electrodes and generate a current.

1.3.1 Development of new photovoltaic technologies

Solar cells based on silicon are now a mature technology, with photovoltaic systems becoming cost-competitive with traditional sources of electricity, particularly in

1.3. Semiconductors for photovoltaic devices

areas of the world with high levels of sunshine duration. This has seen increasing roll-out of photovoltaic generation capacity, with worldwide solar capacity in 2015 standing at 227 GW, representing 1% of global energy demand, with yearly global manufacturing capacity predicted to reach ~ 100 GW by 2020 [32]. Despite the successes of silicon photovoltaics, emerging photovoltaic technologies have generated significant interest in the scientific community. In particular, the past five years have seen a resurgence in the field with the discovery of the suitability of lead-halide perovskites for photovoltaic devices [5, 6]. This has seen certified efficiencies in excess of 22%, surpassing other emerging photovoltaic technologies of dye-sensitized solar cells, quantum dot solar cells and organic photovoltaics [33] and putting perovskite photovoltaics on a comparable level to silicon devices ^a. Thin film perovskite solar cells have the advantages of low-cost solution-processing production methods [34, 35], the ability to tune physical properties by varying chemical composition [36], as well as the potential for use in integrated photovoltaics. Nevertheless, there are issues of long-term stability and moisture sensitivity [37] and commercial devices have yet to be realised.

Photovoltaic devices based on lead-halide perovskites typically employ a heterojunction architecture: an example perovskite solar cell architecture is shown in Figure 1.2(a) [38]. Perovskite solar cells typically consist of a thin layer, $< 1 \mu\text{m}$, of polycrystalline lead halide perovskite between charge selective contacts. TiO_2 is commonly used as an electron-selective contact on top of a fluorine-doped tin oxide (FTO) electrode, while a range of hole-transporting materials (HTM) can be used to allow the conduction of holes to a gold electrode. The choice of suitable selective contacts is determined by the difference in band energies between the selective contacts and the perovskite semiconductor, as shown in Figure 1.2(b), which favour the extraction of an electron to the FTO contact and of a hole to the Au contact. It

^aTypical residential silicon photovoltaic modules, such as the SunPower X22 solar panel, currently have total-area module efficiencies of $\sim 22\%$.

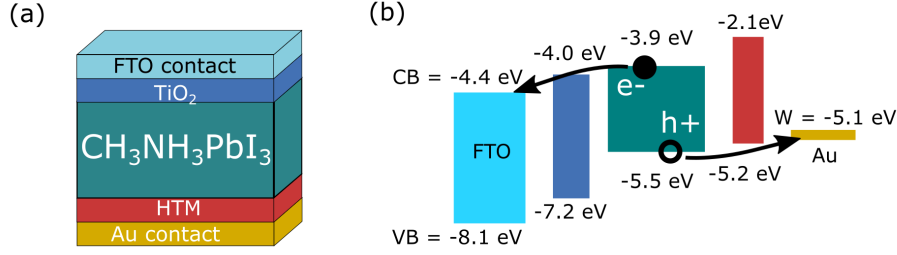


Figure 1.2: Details of a perovskite solar cell device architecture, based on a figure from Green *et al.* [38]. (a) Device architecture of a typical perovskite photovoltaic device, consisting of a layer of perovskite crystal and charge selective contacts of TiO₂ and a hole transporting material (HTM). Fluorine-doped tin oxide (FTO) and gold are often used as external ‘metallic’ contacts. (b) Energy band diagram of the constituent components, showing vacuum potentials of the conduction and valence bands for the semiconductors in the perovskite solar cell, alongside the work function of the gold electrode.

is important to note that a shift in the band energies relative to the vacuum potentials will occur once the constituent materials are connected in equilibrium, as the system must have a continuous chemical potential. This will be discussed in further detail in Chapter 3.

1.4 Outline of the thesis

In this thesis I will investigate the structural and electrical properties of two functional materials using a variety of experimental techniques. The first is the lead-halide perovskite CH₃NH₃PbI₃, the prototypical semiconductor of perovskite photovoltaic devices. I shall present electrical measurements of hysteresis loops on thin film devices and dielectric spectroscopy measurements on single crystals, in order to investigate the potential causes of hysteresis that is observed in perovskite devices. X-ray diffraction and quasielastic neutron scattering measurements are also presented in order to investigate the structural details of CH₃NH₃PbI₃. The implications of these measurements on the operation of perovskite photovoltaic

devices is also discussed. The second material investigated is CuFeO_2 , a magnetic insulator which exhibits a multiferroic phase in applied magnetic field. Electrical measurements are performed to characterise a hysteretic polarisation memory effect and its dependence on the magnetic phase history. A model is proposed based on Monte Carlo simulations of domain wall structures, and the applicability of this model to other multiferroics is discussed.

Chapter 2

Experimental techniques

As part of this thesis, I shall use the experimental techniques of dielectric spectroscopy and quasielastic neutron scattering to perform a detailed study of the electrical and structural properties of $\text{CH}_3\text{NH}_3\text{PbI}_3$. In this chapter, I shall discuss the general theory behind these experimental techniques and discuss in detail the specific models that will be used to interpret and fit the quasielastic neutron data. I shall also discuss the frequency- and temperature-dependent dielectric behaviour of various relaxation and charge carrier processes, to aid discussion of the dielectric spectroscopy data in Chapter 3.

2.1 Quasielastic neutron diffraction

2.1.1 Neutron scattering theory: the scattering cross section

For a neutron interacting with a sample of N atoms of scattering length b , the number of neutrons scattering into solid angle $d\Omega$ with a final energy between E' and $E'+dE'$ is given by the double differential cross section

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{k'}{k} \langle |b|^2 \rangle S(\mathbf{Q}, \omega), \quad (2.1)$$

2.1. Quasielastic neutron diffraction

where $S(\mathbf{Q}, \omega)$ is the dynamical structure factor;

$$S(Q, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \sum_{m'm} \langle \exp\{-i\mathbf{Q} \cdot \mathbf{R}_{m'}(0)\} \exp\{i\mathbf{Q} \cdot \mathbf{R}_m(t)\} \rangle \exp(-i\omega t) dt. \quad (2.2)$$

Here, (E', k') and (E, k) are the final and initial energy and wavevector of the neutron, the energy transfer $\omega = E - E'$ and $\mathbf{Q} = \mathbf{k} - \mathbf{k}'$. $\langle |b|^2 \rangle$ is the average mod-square nuclear scattering length and the sum is over all pairs of the N atoms. $\langle |b|^2 \rangle$ can be separated into two contributions due to coherent and incoherent scattering;

$$\langle |b|^2 \rangle = |\langle b \rangle|^2 + \delta_{m,m'} [\langle |b|^2 \rangle - |\langle b \rangle|^2] = \frac{1}{4\pi} [\sigma_{\text{coh}}^2 + \delta_{m,m'} \sigma_{\text{inc}}^2]. \quad (2.3)$$

For a neutron scattering from a lattice of nuclei, this separation can be understood physically as a separation into scattering from the average scattering length, and scattering due to deviations from the average, which arise due to the nuclear spin orientation and isotopic variation. The average scattering potential of the nuclei gives rise to interference effects, hence the coherent scattering length is given by the mod-square of $\langle b \rangle$. The deviations from the average are randomly distributed and do not give rise to interference, and hence give incoherent scattering proportional to the mean-square deviation $[\langle |b|^2 \rangle - |\langle b \rangle|^2]$ [39].

Therefore, the total scattering cross section can be written as

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{k'}{k} \frac{\sigma_c}{4\pi} S_{\text{coh}}(\mathbf{Q}, \omega) + \frac{k'}{k} \frac{\sigma_i}{4\pi} S_{\text{inc}}(\mathbf{Q}, \omega), \quad (2.4)$$

where

$$S_{\text{inc}}(Q, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \sum_m \langle \exp\{-i\mathbf{Q} \cdot \mathbf{R}_m(0)\} \exp\{i\mathbf{Q} \cdot \mathbf{R}_m(t)\} \rangle \exp(-i\omega t) dt, \quad (2.5)$$

$$S_{\text{coh}}(Q, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \sum_{m'm} \langle \exp\{-i\mathbf{Q} \cdot \mathbf{R}_{m'}(0)\} \exp\{i\mathbf{Q} \cdot \mathbf{R}_m(t)\} \rangle \exp(-i\omega t) dt. \quad (2.6)$$

2.1. Quasielastic neutron diffraction

The incoherent structure factor $S_{\text{inc}}(\mathbf{Q}, \omega)$ can be rewritten in terms of the self correlation function $I_{\text{self}}(\mathbf{Q}, t)$;

$$S_{\text{inc}}(\mathbf{Q}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} I_{\text{self}}(\mathbf{Q}, t) \exp(-i\omega t) dt, \quad (2.7)$$

$$I_{\text{self}}(\mathbf{Q}, t) = \sum_m \langle \exp\{-i\mathbf{Q} \cdot \mathbf{R}_m(0)\} \exp\{i\mathbf{Q} \cdot \mathbf{R}_m(t)\} \rangle. \quad (2.8)$$

For a rigid crystal, $\mathbf{R}_m(0) = \mathbf{R}_m(t)$ for all times t , hence $I_{\text{self}} = N$ and the incoherent scattering is purely elastic:

$$\frac{d^2\sigma}{d\Omega dE'} = N \frac{k'}{k} \frac{\sigma_i}{4\pi} \delta(\omega). \quad (2.9)$$

For a crystal that contains atoms or molecules that can undergo rotational or diffusive motions this is no longer the case and the self correlation functions are time dependent, as shall be shown in the following sections, giving rise to inelastic incoherent scattering.

In order to determine the form of $S(\mathbf{Q}, \omega)$ due to molecular motions within in a crystal, one can consider distinct models of rotation depending on the local crystal field and the resulting form of $I_{\text{self}}(\mathbf{Q}, t)$. For a molecule rotating within a crystal structure, one can consider three regimes of behaviour, depending on the relative energy scales of the potential landscape that the molecule experiences within the crystal and the thermal motion of the molecule. If the potential barrier separating symmetry equivalent orientations of the molecule is large compared to the rotational constant $\hbar^2/2I$, then the molecule will only undergo small angular oscillations about the equilibrium with a high frequency (librational motion). At temperatures where the molecular thermal motion becomes comparable to the potential energy barriers, the molecule will start to jump between equivalent orientations. For a simple model, one can assume that the jumps are instantaneous with an average time τ between jumps, i.e. the probability of reorientation per unit time is $1/\tau$. In this case, the

timescale τ will show thermally activated behaviour with an Arrhenius temperature dependence. Even though in reality jumps are not instantaneous and there will be a probability distribution describing the molecular orientation, the model is expected to give a good description of reorientational behaviour if the number of molecules performing reorientation is much smaller than the number of molecules located in the potential minima [40]. If the rotational potential is small compared to the thermal energy of the molecule, the large fluctuations of the lattice and neighbouring molecules cause large fluctuations of the crystal field and potential barriers. In this case, molecular motion can be described by a rotational diffusion model, where continuous small angle rotations occur and on average there is no preferred orientation in space.

In the following sections, I shall discuss models applicable for the work presented in this thesis; further details of the models can be found in Ref. [40].

2.1.2 Form of $S(\mathbf{Q}, \omega)$ for diffuse rotations and translations within a crystal

2.1.2.1 Isotropic rotational diffusion

For the case of isotropic rotational diffusion on a sphere of radius r , one considers solutions to the diffusion equation for the orientational probability $P(t)$;

$$D_r \nabla^2 P(t) = \frac{\partial P}{\partial t}, \quad (2.10)$$

where D_r is the rotational diffusion constant. The form of $I_{\text{inc}}(\mathbf{Q}, t)$ can be written as

$$I_{\text{inc}}(\mathbf{Q}, t) = \sum_{\Omega_0} \sum_{\Omega} \exp(iQ(r(\Omega) - r(\Omega_0))) P(\Omega, \Omega_0, t) P(\Omega_0), \quad (2.11)$$

2.1. Quasielastic neutron diffraction

where $P(\Omega_0)$ is the distribution of initial orientations of the molecule, $P(\Omega, \Omega_0, t)$ is the probability distribution of orientations after time t , given an initial orientation Ω_0 and $Q = |\mathbf{Q}|$ [40]. The exponential terms can be expanded in terms of spherical harmonics, while one can expand $P(\Omega, \Omega_0, t)$ in terms of the Wigner rotation matrices. Solving the rotational diffusion equation leads to the form of $I_{\text{inc}}(\mathbf{Q}, t)$ [40];

$$I_{\text{inc}}(\mathbf{Q}, t) = \sum_{l=0}^{\infty} (2l+1) j_l^2(QR) \exp(-l(l+1)D_r t), \quad (2.12)$$

where $j_l(QR)$ are the spherical bessel functions of order l . Therefore, for isotropic rotational diffusion on a sphere of radius r , the scattering function, which is the Fourier transform of $I_{\text{inc}}(\mathbf{Q}, t)$, can be written as a sum of spherical harmonic terms;

$$S_{\text{inc}}^{\text{iso}}(\mathbf{Q}, \omega) = j_0^2(Qr) \delta(\omega) + \sum_{l=1}^{\infty} (2l+1) j_l^2(Qr) L(\omega, \tau_l), \quad (2.13)$$

where $L(\omega, \tau_l)$ is the Lorentzian

$$L(\omega, \tau_l) = \frac{1}{\pi} \frac{\tau_l}{1 + \omega^2 \tau_l^2}. \quad (2.14)$$

Here τ_l is the correlation time for the l^{th} spherical harmonic and is given by

$$\frac{1}{\tau_l} = l(l+1)D_r. \quad (2.15)$$

2.1.2.2 Uniaxial rotational diffusion

A similar expression can also be deduced for isotropic rotations on a circle of radius r , referred to as uniaxial rotation [40]. In this case, the form of $S(\mathbf{Q}, \omega)$ is given by

$$S_{\text{inc}}^{\text{uni}}(\mathbf{Q}, \omega) = J_0^2(Qr \sin \theta) \delta(\omega) + 2 \sum_{m=1}^{\infty} J_m^2(Qr \sin \theta) L(\omega, \tau_m), \quad (2.16)$$

2.1. Quasielastic neutron diffraction

where J_m is a bessel function of the first kind of order m , θ is the angle between the scattering vector and the axis of rotation and τ_m is the correlation time for the m^{th} term, given by

$$\frac{1}{\tau_m} = m^2 D_r. \quad (2.17)$$

2.1.2.3 Bound translational diffusion

Another case that shall be considered is if the molecule is able to undergo translational diffusion along an axis, z , restricted between barriers separated by L_z . The form of $S_{\text{inc}}(\mathbf{Q}, \omega)$ can be written [40]

$$S_{\text{inc}}(\mathbf{Q}, \omega) = A_0(Q_z L_z) \delta(\omega) + \sum_{n=1}^{\infty} A_n(Q_z L_z) L(\omega, \tau_n), \quad (2.18)$$

where

$$A_0(Q_z L_z) = \frac{2(1 - \cos(Q_z L_z))}{(Q_z L_z)^2}, \quad (2.19)$$

$$A_n(Q_z L_z) = \frac{4((Q_z L_z)^2)(1 - (-1)^n \cos(Q_z L_z))}{((Q_z L_z)^2 + (n\pi)^2)^2} \quad (2.20)$$

and

$$\tau_n^{-1} = n^2 \pi^2 D_z / L_z^2. \quad (2.21)$$

This form of $S_{\text{inc}}(\mathbf{Q}, \omega)$ corresponds to a maximum of quasielastic scattering along the q_z direction, where the position of the maximum in q_z is related to the width of the bound region L_z .

2.1.2.4 Uncoupled complex motions

When the molecule is able to undergo several uncoupled motions (rotational, vibrational, translational etc.), one can write

$$I_{\text{inc}}(\mathbf{Q}, t) = I_1(\mathbf{Q}, t) \cdot I_2(\mathbf{Q}, t) \cdot \dots \quad (2.22)$$

Therefore the total scattering function $S_{\text{inc}}(\mathbf{Q}, \omega)$ is given by the convolution of the scattering functions for the individual motions

$$S_{\text{inc}}(\mathbf{Q}, \omega) = S_1(\mathbf{Q}, \omega) * S_2(\mathbf{Q}, \omega) * \dots \quad (2.23)$$

These relations can be used to calculate the scattering function when several uncoupled rotational motions are present. One model considered in Chapter 4 is a model of the CH_3NH_3 molecule in $\text{CH}_3\text{NH}_3\text{PbI}_3$ undergoing uniaxial rotations about the molecular threefold axis in addition to the axis undergoing free rotational motion. This motion can be considered as the convolution of uniaxial rotational motion with a radius of rotation r_1 and isotropic rotational diffusion of the axis with a radius of rotation r_2 . In this case, the scattering function is given by

$$S_{\text{inc}}(\mathbf{Q}, \omega) = \int S_{\text{inc}}^{\text{uni}}(\mathbf{Q}, \omega - \omega') S_{\text{inc}}^{\text{iso}}(\mathbf{Q}, \omega') d\omega'. \quad (2.24)$$

The scattering function for a combination of uniaxial rotation plus isotropic rotational

diffusion can therefore be written as

$$\begin{aligned}
S_{\text{inc}}(\mathbf{Q}, \omega) = & \int \int \{ (J_0^2(Qr_1 \sin \theta) j_0^2(Qr_2) \delta(\omega)) \\
& + 2j_0^2(Qr_2) \sum_{m=1}^{\infty} J_m^2(Qr_1 \sin \theta) L(\omega, \tau_m) \\
& + J_0^2(Qr_1 \sin \theta) \sum_{l=1}^{\infty} (2l+1) j_l^2(Qr_2) L(\omega, \tau_l) \\
& + 2 \sum_{l=1}^{\infty} \sum_{m=1}^{\infty} (2l+1) j_l^2(Qr_2) J_m^2(Qr_1 \sin \theta) L(\omega, \tau_{lm}) \} d\theta d\phi
\end{aligned} \tag{2.25}$$

where

$$\tau_{lm}^{-1} = \tau_m^{-1} + \tau_l^{-1}. \tag{2.26}$$

The double integral over θ, ϕ takes into account the spherical averaging of the uniaxial rotation as the axis diffuses in an isotropic manner. Therefore the form of $S_{\text{inc}}(\mathbf{Q}, \omega)$ includes an elastic term, a spherically averaged uniaxial rotation term, an isotropic rotation term and a mixed term arising from the convolution of two Lorentzian energy distributions. When the correlation time of one motion is much shorter than the other, the faster motion will give a sum of Lorentzians with a broad energy distribution while the slower motion will give a sum of narrow Lorentzians. The width of the mixed term will be dominated by the faster motion, and in the limit $\tau_{\text{slow}} \gg \tau_{\text{fast}}$, the mixed term can be incorporated into the amplitudes of the fast motion. Assuming the uniaxial rotation to be the fast motion, the sum of the prefactors is unity for the terms including $\sum_{m=1}^{\infty}$, therefore in the approximation that $\tau_{lm} \approx \tau_m$ it can be written

$$\begin{aligned}
S_{\text{inc}}(\mathbf{Q}, \omega) \approx & \int \int \{ J_0^2(Qr_1 \sin \theta) \left[j_0^2(Qr_2) \delta(\omega) + \sum_{l=1}^{\infty} (2l+1) j_l^2(Qr_2) L(\omega, \tau_l) \right] \\
& + 2 \sum_{m=1}^{\infty} J_m^2(Qr_1 \sin \theta) L(\omega, \tau_m) \} d\theta d\phi.
\end{aligned} \tag{2.27}$$

2.1.3 Form of $S(\mathbf{Q}, \omega)$ for jump rotations between symmetry equivalent orientations

When a molecule undergoes jump motions in a crystal field of a given symmetry, one can use group theory techniques to derive the form of $I_{\text{inc}}(\mathbf{Q}, t)$. This is also true when one is considering a combination of jumps around crystallographic axes as well as rotations about molecular axes, under the assumption that the two types of jumps occur independently, which allows each motion to be described by a characteristic timescale.

For rotations in a crystal field of a given point symmetry, one can define the probability per unit time of a rotation belong to the class ν of the point group as τ_ν^{-1} , where τ_ν represents the average time between jumps. It can be shown that $I_{\text{inc}}(\mathbf{Q}, t)$ can be written as a product of an amplitude A_μ and an exponential decay with a characteristic timescale τ_μ summed over the irreducible representations Γ_μ of the point group [40];

$$I_{\text{inc}}(\mathbf{Q}, t) = \sum_{\mu} A_{\mu}(\mathbf{Q}) \exp(-t/\tau_{\mu}). \quad (2.28)$$

The amplitudes and characteristic timescales are given by

$$A_{\mu}(\mathbf{Q}) = \frac{\chi_{\mu}^E}{g} \sum_{\nu} \chi_{\mu}^{\nu} \sum_{C_{\nu}} \exp\{i\mathbf{Q} \cdot (\mathbf{R} - C_{\nu}\mathbf{R})\}, \quad (2.29)$$

$$\frac{1}{\tau_{\mu}} = \sum_{\nu} \frac{n_{\nu}}{\tau_{\nu}} \left(1 - \frac{\chi_{\mu}^{\nu}}{\chi_{\mu}^E}\right), \quad (2.30)$$

where ν labels the classes of C , C_{ν} is an operator in class ν , g is the order of the point group, χ_{μ}^{ν} is a character of class ν belonging to the irreducible representation μ and n_{ν} is the number of operators in class ν . Therefore, given the atomic coordinates of the molecule, one can calculate the amplitudes $A_{\mu}(\mathbf{Q})$ for a given scattering vector $\mathbf{Q}$ by performing a sum over the translation vectors $\mathbf{R} - C_{\nu}\mathbf{R}$ resulting from applying

2.1. Quasielastic neutron diffraction

the relevant symmetry operations to the molecule.

As $S_{\text{inc}}(\mathbf{Q}, \omega)$ is given by the Fourier transform of $I_{\text{inc}}(\mathbf{Q}, t)$, the resultant form of $S_{\text{inc}}(\mathbf{Q}, \omega)$, in the presence of thermal atomic displacements characterised by $\langle u^2 \rangle$, is given by

$$S_{\text{inc}}(\mathbf{Q}, \omega) = \exp\{-\langle u^2 \rangle Q^2\} \{A_0(\mathbf{Q})\delta(\omega) + \sum_{\mu=1}^n A_{\mu}(\mathbf{Q})L(\omega, \tau_{\mu})\} \quad (2.31)$$

where $L(\omega, \tau_{\mu})$ is the Lorentzian

$$L(\omega, \tau_{\mu}) = \frac{1}{\pi} \frac{\tau_{\mu}}{1 + \omega^2 \tau_{\mu}^2}. \quad (2.32)$$

The $A_0(\mathbf{Q})\delta(\omega)$ term arises from the totally symmetric irreducible representation and is the amplitude for elastic incoherent scattering. The second term sums the products of the amplitudes and Lorentzian energy distributions of scattering for the remaining n irreducible representations and gives rise to quasielastic scattering. The amplitudes describe how the scattering is distributed as a function of scattering vector $\mathbf{Q}$, while the Lorentzian functions describe how this scattering amplitude is distributed as a function of energy transfer ω .

This formalism can also be applied to the motion of a molecule undergoing jump rotations in a crystal point group C as well as rotations about the mobile molecular axis, i.e. rotations in a molecular point group M . In this case, one considers the direct product group $\Gamma = C \times M$ and it can be shown that the form of $I_{\text{inc}}(\mathbf{Q}, t)$ is given by Equation 2.28, but where the sum is performed over irreducible representations of the direct product group Γ [40]. The amplitudes and characteristic timescales are

then given by

$$A_\mu(\mathbf{Q}) = \frac{\chi_\mu^{Ee}}{g} \sum_\nu \sum_\eta \chi_\mu^{\nu\eta} \sum_{C_\nu} \sum_{M_\eta} \exp\{i\mathbf{Q} \cdot (\mathbf{R} - C_\nu M_\eta \mathbf{R})\} \quad (2.33)$$

$$\frac{1}{\tau_\mu} = \sum_\nu \frac{n_\nu}{\tau_\nu} \left(1 - \frac{\chi_\mu^{\nu e}}{\chi_\mu^{Ee}}\right) + \sum_\eta \frac{n_\eta}{\tau_\eta} \left(1 - \frac{\chi_\mu^{E\eta}}{\chi_\mu^{Ee}}\right) \quad (2.34)$$

where ν, η label the classes of C, M and μ labels the irreducible representations of Γ . g is the order of Γ , χ is a character in the direct product group and n_ν is the number of operators in class ν . In a similar manner to the case of purely crystallographic rotations, one can calculate the amplitudes $A_\mu(\mathbf{Q})$ for a given scattering vector $\mathbf{Q}$ by performing a sum over the translation vectors $\mathbf{R} - C_\nu M_\eta \mathbf{R}$ resulting from applying the combined symmetry operations to the molecule for each irreducible representation of the product group.

2.1.4 Quasielastic neutron diffraction on the OSIRIS spectrometer

One method to produce neutrons for experimental research is through neutron spallation, where a high energy proton beam impacts upon a target, producing high energy neutrons. This method is used at the ISIS neutron source at the Rutherford Appleton Laboratory. A synchrotron is used to produce a proton pulse at a frequency of 50 Hz, which impacts upon a tungsten target, producing high energy neutrons. Neutron moderators, such as liquid hydrogen or liquid methane, are used to reduce the energy of the neutrons to energies that are useful for research of condensed matter systems.

The OSIRIS instrument at the ISIS neutron source receives neutrons from a liquid hydrogen moderator cooled to 25 K and therefore receives neutrons with a low energy/long wavelength. Two disc choppers are used to define the energy range of

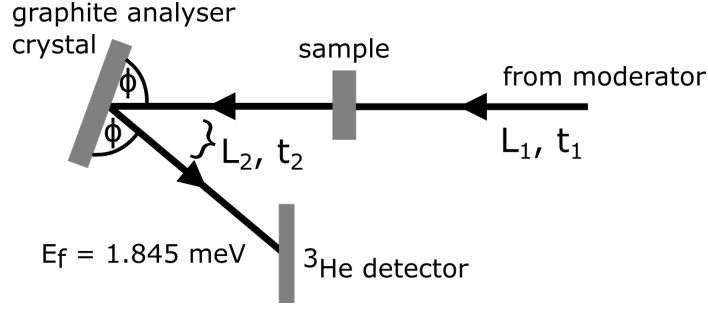


Figure 2.1: Indirect scattering geometry of the OSIRIS spectrometer.

the incident neutrons and also limit frame overlap from neighbouring neutron pulses. Mirror guides focus the neutron beam onto the sample position, giving flux across an area 44 mm high by 22 mm wide. The OSIRIS instrument contains two detector banks, enabling it to be used as either a long-wavelength diffractometer or a high resolution quasielastic spectrometer. For diffraction measurements, a detector bank consisting of 962 ZnS tubes is located at scattering angles $150^\circ < 2\theta < 170^\circ$. For quasielastic spectroscopy measurements an indirect geometry is used, as shown in Figure 2.1. This consists of a graphite crystal analyser array, which is used to select scattered neutrons with one fixed energy, and a detector assembly of 42 ^3He tubes. The spectroscopy detector covers an effective 2θ range of $11^\circ < 2\theta < 150^\circ$ and a vertical range of $\pm 12^\circ$ out of the plane. In the experiments presented in this thesis, the spectrometer of OSIRIS was primarily used to study the molecular motion in $\text{CH}_3\text{NH}_3\text{PbI}_3$ by quasielastic neutron scattering, while the backscattering detector was used at the beginning of the experiment to determine the crystal alignment.

2.1.4.1 Energy and momentum analysis on OSIRIS

In a quasielastic scattering experiment, the final energy E_F of a detected neutron can be written in terms of the flight time t_2 and path length L_2

$$E_F = \frac{1}{2}mv^2 = \frac{1}{2}m\left(\frac{L_2}{t_2}\right)^2, \quad (2.35)$$

where m is the neutron mass. This can be rewritten in terms of the d -spacing of the analyser bank and bragg reflection angle ϕ ;

$$E_F = \frac{1}{2m} \left(\frac{h}{\lambda}\right)^2 = \frac{1}{2m} \left(\frac{h}{2d\sin(\phi)}\right)^2, \quad (2.36)$$

where h is the Planck constant.

Combining the two expressions for E_F leads to an expression for t_2 in terms of known quantities

$$t_2 = 2mL_2d\sin(\phi)/h. \quad (2.37)$$

If the total time of flight from the moderator to detector is given by $t = t_1 + t_2$, the energy transfer can be written in terms of the known parameters L_1 , L_2 , d , ϕ and measured total time of flight t ;

$$\Delta E = E_i - E_f = \frac{1}{2m} \left(\left(\frac{L_1}{t_1}\right)^2 - \left(\frac{L_2}{t_2}\right)^2 \right) = \frac{1}{2m} \left(\left(\frac{L_1}{t - t_2}\right)^2 - \left(\frac{L_2}{t_2}\right)^2 \right) \quad (2.38)$$

During a quasielastic scattering experiment, each detector therefore measures the scattering intensity as a function of total time of flight t , which is converted to energy transfer to give a spectrum of scattering intensity as a function of energy transfer.

In addition to energy transfer, one can determine the momentum transfer $\mathbf{Q}$ during a quasielastic scattering measurement. The momentum transfer is defined as

$$\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f, \quad (2.39)$$

2.1. Quasielastic neutron diffraction

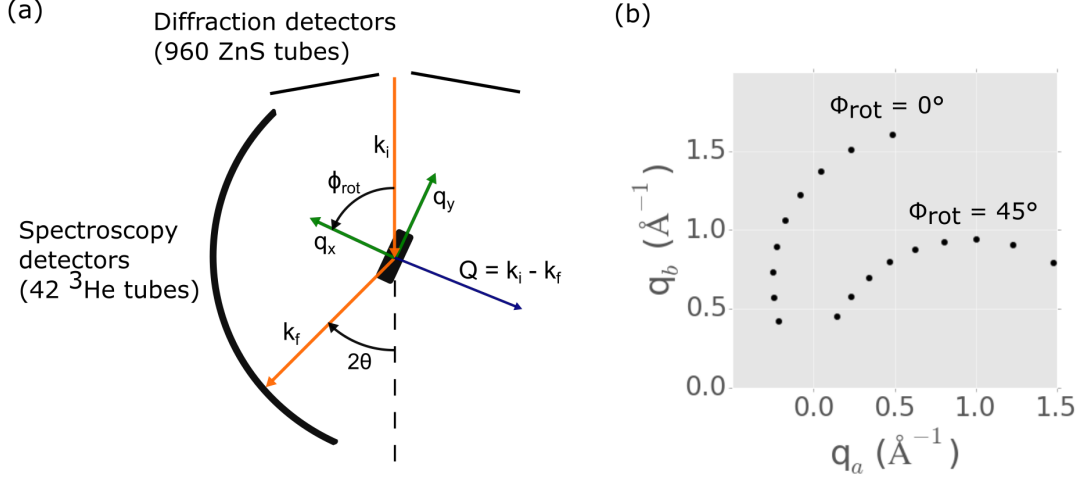


Figure 2.2: (a) Instrumental geometry of a single crystal scattering experiment on OSIRIS. (b) Example paths traced in the scattering plane for a single crystal experiment. Rotating the crystal array allows scattering in different directions in the plane to be mapped.

where $\mathbf{k}_i$ and $\mathbf{k}_f$ are the initial and final neutron wavevectors, as shown in Figure 2.2(a). Conservation of energy requires that

$$\Delta E = E_i - E_f = \frac{\hbar^2 k_i^2}{2m} - \frac{\hbar^2 k_f^2}{2m}, \quad (2.40)$$

where $k = |\mathbf{k}|$. In order to relate the momentum transfer to the energy transfer, one can use the relation

$$|\mathbf{Q}|^2 = k_i^2 + k_f^2 - 2k_i k_f \cos(2\theta). \quad (2.41)$$

Using the fact that

$$\frac{\hbar^2}{2m}(k_i^2 + k_f^2) = E_i + E_f = 2E_f + \Delta E \quad (2.42)$$

and

$$\frac{\hbar^2}{2m}k_i k_f = (E_i E_f)^{\frac{1}{2}} = (E_f(E_f + \Delta E))^{\frac{1}{2}} \quad (2.43)$$

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leads to the relation

$$\frac{\hbar^2 |\mathbf{Q}|^2}{2m} = 2E_f + \Delta E - 2\cos(2\theta)(E_f(E_f + \Delta E))^{\frac{1}{2}}. \quad (2.44)$$

Therefore, scattering at high $|\mathbf{Q}|$ occurs at high angles, while there is also a $|\mathbf{Q}|$ -dependence on energy transfer ΔE .

Quasielastic scattering measurements are typically performed on powder samples, where powder averaging ensures that for a given scattering vector $\mathbf{Q}$, the interaction with the sample is a spherical average over all points in reciprocal space where $|\mathbf{Q}| = |\mathbf{q}|$, where $\mathbf{q}$ is a vector in the reciprocal space of the crystal. For experiments on a single-crystal, one can use the vector nature of $\mathbf{Q}$ to investigate scattering in different directions in reciprocal space. This can be done by rotating a crystal sample, such that $\mathbf{Q}$ is rotated through the reciprocal space defined by the crystal lattice, as shown in Figure 2.2(b). The orientation of the reciprocal lattice can be determined accurately on OSIRIS by observing known Bragg reflections in the backscattering diffraction bank. Knowledge of the orientation can then be used to convert the Q -value for each detector, into a $\mathbf{q}$ -vector for the sample. As such, in a single crystal experiment, the dataset consists of the scattering intensity S as a function of q_x , q_y and ΔE . The OSIRIS spectrometer is not sensitive to the q_z component of the scattered neutrons, and as the detector bank only covers a vertical range of $\pm 12^\circ$ out of the plane, it shall be assumed that $q_z = 0$ for the analysis of the quasielastic scattering data ^a.

2.1.4.2 Sample environment

Samples were mounted onto an aluminium finger on a rotation stage in a closed cycle refrigerator (CCR). The rotation stage allowed rotation of the crystal about the axis normal to the scattering plane. A small amount of helium exchange gas (~ 10 mbar)

^aThe angular variation of quasielastic scattering intensity typically follows a $\cos^2(\theta)$ -type dependence, therefore over 12° the angular variations in intensity will be less than 5%, justifying the assumption.

was used to control the temperature of the CCR, allowing measurements across a temperature range of 10 K to 350 K.

2.2 Dielectric spectroscopy

The dielectric response of a material contains a wealth of information on the dynamics of charged objects within a material. In this Section, I shall define quantities of interest and discuss the dielectric response of a number of regimes of behaviour relevant for the work presented in this thesis.

2.2.1 Theory of dielectric relaxation in solids

The electrical displacement $\mathbf{D}$ is defined as

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P}, \quad (2.45)$$

where $\mathbf{E}$ is an external electric field, $\mathbf{P}$ is the polarisation density of the material and ϵ_0 is the permittivity of free space. Here $\mathbf{P}$ includes permanent polarisation density, such as from a ferroelectric polarisation, and polarisation density induced by the electric field.

In a linear dielectric, the induced polarisation is related to the electric field by the susceptibility χ ;

$$\mathbf{P} = \epsilon_0 \chi \mathbf{E}. \quad (2.46)$$

In this case, one can define the dielectric permittivity ϵ , which relates the electrical displacement to $\mathbf{E}$;

$$\mathbf{D} = \epsilon \mathbf{E}. \quad (2.47)$$

In general, the dielectric permittivity is a complex rank-2 tensor, which is also frequency dependent (the same is true of χ). It is also useful to define the

dimensionless relative complex permittivity $\tilde{\epsilon}_r$:

$$\tilde{\epsilon}(\omega) = \tilde{\epsilon}_r(\omega)\epsilon_0 = \epsilon'(\omega) + i\epsilon''(\omega). \quad (2.48)$$

When considering systems with a frequency dependence, it is usually more intuitive to consider the relative frequency-dependent susceptibility $\tilde{\chi}(\omega)$, defined by Jonscher [41] as

$$\tilde{\chi}(\omega) = (\tilde{\epsilon}(\omega) - \epsilon_\infty)/\epsilon_0 = \chi'(\omega) + i\chi''(\omega), \quad (2.49)$$

where ϵ_∞ is the frequency-independent value of ϵ at high frequencies. By removing the static high-frequency dielectric constant, the true frequency dependence of χ due to a given physical mechanism is often more evident [41].

In general, one can identify two distinct types of dielectric relaxation; dipolar-type relaxation and charge carrier behaviour. Dipolar polarisation does not leave any residual polarisation upon discharging, whereas charge carrier behaviour typically leaves a finite polarisation within the material [41]. I shall discuss the characteristic dielectric responses of the two types of behaviour in the following sections.

2.2.2 Dipolar relaxation

Debye first introduced a model to describe the dielectric response of a noninteracting system of dipoles to an external electric field [42]. The response is given by

$$\tilde{\chi}(\omega) = \frac{\chi_s}{1 + i\omega\tau} = \frac{\chi_s}{1 + \omega^2\tau^2} - i\frac{\chi_s\omega\tau}{1 + \omega^2\tau^2} \quad (2.50)$$

where χ_s is the ‘static’ susceptibility (i.e. the susceptibility for $\omega \rightarrow 0$) and τ is the characteristic relaxation time of the dipole, assumed to be the same for each dipole. The Debye response calculated from Equation 2.50 is plotted in Figure 2.3. The form of susceptibility corresponds to a smooth step-like reduction in the real part of χ , and

2.2. Dielectric spectroscopy

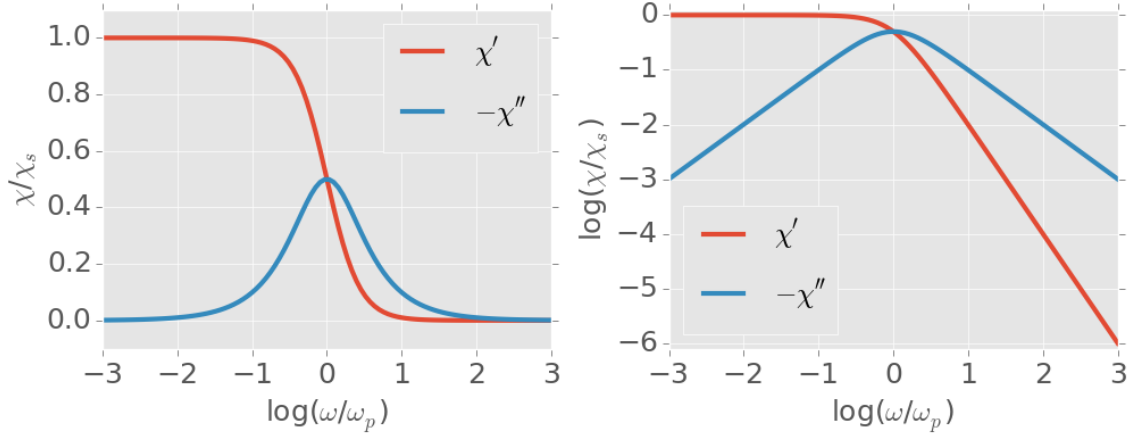


Figure 2.3: (a) Frequency dependence of the real and imaginary parts of the dielectric susceptibility for a system of ideal non-interacting dipoles with a characteristic relaxation time $\tau = 1/\omega_p$ (the Debye model). As χ'' is a measure of the dielectric loss, it has a negative phase relative to χ' ; $-\chi''$ is therefore equal to the magnitude of χ'' , which is the experimentally measured quantity (through ϵ''). (b) When plotted on a log-log scale, the imaginary part of χ has a gradient of ± 1 on either side of the maximum susceptibility, while the real part of χ has a gradient of -2 above the relaxation peak.

a peak in the imaginary part of χ , with the loss peak centred at a frequency $\omega_p = 1/\tau$. When plotted on a log-log scale, for $\omega \lesssim 10\omega_p$, $-\chi''$ has a gradient of 1 while χ' is frequency independent. However, for $\omega \gtrsim 10\omega_p$, $-\chi''$ has a gradient of -1 while χ' has a gradient of -2; this fact is important in distinguishing the frequency dependence of a Debye-type relaxation from charge carrier behaviour, as shall be discussed in the following section.

In real systems there is typically some interaction between dipoles and a distribution of relaxation times, which leads to a broadening of the Debye-type response that can be most generally described by the empirical Havriliak-Negami relaxation model. This introduces both symmetric and asymmetric broadening, with a susceptibility of the form

$$\tilde{\chi}(\omega) \propto [1 + (i\omega\tau)^m]^{(n-1)/m}, \quad (2.51)$$

which corresponds to a loss peak with a frequency dependence of $\chi''(\omega) \propto \omega^m$ for $\omega \ll 1/\tau$, and $\chi''(\omega) = \cot(n\pi/2)\chi'(\omega) \propto \omega^{n-1}$ for $\omega \gg 1/\tau$, where n, m are in the range 0 to 1 [41].

The dipolar-type response is not limited to electronic or molecular dipoles, but can apply to any physical system where a dipolar electrical polarisation occurs with a characteristic relaxation time. For example, the Debye response is also observed for an ideal resistor R and capacitor C in series, as the charge stored across the capacitor is an electric dipole and there is a characteristic time for depolarisation through the resistor with a time constant $t = RC$, giving a Debye response with a relaxation frequency $\omega_p = 1/RC$.

The Debye-type response is therefore important to consider for materials which have bulk conductive regions in addition to interfacial capacitive regions, such as grain boundaries, which can lead to a dipolar response with a large dielectric constant that is sometimes referred to as Maxwell-Wagner polarisation. Another example of a dipolar-type response is due to electrode polarisation, where an insulating layer at the electrodes causes an electric polarisation to develop due to the build up of charge carriers, a model which is particularly relevant to ionic conductors [43].

2.2.3 Charge carrier behaviour and the universal dielectric response

In the presence of conductive charge carriers, the electrical conductivity gives a contribution to the imaginary part of the dielectric constant;

$$\epsilon(\omega) = \epsilon'(\omega) + i \frac{\sigma(\omega)}{\omega}. \quad (2.52)$$

Therefore for the case of DC conduction, $\sigma(\omega) = \sigma_{DC}$, and one expects $\epsilon'' \propto 1/\omega$. However, for a system of hopping charge carriers, such as ions or hopping electrons,

2.2. Dielectric spectroscopy

dispersion is typically observed in the frequency spectrum and a ‘universal’ dielectric response is often observed.

The existence of a ‘universal’ dielectric response has been discussed in detail by Jonscher [41], where it is observed that under a wide range of circumstances, including in dipolar and hopping carrier systems, the frequency dependence of the complex susceptibility $\tilde{\chi}(\omega)$ at high frequencies follows a fractional power law

$$\tilde{\chi}(\omega) \propto (i\omega)^{(n-1)}, \quad (2.53)$$

where n is typically in the range $0.7 < n < 0.9$, i.e. a fairly flat frequency dependence compared to a Debye-type response. The frequency dependence leads to a Kramers-Kronig relation between the real and imaginary susceptibilities

$$\chi''(\omega)/\chi'(\omega) = \cot(n\pi/2), \quad (2.54)$$

where both the real and imaginary parts of χ follow the same power law frequency-dependence.

Jonscher also notes that for materials where the conduction is due to hopping charge carriers (electronic or ionic carriers), two distinct power law regions are observed in the frequency spectrum. At high frequencies, a low level of dispersion is observed, and a power law with high values of n is observed. As the frequency reduces, there is a transition to a second regime, where behaviour known as low-frequency dispersion (LFD) is observed. LFD is characterised by small values of n , typically between 0.1 and 0.01, indicating a conductivity with a weak frequency dependence $\sigma(\omega) \propto \omega^n$ [41]. This behaviour is distinct from true DC conductivity, for which $n = 0$. Importantly, the increase in $\chi'(\omega)$ as the frequency reduces implies reversible charge storage in the material, whereas in DC conduction there is no stored charge and χ' is independent of frequency. The physical origin of the

2.2. Dielectric spectroscopy

fractional power law is due to the fact that the ratio of the imaginary to real components of the susceptibility, as given by Equation 2.54, is equal to the ratio of the energy loss (associated with conduction) to the electrostatic energy stored within the dielectric. The frequency independence of n occurs when the energy lost in every microscopic reversal of polarisation is independent of the rate of reversals [44].

LFD is widely observed for ionic conductors, however there are examples of LFD arising from hopping electronic systems [45]. Reports in the literature of LFD due to electronic hopping are limited to organic charge transfer complexes (CTC), as opposed to covalent or ionic compounds [45]. Furthermore, the rise in $\chi'(\omega)$ at low frequency in electronic systems implies that the electrons can only hop within the material and that some blocking must occur at the contacts, which may be relevant for electrons hopping between organic molecules in an organic CTC but is not obviously applicable to electronic transport in semiconductors. For ionic conduction, the conductivity is thermally activated with an Arrhenius-like activation [30]:

$$\sigma = nq\mu = nq\frac{qD}{k_BT}, \quad (2.55)$$

$$D = D_0\exp(-E_a/k_BT), \quad (2.56)$$

where n is the density of vacancies of charge q . D is the diffusion coefficient, which is thermally activated, where E_a is the activation energy to overcome the potential barrier between neighbouring sites.

An approximate expression for the D_0 constant can be determined by considering an atom attempting to overcome a barrier of height E_a between potential minima. If the atom vibrates in the potential minima with a frequency f_0 , the probability per unit time that the atom will have the thermal energy to pass over the barrier is given by $f_0\exp(-E_a/k_BT)$ [30]. Hence, the rate of jumps Γ for an atom with z nearest

2.2. Dielectric spectroscopy

neighbours is given by

$$\Gamma = z f_0 \exp(-E_a/k_B T). \quad (2.57)$$

In order to relate this to an approximate diffusion coefficient, one can use the Einstein-relation for the time-dependent mean-square displacement due to diffusion:

$$\langle (\delta x(t))^2 \rangle = 2dDt, \quad (2.58)$$

where d is the dimensionality of the diffusive motion. Setting the mean square distance to be equal to the jump distance a , one can combine Equations 2.57 and 2.58 to obtain a 3D diffusion coefficient

$$D \approx \frac{z}{6} f_0 a^2 \exp(-E_a/k_B T). \quad (2.59)$$

Therefore, the conductivity can be written

$$\sigma \approx \frac{z f_0 a^2 n q^2}{6 k_B T} \exp(-E_a/k_B T). \quad (2.60)$$

In summary, the theory of dielectric relaxation of solids gives a clear distinction between dipolar and hopping charge carrier behaviour. In particular, at lower frequencies a dispersion is typically observed for hopping charge carriers, where both χ' and χ'' follow the same fractional power law giving large values of susceptibility at low frequency and implying a reversible storage of charge within the material.

Chapter 3

Ionic conduction and electrical hysteresis in $\text{CH}_3\text{NH}_3\text{PbI}_3$

3.1 Introduction

Amongst the wide range of materials studied for use in photovoltaic devices, the lead halide perovskites have received widespread attention in the scientific community over the past five years. This family of materials has the ABX_3 perovskite crystal structure, where B is a metallic cation (typically lead), X is a halide anion (iodide, bromide or chloride) and A is a cation (typically an organic molecule such as methylammonium ($\text{MA} = \text{CH}_3\text{NH}_3$) or formamidinium ($\text{FA} = \text{CH}(\text{NH}_2)_2$)). Initially investigated as a light harvester in electrolytic solar cells [46], it was discovered that solid-state solar cells consisting of a layer of $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanocrystals were able to produce devices with power conversion efficiencies (PCEs) above 9% [5,6]. Since this discovery, intensive research activity has seen rapid increases in efficiency for halide-perovskite based devices, with PCEs above 20% now regularly reported and a highest certified efficiency of 22.1% [33]. This rapid increase in efficiency, combined with the low cost of solution processing methods used to create halide-perovskite photovoltaic devices,

has made halide-perovskite devices commercially viable, with several companies now commercialising perovskite photovoltaic devices.

3.1.1 $\text{CH}_3\text{NH}_3\text{PbI}_3$ as a photoabsorber for photovoltaic devices

Several physical properties make lead halide perovskites good materials for use in photovoltaic devices; a suitable band gap, highly mobile charges with low recombination and the ability to tune the band gap by creating compounds with mixed ratios of the halide ions, such as $\text{CH}_3\text{NH}_3\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$. The prototypical halide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ has a band gap of $\sim 1.55\text{ eV}$ [6, 47], which is fairly close to the optimal band gap of 1.34 eV for a single-layer photovoltaic device as determined by the Shockley-Queisser limit [29]. Furthermore, the band gap can be reduced to 1.48 eV by replacing MA with FA [47], while chemical tuning of the band gap is possible through varying the halide ion fraction x in $\text{CH}_3\text{NH}_3\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$ and $\text{CH}(\text{NH}_2)_2\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$ devices [47, 48]. Together this enables the band gap to be tuned in the range 1.48 eV to 2.28 eV , making halide perovskites suitable for both single layer devices and as part of multi-layer tandem devices.

Alongside their favourable optical properties, the halide perovskites display remarkably good electronic properties in photovoltaic devices. Upon photoexcitation, excitons rapidly dissociate and the high carrier mobilities and diffusion lengths allow photoexcited charges to be efficiently extracted under device operating conditions [49–51]. This is due to several factors. First, it is evident from many studies that a halide perovskite layer with a large crystal grain size up to $1\text{ }\mu\text{m}$ can be formed from a variety of solution processing and vapour deposition methods [35, 52–55]. The ability to form high quality films causes minimal electronic trap states within the band gap, as evidenced by a sharp onset in absorption at the band edge [56] and large diffusion lengths [50]. As well as low rates of

3.1. Introduction

mono-molecular recombination (due to trap-assisted recombination), low rates of bi-molecular (electron-hole) recombination were also determined from THz spectroscopy studies [31]. The measured bi-molecular recombination rates in $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{Pb}(\text{Cl}_x\text{I}_{1-x})_3$ were found to exceed the Langevin recombination limit ^a by four orders of magnitude, enabling a diffusion length of above one micron in the low carrier density regime, which was suggested to arise from spatial separation of electrons and holes within the crystal structure of $\text{CH}_3\text{NH}_3\text{PbI}_3$ [31].

Despite the excellent physical properties of the halide perovskites for photovoltaic applications, a number of issues still need to be addressed. One issue is thermal stability and sensitivity to moisture. Rapid degradation is observed when perovskite photovoltaics are aged under sunlight without suitable encapsulation due to the effect of moisture [37]. Degradation is also observed at elevated temperatures, hence the stability of perovskite based devices under environmental conditions is an important issue to address for the long-term stability of photovoltaic devices [57–59]. Another issue identified in the literature is the issue of current-voltage hysteresis and anomalous electronic properties of devices, such as a low-frequency giant dielectric constant and interfacial charging [11, 60–62]. Investigating the underlying mechanisms causing these unusual electronic properties of $\text{CH}_3\text{NH}_3\text{PbI}_3$ photovoltaic devices is the focus of this chapter.

3.1.2 The issue of current-voltage hysteresis and anomalous electronic properties

Current-voltage hysteresis is defined as a difference in the current-voltage characteristics of a photovoltaic device, depending on the direction of voltage scan

^aThe Langevin recombination limit is a classical result which states that higher carrier mobilities lead to an increased recombination rate due to the increased likelihood of collisions between electrons and holes, thereby limiting the diffusion length.

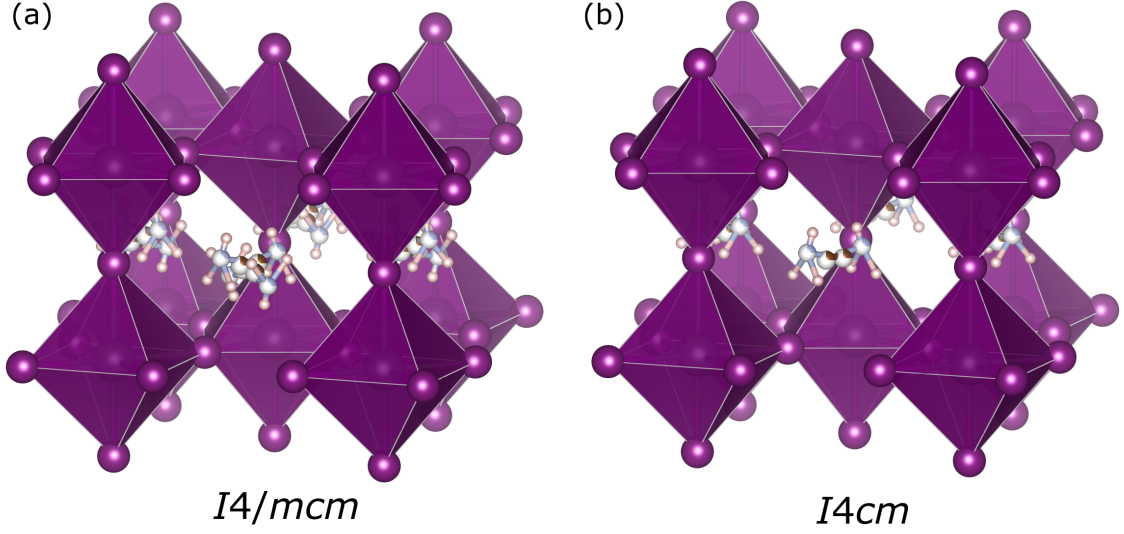


Figure 3.1: (a) *I4/mcm* tetragonal structure of CH₃NH₃PbI₃ at 180 K between $z = 0$ and $z = 0.5$ as reported in the literature [63]. The methylammonium molecule can occupy one of four symmetry equivalent positions, two of which correspond to a molecular dipole with a component along $+c$, and two which have an equivalent component along $-c$. (b) Atomic arrangement for an *I4cm* tetragonal structure of CH₃NH₃PbI₃ between $z = 0$ and $z = 0.5$ as assigned in [64]. In this structure, the methylammonium molecular dipole occupies one of two symmetry equivalent positions, both with a dipole component along $+c$. A displacement of the iodine atoms along $\pm c$ is also allowed.

between forward bias and short circuit configurations (i.e. the history of the device). This effect was characterised in detail by Snaith *et al.* [11], where the magnitude of hysteresis was shown to depend on scan rate, biasing history, contact material and lighting conditions. Resolving and understanding the hysteresis issue was said to be essential to further progress in perovskite photovoltaics [11]. Several explanations were proposed as the origin of the hysteresis effect; an intrinsic ferroelectric nature of the perovskite material, charge traps at the perovskite surface or ionic migration leading to electronic band bending at the perovskite-electrode interface.

The possibility of ferroelectric behaviour has been proposed as the general cubic perovskite crystal structure is able to undergo polar distortions which cause a ferroelectric polarisation to develop, such as for the type-I ferroelectrics BaTiO₃ and

3.1. Introduction

BiFeO₃. The theory of a ferroelectric behaviour of CH₃NH₃PbI₃ gained momentum after a crystallographic study of the room temperature tetragonal phase assigned the polar *I4cm* space group alongside claims of a ferroelectric current response [64], as opposed to the previously accepted non-polar *I4/mcm* space group [65,66].

In general, the perovskite crystal structure and presence of a polar molecule such as CH₃NH₃⁺ give two potential mechanisms for ferroelectricity in the halide perovskites; a polar distortion of the Pb-X framework, or a molecular ferroelectricity due to orientational ordering of the MA/FA molecular dipoles. A comparison of the molecular orientations in the *I4/mcm* and *I4cm* structures is shown in Figure 3.1. In the *I4/mcm* structure, the CH₃NH₃ molecular dipole occupies one of four symmetry equivalent orientations, with an average dipole moment of zero, however in the *I4cm* structure there are only two symmetry equivalent orientations, both of which have a dipole moment along the +*c* direction. Furthermore, *ab initio* studies of CH₃NH₃PbI₃ have predicted ferroelectric polarisations of 4.4 μC cm⁻² [67] and 38 μC cm⁻² [68]. There have also been several reports in the literature of electrical measurements of CH₃NH₃PbI₃ films that are claimed by the authors to indicate a ferroelectric response [64,69]. However in order to conclusively provide evidence of a ferroelectric response, it is necessary to measure the ferroelectric hysteresis loop, of which there have been no definitive measurements in the literature.

In this chapter I will investigate the potential ferroelectric response of the prototypical halide perovskite CH₃NH₃PbI₃ through hysteresis loop measurements of CH₃NH₃PbI₃ thin films. I shall also present dielectric spectroscopy measurements on crystals which reveal the extent of ionic conduction in the halide perovskites and discuss the relationship between ionic migration and current-voltage hysteresis. The issues of crystallography and space group symmetry are addressed in Chapter 4. The thin film measurements presented in this chapter were published in the following article [70].

3.2 Hysteresis loop measurements on thin film $\text{CH}_3\text{NH}_3\text{PbI}_3$

The defining property of ferroelectricity is the existence of a macroscopic electrical polarisation that can be reversed with an applied electric field. As such, the definitive experimental measurement of ferroelectricity is the measurement of a polarisation electric-field hysteresis loop. In the simplest case, this can be done by applying a sinusoidal voltage waveform across the material and measuring the surface charge density due to polarisation reorientation during the measurement. However, the electric fields needed to switch a ferroelectric polarisation are often large, causing additional contributions to the charge density due to effects including dielectric polarisation and conduction, which can be a significant issue for poor insulators and thin film samples.

3.2.1 The Double Wave Method for measuring hysteresis

For measurements of the potential ferroelectric response of $\text{CH}_3\text{NH}_3\text{PbI}_3$, the double-wave method (DWM) was used to separate hysteretic effects from non-hysteretic effects [71]. In the DWM, a voltage waveform is applied to the material of interest using a Sawyer-Tower circuit as shown in Figure 3.2(a). The waveform was generated by a voltage output of a computer and was applied across a $\text{CH}_3\text{NH}_3\text{PbI}_3$ 350 nm thick film, fabricated by vapour-assisted solution processing [72]. X-ray diffraction characterisation of the film revealed a polycrystalline nature of the processed film, therefore any polarisation measured would be a powder averaged value ^b. The film was contacted on one side with fluorine-doped tin oxide (FTO) and on the other side with a gold electrode (i.e. the film was solely a layer of $\text{CH}_3\text{NH}_3\text{PbI}_3$ between two electrodes and did not include the electron/hole blocking layers of a typical

^bI am grateful to Dr. Giles Eperon for fabricating the $\text{CH}_3\text{NH}_3\text{PbI}_3$ films and performing the growth characterisation by X-ray diffraction.

3.2. Hysteresis loop measurements on thin film $\text{CH}_3\text{NH}_3\text{PbI}_3$

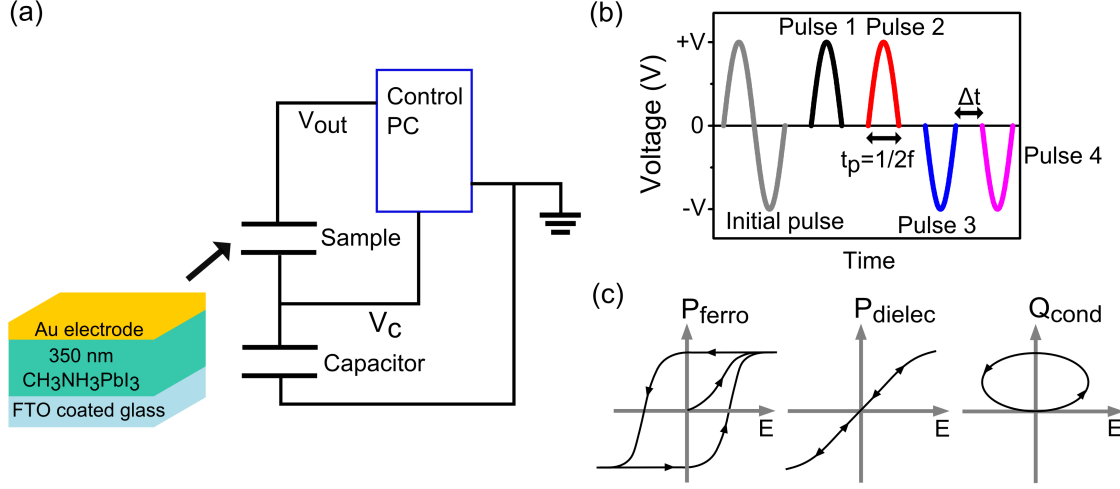


Figure 3.2: (a) Sawyer-Tower circuit arrangement for hysteresis loop measurements. A voltage waveform (b) is applied across the sample which is in series with a reference capacitor that acts as a charge integrator. The DWM waveform allows the hysteretic and non-hysteretic contributions to be separated analytically. (c) The expected E -field dependence of accumulated charges due to ferroelectric polarisation, dielectric polarisation and diode conduction. In semiconductors such as $\text{CH}_3\text{NH}_3\text{PbI}_3$, electronic conduction can cause $Q_{\text{cond}} \gg Q_{\text{ferro}}$, particularly at low measurement frequencies.

photovoltaic device). The film was connected in series with a capacitor, with one side of the capacitor connected to ground, while the capacitor voltage was measured via a voltmeter on a computer. The capacitor acts as an integrator of the surface charge due to dielectric and ferroelectric polarisation, in addition to any conductive current through the film during the measurement:

$$V_c(t) = Q_c(t)/C_{\text{ref}} = [(P(t) \times A) + \int_0^t I_{\text{cond}}(t)dt]/C_{\text{ref}}. \quad (3.1)$$

The waveform of the DWM, shown in Figure 3.2(b), allows separation of hysteretic from non-hysteretic processes. The waveform consists of a sine wave of one period, followed by two half period sine waves with positive voltage and two half period sine waves with negative voltage; these are referred to as the initial pulse and pulses 1-4. The initial pulse acts to pole the sample in the negative direction. The integrated

charge from the first pulse contains any hysteretic switching behaviour in addition to non-hysteretic contributions, such as from dielectric polarisation or conduction. The expected E -field dependence of these contributions are shown in Figure 3.2(c). During the second pulse, only the non-hysteretic contributions are measured, and subtraction of the second signal from the first yields the underlying hysteretic behaviour. This is repeated for pulses 3 and 4, enabling the full hysteresis loop to be analytically reconstructed. A peak voltage of 2 V was used for the measurements, corresponding to an E -field of 5.7 kV mm^{-1} . Higher voltages were found to irreversibly damage the films. During the measurements, C_{ref} was chosen such that $R_{\text{sample}}C_{\text{ref}} \gg t_{\text{pulse}}$, to avoid additional transient responses being introduced into the measurement, which limited the capacitor voltage to 0.2 V. Furthermore, gap times of 10 s were used between pulses to discharge C_{ref} and avoid the introduction of additional hysteretic behaviour. Measurements were made under dark conditions to eliminate photocurrent and measure the intrinsic properties of the films.

3.2.2 Frequency-dependent hysteresis measurements

Hysteresis loops of $\text{CH}_3\text{NH}_3\text{PbI}_3$ films were measured by the DWM across a frequency range from 150 Hz to 0.1 Hz. An example of the capacitor voltage as a function of applied voltage for the four DWM pulses at 2 Hz is shown in Figure 3.3(a).

It is clear that the signal is dominated by non-hysteretic conduction, as a large conductive contribution is seen in all pulses, while the diode-like characteristics of the film cause a larger current flow for negative applied voltages. Nevertheless, there is a clear difference between pulses 1 & 2, and pulses 3 & 4, with a larger increase in the capacitor voltage for pulses 1 & 3, indicating a hysteretic contribution. Analytically subtracting pulses 2 & 4 from pulses 1 & 3 gives the hysteresis loop shown in Figure 3.3(b). The hysteresis loop is plotted in units of $\mu\text{C cm}^{-2}$ to compare to known ferroelectrics. Qualitatively, the shape of the hysteresis loop

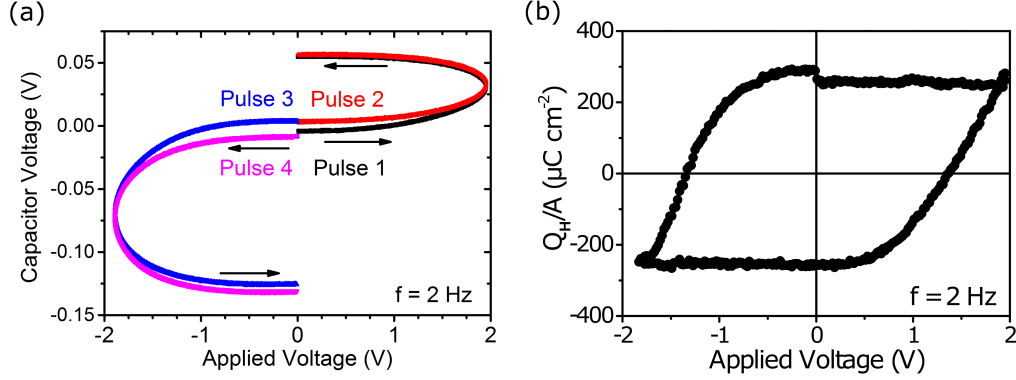


Figure 3.3: DWM measurements on a thin film of $\text{CH}_3\text{NH}_3\text{PbI}_3$. (a) Measured capacitor voltage as a function of applied voltage during the four pulses of the DWM, showing a large conductive contribution but with a clear difference between pulses 1 & 2, and between pulses 3 & 4. (b) Hysteresis loop obtained by analytical subtraction of the DWM pulses. The hysteresis loop is plotted in units of charge density (Q_H/A) to compare to known ferroelectrics. The hysteresis loop shows a response similar to an unsaturated ferroelectric hysteresis loop, but with a large magnitude of charge density.

appears similar to that of an unsaturated ferroelectric hysteresis loop. However, the magnitude of hysteresis far exceeds the best ferroelectrics, particularly at low frequencies.

The frequency dependence of the hysteretic charge density was investigated, the results of which are shown in Figure 3.4. At very low frequencies, the hysteretic charge density exceeds $1000 \mu\text{C cm}^{-2}$, over an order of magnitude larger than the best known ferroelectrics. For example, the perovskite ferroelectric BaTiO_3 has a bulk polarisation of $15 \mu\text{C cm}^{-2}$ [73], which is enhanced to $70 \mu\text{C cm}^{-2}$ in thin films [74], while the largest reported polarisation is $150 \mu\text{C cm}^{-2}$ for thin films of the perovskite ferroelectric BiFeO_3 [75]. Between 150 Hz and 4 Hz, the hysteretic charge density was observed to be linear in $1/f$ (i.e. linear in the time of applied voltage), while there is some saturation of the hysteretic charge density below 0.4 Hz. This behaviour is uncharacteristic of thin-film ferroelectric switching, where the ferroelectric hysteresis is expected to be largely frequency independent [76]. The linearity of Q_H vs $1/f$

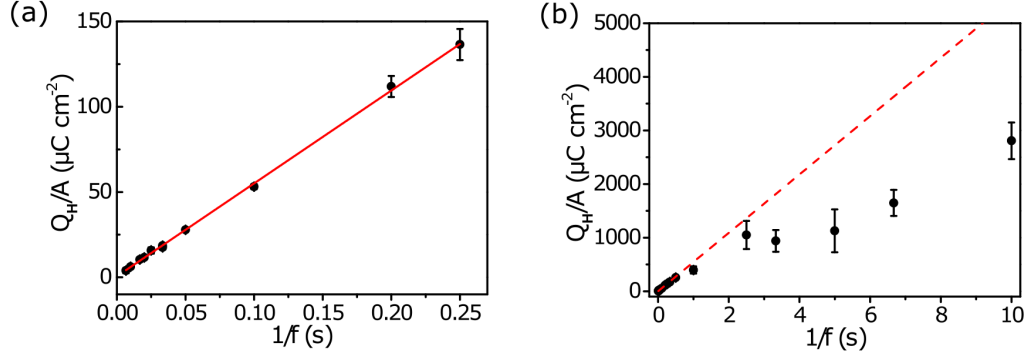


Figure 3.4: Frequency dependence of the hysteretic charge density, in the range 150 Hz to 4 Hz (a), and 150 Hz to 0.1 Hz (b), plotted as a function of $1/f$. The frequency dependence of Q_H/A is linear in $1/f$ for frequencies above 4 Hz, as indicated by the red fitted line, while some saturation of Q_H/A is observed at low frequencies. Error bars indicate the range of measured values of Q_H/A at each frequency. The frequency dependence of Q_H and large magnitude at low frequencies are uncharacteristic of a ferroelectric response and indicate a conductive mechanism for the hysteresis.

and large values of Q_H at low frequency implies that the observed hysteresis arises from a conductive mechanism within the film. As conduction is minimised at high frequencies, an upper limit to any intrinsic ferroelectric response is defined by the intercept of the Q_H vs $1/f$ fit. A linear fit was found to pass through the origin within error, with the uncertainty putting an upper limit on an intrinsic ferroelectric polarisation of $1 \mu\text{C cm}^{-2}$.

In order to understand the origin of the hysteretic charge density, it is helpful to consider the current density of the film during the measurement, rather than the accumulated charge. This was calculated by taking the differential of the capacitor voltage during the DWM measurement; an example current-voltage curve is plotted in Figure 3.5. The charge-voltage hysteresis is now visible as a difference in the current density through the film between the first and second pulses, and between the third and fourth pulses. The linearity of Q_H vs $1/f$ corresponds to a frequency independent difference in the current-voltage curves at high frequency, with the current difference reducing at low frequencies. This investigation therefore shows how hysteresis in the

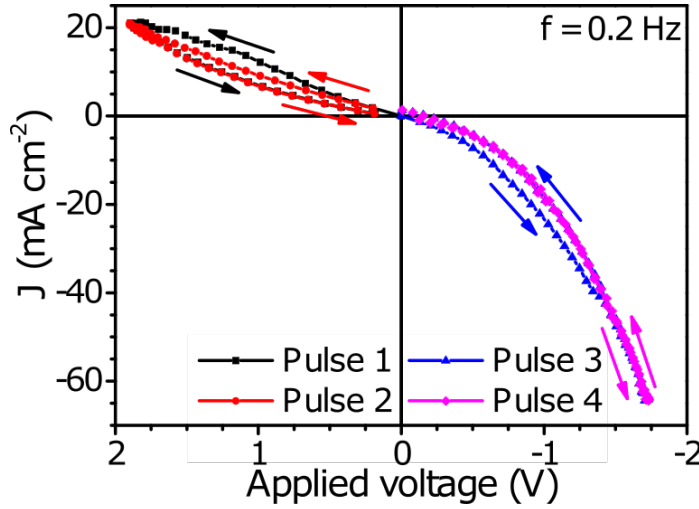


Figure 3.5: A DWM measurement at 0.2 Hz plotted as current-voltage curves. Arrows indicate the sweep direction. The hysteresis is now visible as a difference in current density in each direction.

current-voltage curve of a thin film device, as reported in the literature, can appear to produce hysteresis loops which look similar to ferroelectric hysteresis loops. However, investigation of the magnitude and frequency dependence using the DWM allows one to rule out ferroelectric hysteresis as the dominant mechanism, instead indicating a conductive mechanism as the cause of the current voltage hysteresis.

3.2.3 Time-dependent fixed voltage switching

To further investigate the origin of current-voltage hysteresis, the response of the film was measured upon switching with a fixed voltage V , for a set of voltages. A pre-poling voltage of $-V$ was applied to the film, followed immediately by the application of positive voltage V (at time $t = 0$), representing DC switching. The switching behaviour was investigated for a series of voltages between 0.5 V and 1.5 V, and the results are shown in Figure 3.6(a). Fixed voltages above 1.5 V were found to damage the films, while the steady state current measured was found to be reduced compared to the DWM measurements, which was attributed to film degradation over time. In

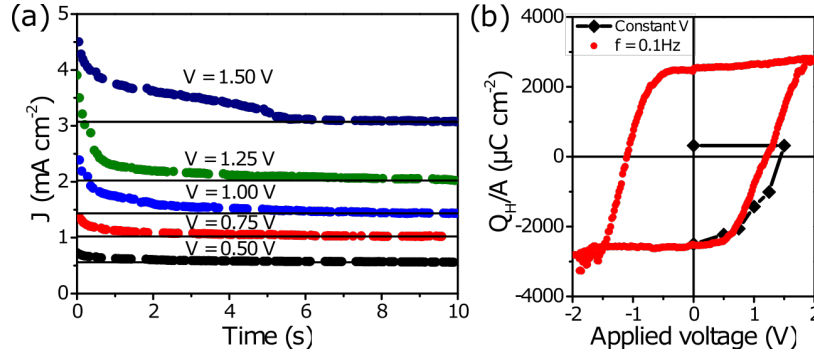


Figure 3.6: (a) Time-dependent current after fixed voltage switching from $-V$ to $+V$ at $t = 0$, at a series of voltages. A steady state current is only reached after approximately 10 seconds (shown by the solid lines). (b) Comparison of the integrated time dependent current (above the steady state background) as a function of voltage, with the hysteresis loop measured at 0.1 Hz. The integrated current plot is shifted by $-2500 \mu\text{C cm}^{-2}$ to give both plots a common origin, showing good general agreement of the magnitude and voltage dependence of the time-dependent current with the hysteresis loop.

the fixed voltage switching measurements, it was observed that the initial current is larger than the steady state value, which is reached after approximately 10 seconds. A voltage dependence of the time-dependent current is also evident. By integrating the time-dependent current (i.e. that above the steady state background defined above 10 s), one can calculate the corresponding charge density as a function of voltage. Figure 3.6(b) shows a comparison of this charge density as a function of voltage with the lowest frequency hysteresis loop. Good general agreement is observed for both the magnitude and voltage dependence of the time-dependent current measurements and hysteresis loop measurements.

Together, these measurements show that the hysteresis arises from a charge trapping process at the electrode-film interfaces that saturates on a timescale of seconds. This could in principle be due to electronic or ionic charge trapping, however given the high carrier mobilities in this compound, one would expect electronic charge trapping on the order of nanoseconds [77]. Furthermore, ionic charge trapping has been previously reported to occur on a timescale of seconds in

3.2. Hysteresis loop measurements on thin film $\text{CH}_3\text{NH}_3\text{PbI}_3$

$\text{CH}_3\text{NH}_3\text{PbI}_3$ devices [78], while similar halide perovskites such as CsPbBr_3 are known to be ionic conductors [79]. If ionic migration is indeed possible in $\text{CH}_3\text{NH}_3\text{PbI}_3$, the applied E -field of 5.7 kV mm^{-1} would be expected to introduce significant migration, which would cause an accumulation of ionic charge at the electrodes. In this scenario, due to the time dependent nature of the DWM, at later times the ionic conduction at a given voltage would always be reduced, causing a difference once the pulses are subtracted. Furthermore, accumulation of ionic charges is expected to cause n/p doping of the contacts, causing a change in the electron/hole extraction efficiencies and modifying the steady state current through the device. This causes difficulties when trying to determine the extent to which the slow time response is a direct measurement of the ionic conductivity, or a secondary effect arising from a modification to the electrical properties at the film-electrode interfaces. Taking the maximum hysteretic charge density of $2500 \mu\text{C cm}^{-2}$ and I^- vacancies as the ionic species, one can calculate that this charge density corresponds to 3.7% of the I^- ions in the film. Therefore the measured charge density is too large to be explained purely by the accumulation of ionic vacancies, and the measurements presented thus far contain a mixture of direct and secondary ionic effects due to the modification of the electronic charge extraction at the surface (this shall be explored further in Section 3.4).

Dielectric spectroscopy, as discussed in Chapter 2, can enable in-depth studies of the nature of conduction in electronic/ionic conductors. In the remainder of this chapter, I will present dielectric measurements on single crystal $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$, which are far more insulating compared to thin films and enable the effects of ionic migration to be investigated. I will then discuss the implications of the hysteresis loop and dielectric measurements on the properties of halide perovskite photovoltaic devices.

3.3 Dielectric spectroscopy of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$

Previous studies have investigated the dielectric response of halide-perovskite thin films, where a giant dielectric response has been observed at low frequency [60,61,80]. A number of explanations have been proposed for this response including a highly polarisable lattice, ionic conduction and interfacial charging [60,61,80–82]. However, due to the relatively high electrical conductivity of thin-film devices, electronic carriers will dominate the dielectric response at low frequency and also lead to additional dipolar-type relaxations at interfaces at higher frequencies. In order to investigate the potential for an intrinsic ionic conductivity, it is therefore necessary to measure bulk single-crystals. As discussed in the following section, the number of electronic defect states within the band gap is expected to be minimal, giving a much higher electrical resistance and enabling the effects of ionic conduction to be observed.

3.3.1 Defect physics of $\text{CH}_3\text{NH}_3\text{PbI}_3$

As the experimental investigation of the electrical properties of $\text{CH}_3\text{NH}_3\text{PbI}_3$ has intensified, a number of theoretical studies have investigated the possibility of ion migration and the potential for forming elemental defects within $\text{CH}_3\text{NH}_3\text{PbI}_3$. One study calculated the energy profile for migration of defects of Pb, I and CH_3NH_3 between adjacent sites [83]. This study determined activation energies of 0.58 eV, 0.84 eV and 2.31 eV for I, CH_3NH_3 and Pb migration, and calculated a much higher diffusion coefficient for I ($10^{-12} \text{ cm}^2 \text{ s}^{-1}$) than CH_3NH_3 ($10^{-16} \text{ cm}^2 \text{ s}^{-1}$). This builds on an earlier theoretical study which found that the predominant disorder in $\text{CH}_3\text{NH}_3\text{PbI}_3$ is ionic rather than electronic disorder, even for stoichiometric samples, due to the low formation energy of defects [84]. Schottky defects (a vacancy of a stoichiometric unit) and partial defects of $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 were

calculated to have formation energies of 0.14 eV, 0.08 eV and 0.22 eV respectively. This corresponds to high levels of vacancies at room temperature; 0.4%, 3.82% and 0.02% for the respective defect types. Importantly, for each of these vacancy processes the sum of the charged vacancies is neutral and so no electron or hole carriers are generated. Further studies have also calculated that any defects formed (such as lone I vacancies and interstitials) may have low formation energies but also only give shallow donor levels (< 0.1 eV) [85], whilst Schottky defects do not give any donor levels within the band gap [86]. It was theoretically shown that solar cells could be switched from n to p -type at room temperature based on the growth conditions, which affect the type of defects [86].

The implication of these studies is that the halide perovskites are expected to have high levels of defects that do not necessarily lead to electron or hole doping or to the formation of defect levels within the bandgap (low levels of sub-band defects are indeed observed, as evidenced by a sharp absorption onset at the band gap). The presence of vacancies therefore creates the potential for vacancy assisted ionic migration within the material.

3.3.2 Experimental technique and development of accurate dielectric measurements

Measurements were performed on mm-sized cuboid-shaped single crystals of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_3$. Electrodes were painted onto the crystals using conductive silver paint. Dielectric measurements were made with a high-accuracy capacitance bridge (Andeen-Hagerling 2700A (AH2700)). This allowed measurements in the 50 Hz to 20 kHz range using a three terminal method. During an impedance measurement, additional stray impedances can also contribute to the measured impedance. This can arise from a variety of sources, such as stray capacitance between the sample connections and other materials in their vicinity,

while external electrical noise can also be picked up if the circuit is partially unshielded. In the three terminal method, the unknown impedance is measured between two terminals, while a third terminal acts as a guard, which is connected to ground. Any impedance between the conductors connecting the sample to the two terminals and the guard terminal do not contribute to the measured impedance, which can be understood by considering the measurement circuitry. Figure 3.7(a) shows a diagram of the measurement circuit essentials. The ratio transformer and location of taps 1 and 2 determine the voltages applied across the variable RC circuitry (which can be considered as a simple parallel RC circuit) and the measured impedance. The variable resistor and capacitor are varied by a microprocessor until the circuit is balanced i.e. the detector records a null voltage for both the in-phase and quadrature components. By considering the in-phase and quadrature voltage drops across legs 3 and 4, the ratio R_x/R_0 is then given by V_2/V_1 , while the ratio C_x/C_0 is given by V_1/V_2 . The design of the instrument is such that any impedance between the high terminal and ground causes an additional load to the ratio transformer, however the ratio transformer has a low impedance and as such additional impedance will only cause a noticeable error for large capacitances, high measurement frequencies or long measurement cable lengths. Any impedance between the low terminal and ground acts as a shunt to the detector, which will introduce additional noise into the detected voltage [87]. Furthermore, if one designs the experimental setup such that the guard terminal effectively shields the two measurement terminals at all points along the circuitry, one can eliminate the effect of any stray capacitances to accurately measure dielectric response of the sample under investigation. Practically, shielded cables must be used, where the shields are connected to the ground of the capacitance bridge and also act to fully isolate the sample, as well as shielding the high and low connectors from one another. The effect of an unshielded arrangement can be seen in Figure 3.7(b), which shows a

3.3. Dielectric spectroscopy of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$

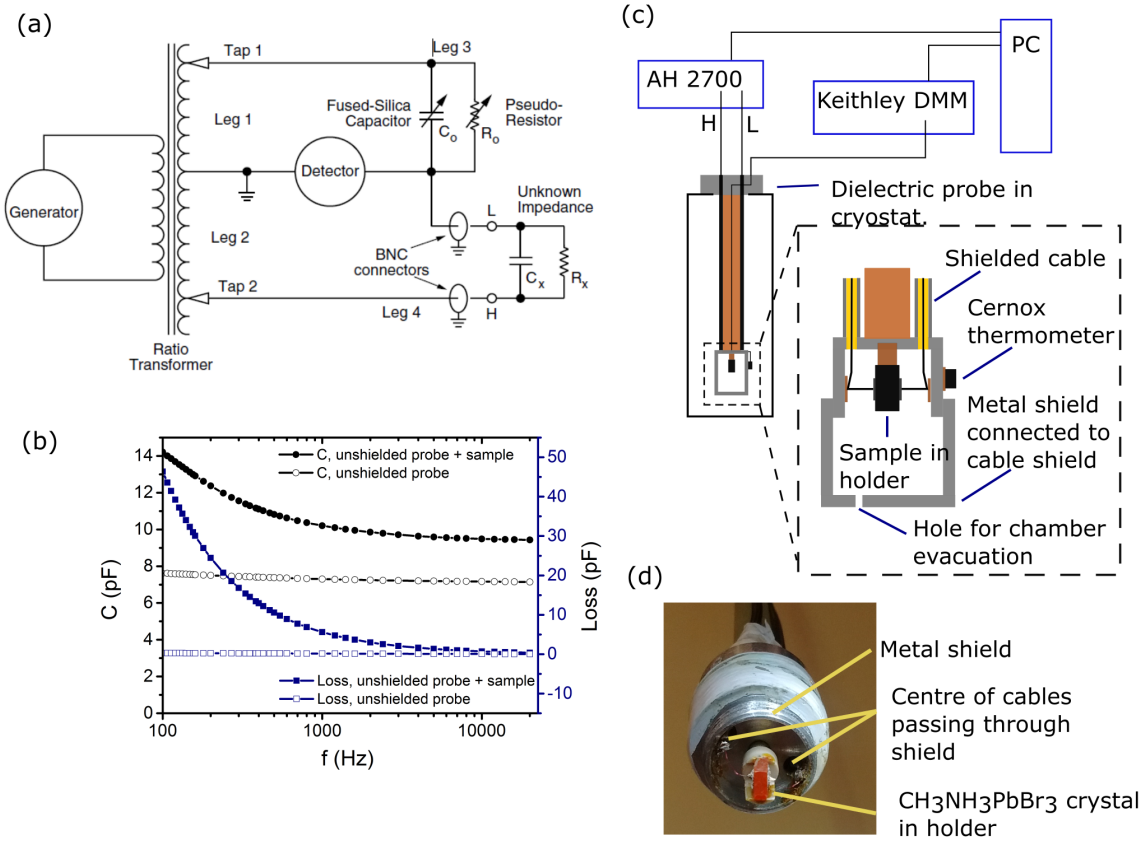


Figure 3.7: (a) Figure reproduced from Andeen-Hagerling 2700A (AH2700) manual [87]. Bridge circuit used by the AH2700 capacitance bridge. A variable capacitor and resistor is used to balance the in-phase and quadrature components of the unknown impedance and give a null voltage across the detector. (b) Example of a measurement on an unshielded probe, with and without a sample of $\text{CH}_3\text{NH}_3\text{PbI}_3$. The response of the probe has a frequency-dependent capacitance varying between 7.1 pF and 7.6 pF, and a loss between 0.04 pF and 0.27 pF in the frequency range 20 kHz to 50 Hz, which contributes a large parallel capacitance to the measurement of a sample with an expected capacitance ~ 2 pF. (c) Schematic of experimental setup used to measure dielectric response using a shielded probe. In order to accurately measure capacitance, I designed and configured a shielded probe in order to perform a three terminal measurement. Shielded wires were used down the length of the probe, and the wire shields were connected to a metallic shield that completely enclosed the sample. BNC connectors were used at the head of the probe and BNC cables were used to connect to the AH2700 capacitance bridge. A calibrated Cernox resistor was mounted to the outside of the metal shield, and the temperature was determined by taking four point resistance measurements of the cernox resistor using a Keithley digital multimeter (DMM). (d) Photograph of the sample end of the dielectric probe, with the shield removed.

3.3. Dielectric spectroscopy of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$

comparison of a frequency-dependent dielectric measurement on an unshielded probe of a single crystal of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and a measurement of the dielectric response of the probe without a sample. The response of the unshielded probe gives a frequency-dependent capacitance ranging between 7.1 pF and 7.6 pF and a loss between 0.04 pF and 0.27 pF, in the frequency range 20 kHz to 100 Hz. As can be seen from the measurement with the $\text{CH}_3\text{NH}_3\text{PbI}_3$ sample, the probe contributes a large parallel capacitance to the sample measurement (the sample itself is expected to have a capacitance ~ 2 pF) and must be eliminated for accurate dielectric characterisation.

In order to implement a shielded three terminal measurement, I designed and configured a shielded dielectric probe. A schematic of the dielectric probe experimental setup is shown in Figure 3.7(c). This consisted of a probe of suitable dimensions and thermal shielding for use in a He flow cryostat, with two shielded wires running from BNC connectors at the head of the probe to a metal sample chamber. The shields of the wires were connected to the metal chamber, which included a metal screw cap to completely enclose the sample except for a hole to allow evacuation. The centre of the wires run through two holes at the top of the shield and connect to solder pads at opposite sides of the chamber. The sample in an ampule screws into the centre of the chamber between the two solder pads, and a short wire connects between a silver paint contact on the sample surface and the solder pads. A pre-calibrated cernox resistor was mounted on the outside of the metal shield, and was connected to a four-pin LEMO connector at the head of the probe. A four point resistance measurement of the cernox resistor was taken using a Keithley digital multimeter (DMM) to determine the temperature. Shielded BNC cables were used to connect between the capacitance bridge and the probe, and the data was logged with a computer. The background capacitance of the shielded probe was measured to be below 0.02 pF and the loss below 0.002 pF across the

measurement range of the AH2700.

3.3.3 Dielectric spectroscopy of $\text{CH}_3\text{NH}_3\text{PbI}_3$

The temperature-dependent dielectric response of $\text{CH}_3\text{NH}_3\text{PbI}_3$ was measured on a 1.1 mm thick crystal across the tetragonal $\pm(112)$ faces ((101) faces of the cubic cell), using silver paint to form contact electrodes of area 6.3 mm^2 . Here the tetragonal axes refer to the axes of the dominant tetragonal crystal, however as the crystal was grown in the cubic phase, significant symmetry twinning will occur upon cooling (this is explored further in Chapter 4). Therefore, the measured ϵ will be a sum of the contributions of the three twins, two of which give (112)-equivalent directions and the third a (100)-equivalent direction along the measurement direction. Therefore, in the dielectric measurements I shall just consider the magnitude of the dielectric constant.

Figure 3.8 shows the temperature dependence of the real and imaginary parts of the dielectric constant, at a measurement frequency of 20 kHz. The data below 300 K was taken upon warming in a Physical Property Measurement System (Quantum Design), while the data above 300 K was taken upon cooling from 350 K in a cryostat chamber at ambient pressure. In the real part of the relative dielectric permittivity, a large change in the dielectric constant can be seen at 163 K, in agreement with previous temperature-dependent dielectric measurements on $\text{CH}_3\text{NH}_3\text{PbI}_3$ powder samples [88]. At the cubic-tetragonal phase transition, no sharp features are observed. A small feature at 329 K of magnitude $\delta\epsilon'_r = 0.1$ was observed, while a weak broad hump between 315 K and 335 K is also evident (see inset of Figure 3.8(a)). The small jump at 196 K is an artefact and is attributed to the loss of a small section of silver-paint contact. The general temperature dependence can be understood as a Curie-Weiss type behaviour, indicative of a paraelectric nature of the molecular dipoles, following by a freezing of the dipolar motion at $T_1 = 163 \text{ K}$. Below T_1 no features were observed in the data down to 10 K.

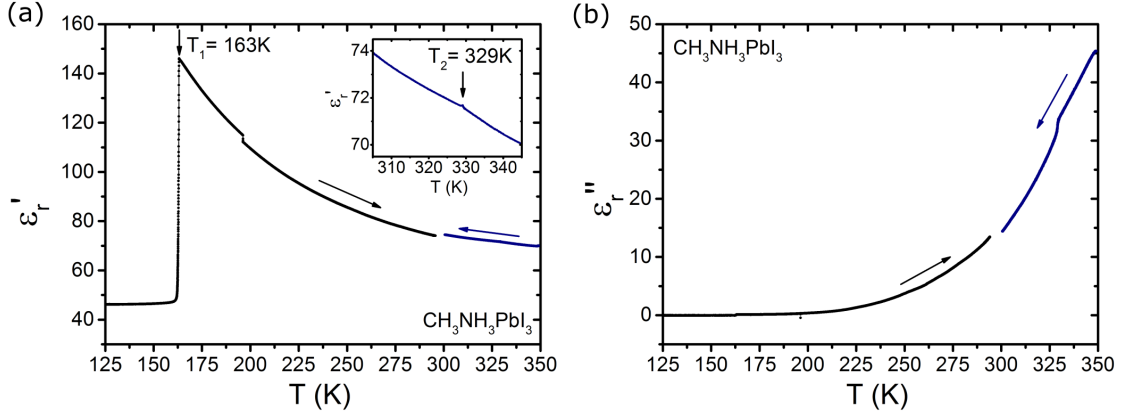


Figure 3.8: Temperature dependence of the real (a) and imaginary (b) parts of the dielectric constant of $\text{CH}_3\text{NH}_3\text{PbI}_3$, measured at 20 kHz. The temperature dependence of the real part of ϵ shows the paraelectric nature of the dipoles until the freezing of the dipolar motion at the orthorhombic-tetragonal phase transition at 163 K. No large features are seen at the cubic-tetragonal phase transition (inset, (a)). The imaginary part of ϵ shows thermally activated behaviour with an onset at ~ 200 K.

The imaginary part of the dielectric loss, shown in Figure 3.8, reveals a thermally activated behaviour with increasing temperature. No loss peaks corresponding to dipolar-type responses were observed, and the behaviour can be attributed to conductive behaviour, which will become evident in the discussion of the frequency-dependent behaviour. It is important to note that the test frequency (20 kHz) is much lower than the expected frequency of molecular dipole rotation ($\sim$ GHz). Therefore the measurement frequency is far below the Debye peak for the molecular motion and the contribution to ϵ from molecular motion is purely real, while the dielectric loss is dominated by conduction.

The frequency dependence was investigated on a second crystal, of thickness 1.1 mm and area 2.7 mm². Contacts were painted onto a cubic (100) face (twinned tetragonal (110) face plus (110) and (001) symmetry equivalent twins). Figure 3.9(a) shows the frequency-dependent dielectric response at room temperature between 100 Hz and 20 kHz, measured with the AH2700 capacitance

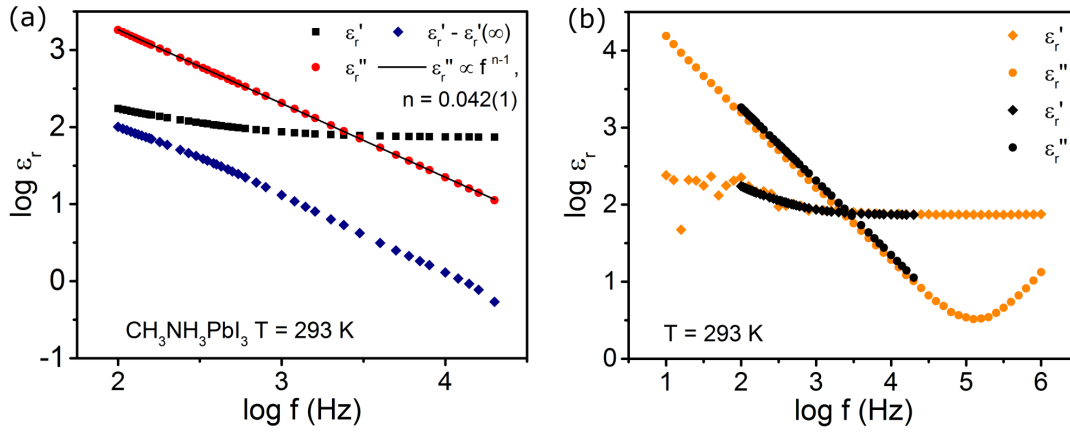


Figure 3.9: (a) Frequency dependence of the real and imaginary parts of ϵ of $\text{CH}_3\text{NH}_3\text{PbI}_3$ at room temperature. The blue curve is obtained by subtracting a constant high-frequency static permittivity (73.4) from ϵ_r' , which reveals that the frequency-dependent component of ϵ_r' follows the same frequency dependence at ϵ_r'' . A linear fit to the ϵ_r'' data gave a value of $n = 0.042(1)$, characteristic of low-frequency dispersion due to ionic conduction. (b) A comparison of the dielectric response measured with the high-accuracy capacitance bridge (black data points) and the dielectric response measured over a larger frequency range using an impedance analyser (orange data points). This showed the continued increase of ϵ_r'' at lower frequency, and the start of a higher frequency process above 100 kHz.

bridge and plotted on a log-log scale. As the frequency is reduced, the dielectric loss rapidly increases, corresponding to a linear increase on a log-log plot. The real part of the dielectric constant is almost constant at high frequency, but increases from ~ 74 at 20 kHz to 174 at 100 Hz. A fit of the data to $\log(\epsilon_r'') \propto (n - 1)\log(f)$ gave an excellent fit to the data with $n = 0.042(1)$, revealing almost DC-like conduction. As previously explained, in order to see the true frequency dependence of ϵ_r' , one should subtract the high frequency static ϵ . Taking a value of 73.4 as the static high frequency permittivity and subtracting from ϵ_r' gives the blue dataset in Figure 3.8(a). This reveals the true frequency-dependent component of ϵ_r' which follows the same frequency dependence as ϵ_r'' . Fitting the power law relation to the real part of the dielectric constant gave similar exponents to the imaginary part, however the value of the fitting parameter was highly sensitive to the value of the high frequency static ϵ used, which cannot be accurately determined from the data. In the following temperature dependent study, only fits to the imaginary part were used to determine the exponent n . One can also calculate n by evaluating the ratio $\chi''(\omega)/\chi'(\omega)$ and using the Kramers-Kronig relation (Equation 2.54), which gives a mean value of $n = 0.039(3)$, in good agreement with the value obtained by fitting ϵ_r'' .

It is clear that both the real and imaginary parts of ϵ follow the same power law behaviour, with a small value of n that is characteristic of low-frequency dispersion. This distinguishes the behaviour from DC electronic conduction, which has a power-law exponent of -1 (i.e. $n = 0$) and does not cause a corresponding increase in ϵ_r' . To verify the LFD behaviour over a larger frequency range, measurements of the dielectric response were made on an impedance analyser (Solartron 1200) between 10 Hz and 1 MHz. The resulting response, alongside the response measured on the AH2700, is shown in Figure 3.8(b). The imaginary part continues to increase linearly at lower frequencies, however the corresponding increase in ϵ_r' is less clear due to significant noise in the data. At higher frequencies above 100 kHz, another response starts to

enter the measurement range, and ϵ_r'' starts to increase with frequency. While only the tail of this response can be seen, it appears to be a Debye-type response, with a constant ϵ_r' and ϵ_r'' proportional to ω . This is likely to be the start of the CH_3NH_3 dipole relaxation. Previous high-frequency dielectric measurements by Poglitsch and Weber [65] reveal that ϵ_r' has reduced to value of ~ 32 at 90 GHz, therefore the observed feature is likely to be the onset of a Debye loss peak due to CH_3NH_3 dipolar relaxation, accompanied by a step-like reduction in ϵ_r' to the value of the lattice polarisability.

In order to investigate the thermal activation of the LFD, the frequency dependence of ϵ_r'' was investigated between 195 K and 290 K, using the high-accuracy AH2700 capacitance bridge. Figure 3.10(a) shows a log-log plot of ϵ_r'' against frequency for the temperatures measured. At each temperature, a good linear fit could be made to the data. The fit was restricted to values of $\log(\epsilon_r'') > 0$, as significant noise in ϵ_r'' was seen below this value. Additionally, this stopped the fit from including the high-frequency region where ϵ_r'' starts to increase again. This can be seen more clearly from the plot of $\log(\sigma)$ against $\log(f)$ in Figure 3.10(b). At the lowest temperatures, an increase in σ is seen at higher frequencies due to the onset of the higher-frequency relaxation process that was observed in the room temperature measurements at $f > 100$ kHz. The fitting exponents obtained are shown in Figure 3.10(c). This reveals that $0.032 < n < 0.055$ at all temperatures measured, indicative of dispersive hopping conduction, which combined with the observation of a large rise in ϵ_r' is strongly suggestive of ionic conduction in $\text{CH}_3\text{NH}_3\text{PbI}_3$. The higher values of n at low temperature may be due to the effect of the tail of the high frequency process causing an increase in ϵ . Figure 3.10(d) shows the thermally activated nature of the conductivity. σ_0 is the value of the conductivity at $\omega = 1$, determined from the $\log(\epsilon_r'')$ vs $\log(f)$ fit. A linear fit to $\ln(\sigma_0 T)$ vs $1/T$ was used to determine an activation energy of ionic conduction of

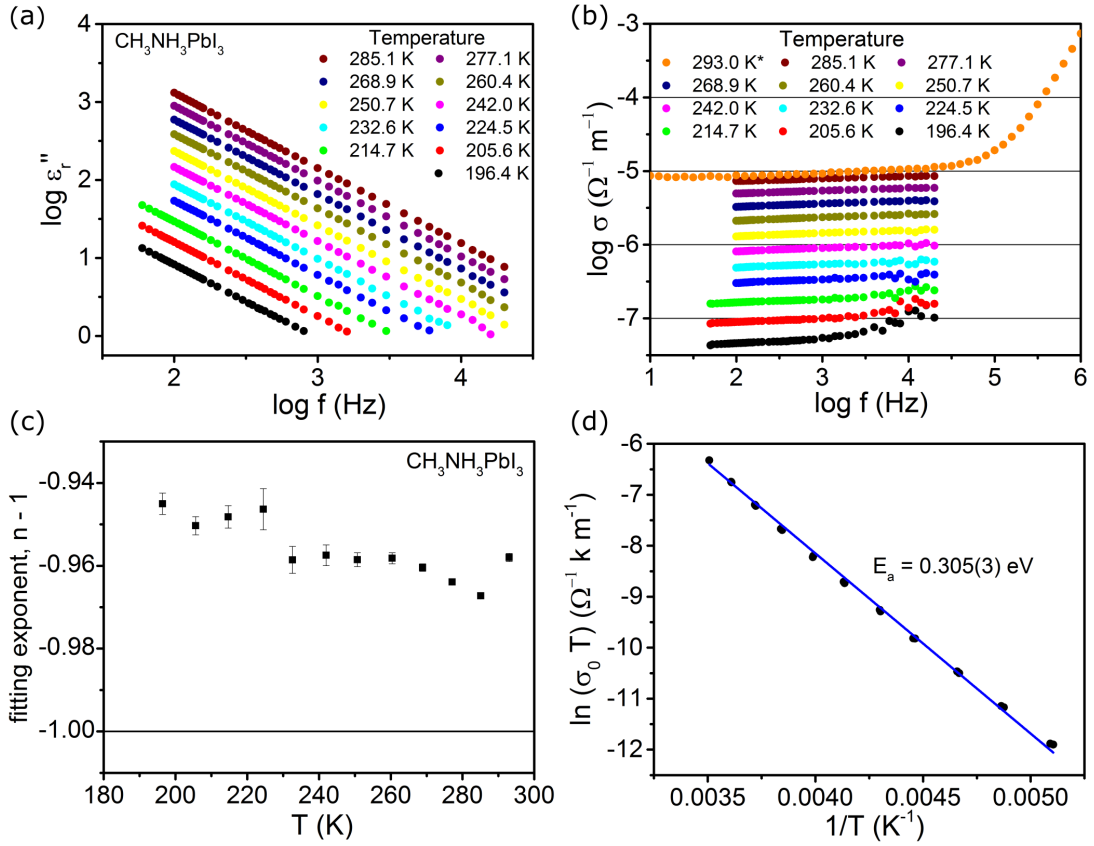


Figure 3.10: (a) Frequency dependence of ϵ'' , plotted on a log-log scale, showing linear behaviour at all temperatures. (b) Converting to conductivity, using the relation $\sigma = \epsilon_0 \epsilon'' \omega$, shows the gradual increase of ω with frequency, corresponding to $\sigma(\omega) = \sigma_0 \omega^n$ with small values of n . The data measured over a larger frequency range at room temperature is also shown for comparison. At low temperatures, the tail of the high frequency process is in the measured frequency range; this was excluded from the fits of ϵ'' . (c) The fitting exponents obtained from the linear fit $\log(\epsilon'') = A + (n-1)\log(f)$, showing little variation with temperature. (d) The activation energy was determined from a fit of $\ln(\sigma_0 T)$ vs $1/T$, giving an activation energy $E_a = 0.305(3) \text{ eV}$.

0.305(3) eV. Furthermore, the value of σ_0 at room temperature can be estimated from the fit as $7.9 \times 10^{-6} \Omega^{-1} \text{ m}^{-1}$.

3.3.4 Dielectric spectroscopy of $\text{CH}_3\text{NH}_3\text{PbBr}_3$

The dielectric response of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ was measured on a 1.75 mm thick single crystal along the cubic a axis, using silver paint to form contact electrodes of area

7.5 mm². The real and imaginary parts of the dielectric response, measured as a function of temperature at a rate of change of 1 K/min, are shown in Figure 3.11.

In the real part of the relative dielectric permittivity, one can identify three features associated with the known crystallographic phase transitions, in agreement with previous dielectric studies [88]. At room temperature, $\text{CH}_3\text{NH}_3\text{PbBr}_3$ forms a cubic crystal structure with $Pm\bar{3}m$ space group symmetry [65]. Between 154 K and room temperature, Curie-Weiss-type behaviour is observed in addition to a feature at the cubic-tetragonal phase transition at 229 K. At 154 K and 149 K, large reductions are seen in the dielectric response, and below 149 K the response is almost constant, with no further features observed. These features correspond to the reported structural transitions from $I4/mcm \rightarrow P4/mmm \rightarrow Pnma$. [65, 89]. As in the case of $\text{CH}_3\text{NH}_3\text{PbI}_3$, the Curie-Weiss-type behaviour and subsequent large reductions in ϵ_r can be attributed to the rotational dynamics and subsequent freezing of the CH_3NH_3 molecular dipoles in the low temperature orthorhombic phase.

Regarding the feature at the cubic-tetragonal phase transition at 229 K, it is unclear whether this corresponds to a change in the lattice polarisability or a reduction in the rotational freedom of the CH_3NH_3 molecule. Previous reports of measurements on a powder sample did not reveal any sharp features at the cubic-tetragonal phase transition in $\text{CH}_3\text{NH}_3\text{PbBr}_3$ [88], therefore this may indicate a slight anisotropy of the dielectric constant in the tetragonal phase, potentially due to the reduction in site symmetry of the CH_3NH_3 molecule and preferential orientation in the ab plane.

The imaginary part of the dielectric constant reveals that the material has low loss across the whole temperature range studied. No loss peaks corresponding to a dipolar-type response are observed, while there is a large, thermally activated increase in the loss as temperature is increased, corresponding to conductive behaviour.

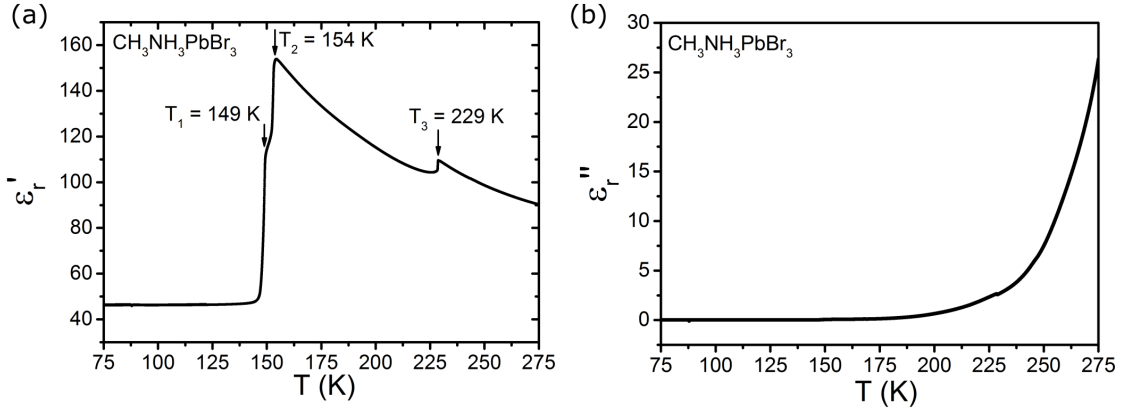


Figure 3.11: Temperature dependence of the real (a) and imaginary (b) part of the relative dielectric permittivity of $\text{CH}_3\text{NH}_3\text{PbBr}_3$, measured at 1 kHz. Three features are observed in the real part of ϵ at the crystallographic phase transitions [65], while the large increase in ϵ'_r upon reducing T down to T_2 indicates a predominantly disordered nature of the CH_3NH_3 dipoles in the tetragonal ($I4/mcm$) and cubic phases. The imaginary part of ϵ shows thermally activated behaviour with an onset at ~ 180 K.

The frequency dependence of the dielectric response was investigated in the range 50 Hz to 20 kHz. Figure 3.12 (a) shows the frequency-dependent response at room temperature, plotted on a log-log scale. As the frequency is reduced, the dielectric loss rapidly increases, corresponding to a linear increase on a log-log plot. A fit to the data of $\log(\epsilon''_r) \propto (n - 1)\log(f)$ gave an excellent fit with $n = 0.022(5)$. The real part of the dielectric constant is predominantly flat at high frequencies, with a value of 83.3 at 20 kHz, and increases somewhat as the frequency is reduced, with a value of 143.4 at 50 Hz. As previously explained, in order to see the true frequency dependence of ϵ'_r , one should subtract the high frequency static ϵ . Taking the value of ϵ'_r at 20 kHz to be the static high frequency permittivity and subtracting this from ϵ'_r reveals the underlying frequency-dependent $\epsilon'_r(\omega)$, as shown by the blue curve in Figure 3.12(a). It is clear that both the real and imaginary parts of ϵ follow the same power law behaviour, with a small value of n that is characteristic of low-frequency dispersion. The value of n was also determined by evaluating the ratio $\chi''(\omega)/\chi'(\omega)$

3.3. Dielectric spectroscopy of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$

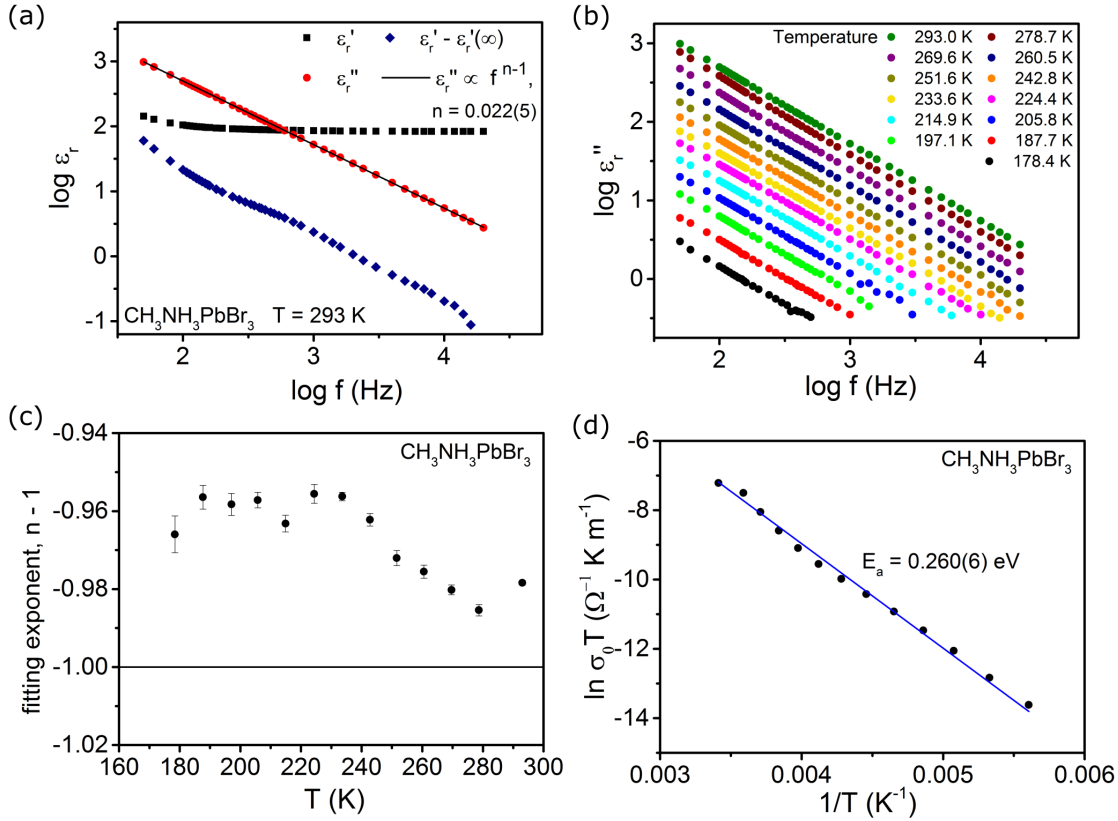


Figure 3.12: Frequency-dependent dielectric response of $\text{CH}_3\text{NH}_3\text{PbBr}_3$. (a) Frequency-dependent response at room temperature. After subtracting the high frequency static ϵ , both ϵ_r' and ϵ_r'' follow the same power law behaviour with a low n , characteristic of low-frequency dispersion. (b) Frequency-dependent loss as a function of temperature, plotted on a log-log scale, showing good power law behaviour. (c) The temperature dependence of the power law exponent $n - 1$. At all temperatures, the behaviour is distinct from true DC behaviour where $n = 0$ (solid line). A slight reduction in n is observed as T is increased, corresponding to higher dielectric loss due to conduction. (d) Plotting $\log(\sigma_0 T)$ against $1/T$ revealed thermally activated behaviour, consistent with ionic conduction with an activation energy $E_a = 0.260(6)$ eV.

and using the Kramers-Kronig relation (Equation 2.54), which gives a mean value of $n = 0.026(3)$, in excellent agreement with the value obtained by fitting ϵ_r'' .

In order to investigate the thermal activation of the LFD, the frequency dependence of ϵ was investigated between room temperature and 178 K. At lower temperatures, it was not possible to measure the loss with sufficient accuracy over a

wide frequency range to achieve good fits. Figure 3.12(b) shows the frequency-dependent loss at a series of temperatures. A frequency dependence of the conductivity $\sigma(\omega) = \sigma_0\omega^n$ was assumed, and linear fits of $\log(\epsilon_r'')$ against $\log(f)$ were used to determine σ_0 and n . Figure 3.12(c) shows the temperature dependence of the fitted exponent $n - 1$. A slight increase is seen for higher temperatures, however the value of $n - 1$ is always significantly greater than -1 , distinguishing the LFD behaviour from DC conductivity. As n is proportional to the stored charge, a reduction in n as temperature is increased is expected, as the increased conduction will cause ions to move in extended paths through the crystal, giving higher dielectric loss. Plotting $\log(\sigma_0 T)$ against $1/T$ (Figure 3.12(d)) reveals thermally activated behaviour consistent with ionic conduction, with an activation energy $E_a = 0.260(6)$ eV determined from a linear fit. From the data, the value of σ_0 at room temperature is $2.5 \times 10^{-6} \Omega^{-1} \text{m}^{-1}$.

3.3.5 Discussion of dielectric behaviour

These measurements reveal that both $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$ show characteristic low-frequency dispersion corresponding to thermally activated hopping conduction. The rise in ϵ_r' at low frequency implies a significant amount of stored charge within the material, which can be understood as the motion of charge carriers creating a large reversible dipole moment. In principle, low frequency dispersion can arise from hopping electronic carriers, however there are limited possibilities for electron hopping in the halide perovskites within the experimentally measured activation energies. On the other hand, other lead halides are known to exhibit halide vacancy conduction [79], while ionic conduction was reported in $\text{CH}_3\text{NH}_3\text{PbI}_3$ powder pellets [90].

To discount the possibility of hopping electron conduction, one must consider whether electronic defects levels introduced by the presence of atomic vacancies

could cause the measured dielectric response. With the halide perovskites, any impurity contribution is likely to be dominated by vacancies or interstitial siting of I, Pb or CH_3NH_3 , which may give either compensated or uncompensated charged sites within the crystal. For the case of thermally activated band conduction from impurity levels, the band nature of the electrons would lead to DC conduction, as opposed to hopping conduction. The type of electronic hopping conduction that one must consider is hopping conduction between impurity levels deeper within the band gap, i.e. those that are too deep in energy to be thermally excited into the conduction band. Impurity conduction is defined as the direct tunnelling of an electron between impurity sites due to a small overlap of the electronic wavefunctions, without thermal activation into the conduction band [91]. However, as detailed by Mott [91], impurity conduction tends only to be the dominant conduction mechanism at very low temperatures ($< 20\text{ K}$) with associated low activation energies on the order of $1 \times 10^{-3}\text{ eV}$. The impurity levels in halide perovskites can be inferred from previous studies on thin films. Very low monomolecular recombination rates, associated with charge trapping, were observed to occur with an activation energy of 0.02 eV [92], while another study determined defect states within 0.03 eV of the band gap in the orthorhombic phase [93]. This is consistent with previous studies of a sharp absorption onset and lack of deep electron levels within the band gap [56], alongside very large electron diffusion lengths in single-crystal $\text{CH}_3\text{NH}_3\text{PbI}_3$ that indicate a negligible level of shallow states [77]. Therefore, the most consistent explanation for the observed dielectric behaviour is that it arises due to ionic conduction within the material.

The activation energy of migration in $\text{CH}_3\text{NH}_3\text{PbI}_3$ is found to be slightly higher than in $\text{CH}_3\text{NH}_3\text{PbBr}_3$, however at room temperature the ionic conductivity is found to be three times greater in $\text{CH}_3\text{NH}_3\text{PbI}_3$, implying a higher level of vacancy defects. The determined activation energies are comparable to those of lead halide

3.3. Dielectric spectroscopy of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$

Compound	Activation Energy (eV)
CsPbBr_3 [79]	0.25
CsPbCl_3 [79]	0.29
PbBr_2 [79]	0.23
PbCl_2 [79]	0.20
$\text{CH}_3\text{NH}_3\text{PbI}_3$	0.305(3)
$\text{CH}_3\text{NH}_3\text{PbBr}_3$	0.260(6)

Table 3.1: Experimental activation energies for lead halide compounds as reported in the literature [79], in addition to the measured activation energies determined from the measurements in this Chapter.

compounds and inorganic lead halide perovskites, as shown in Table 3.1. As discussed in Chapter 2, one can relate the conductivity to the vacancy concentration by the Arrhenius-type relation:

$$\sigma = nq\mu = nq\frac{qD}{k_BT} \approx \frac{za^2f_0nq^2}{6k_BT}\exp(-E_a/k_BT) \quad (3.2)$$

where n is the density of vacancies of charge q , z is the number of nearest neighbours in the lattice, a is the jump distance, f_0 is the vibration frequency of the atom and E_a is the activation energy to overcome the potential barrier. For the value of f_0 , I shall use the experimentally determined vibration band due to Pb-I-Pb bending that occurs at 62 cm^{-1} for $\text{CH}_3\text{NH}_3\text{PbI}_3$ [94], corresponding to a frequency of approximately $1.9 \times 10^{12}\text{ s}^{-1}$.

For $\text{CH}_3\text{NH}_3\text{PbI}_3$, the intersect of the plot of $\ln(\sigma_0 T)$ against $1/T$ was used to determine the vacancy concentration $n \approx 4.2 \times 10^{23}\text{ m}^{-3}$, giving a vacancy fraction of 3.5×10^{-5} , assuming I vacancies to be the conductive species. From the relation between conductivity and the diffusion constant, the room temperature diffusion coefficient is determined to be $D \approx 3.0 \times 10^{-12}\text{ m}^2\text{ s}^{-1}$, which corresponds to a room temperature mobility of $1.2 \times 10^{-10}\text{ m}^2\text{ V}^{-1}\text{ s}^{-1}$. For $\text{CH}_3\text{NH}_3\text{PbBr}_3$, the vacancy concentration was determined to be $n \approx 2.7 \times 10^{22}\text{ m}^{-3}$, corresponding to a vacancy fraction of 1.8×10^{-6} , assuming Br vacancies to be the conductive species. This

corresponds to a room temperature diffusion coefficient $D \approx 1.5 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ and room temperature mobility $\mu \approx 5.8 \times 10^{-10} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$.

The activation energies and implied defect densities determined from the dielectric measurements clearly rule out the very low defect formation enthalpies suggested in a previous computational study [84]. At the low temperatures measured, the ionic conduction is in the extrinsic region, where the vacancy concentration is fixed. In the intrinsic region, where vacancy formation is thermally activated, the activation energy obtained from $\log(\sigma T)$ vs $1/T$ is given by $E_a + \Delta H/5$ for materials with the ABX_3 chemical formula, where ΔH is the enthalpy of vacancy formation of a Schottky defect [79]. No crossover from extrinsic to intrinsic behaviour is seen in either material in the measured temperature range. If the measured defect density was determined by a Schottky equilibrium condition during growth, the vacancy fractions would correspond to enthalpies of vacancy formation of 0.31 eV for $\text{CH}_3\text{NH}_3\text{PbI}_3$ and 0.40 eV for $\text{CH}_3\text{NH}_3\text{PbBr}_3$ (for growth at $T = 350 \text{ K}$). These values are much lower than the formation enthalpies of $> 2.0 \text{ eV}$ determined experimentally for the caesium lead halides [79]. This would also imply that the ionic activation energy is even lower than that determined from the activated conductivity, as one would be in the intrinsic region and therefore ΔH would give a contribution to the activation plot. A much more plausible scenario is that a non-equilibrium extrinsic defect density is produced during the growth process, which could in theory be reduced by an equilibrium growth process.

Another experimental study has investigated the electronic and ionic conductivity in $\text{CH}_3\text{NH}_3\text{PbI}_3$ pressed pellets by using an ion blocking method [90]. This determined a room temperature ionic conductivity of $7.7 \times 10^{-7} \Omega^{-1} \text{ m}^{-1}$ and an electronic conductivity $1.9 \times 10^{-7} \Omega^{-1} \text{ m}^{-1}$. The mobile ion was determined to be I, while the bulk conductivity had an activation energy of 0.43 eV, however this was only determined over a 40°C temperature range above room temperature. The

reported conductivity in this study is an order of magnitude lower than the conductivity determined here by impedance spectroscopy measurements ($7.9 \times 10^{-6} \Omega^{-1} \text{m}^{-1}$), however the conductivity is dependent on the defect density and hence will differ depending on the crystal growth conditions. The diffusion coefficient was determined to be $2.4 \times 10^{-12} \text{m}^2 \text{s}^{-1}$ by Yang *et al.* [90], which implies $n = 5 \times 10^{22} \text{m}^{-3}$. The diffusion coefficient is in close agreement to the value determined from dielectric measurements, while the reduced defect density and conductivity can be attributed to the extrinsic nature of defect formation.

To summarise, the observed hopping conductivity, implied charge storage within the crystal and activation energy in agreement with that of other ionic-conducting lead halide compounds is strong evidence of ionic conductivity as the dominant conduction mechanism within crystalline $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$.

3.4 Implications for conduction in $\text{CH}_3\text{NH}_3\text{PbI}_3$ films

Many theoretical and computational studies have considered the potential role of various physical properties of $\text{CH}_3\text{NH}_3\text{PbI}_3$ on device operation and performance [68, 81–83, 95–97]. However, this is often in the absence of conclusive experimental determination of key parameters such as the magnitude of a potential ferroelectric polarisation or the activation energy of ionic conduction. Now that we have built a clearer picture of the electrical properties of $\text{CH}_3\text{NH}_3\text{PbI}_3$, the effects on $\text{CH}_3\text{NH}_3\text{PbI}_3$ device operation can be determined. In this section I shall briefly discuss the main implications of the experimental results in the context of photovoltaic device operation.

3.4.1 Calculation of ionic defect migration times

For a vibrating atom that can hop to another site in a lattice by overcoming a potential barrier E_a , the hopping rate k is given by

$$k = f_0 \exp(-E_a/k_B T). \quad (3.3)$$

In the $\text{CH}_3\text{NH}_3\text{PbI}_3$ structure, iodine vacancy hopping is possible between eight sites, therefore using the activation energy of 0.305 eV as determined by impedance spectroscopy, the total hopping rate Γ is $8.8 \times 10^7 \text{ s}^{-1}$ at room temperature, assuming instantaneous migration.

For a simple calculation, I shall consider migration along the tetragonal c axis (cubic a axis). When the I^- vacancy is at a site where $z = 0.25$ or 0.75 , it can either move up or down the c direction onto four sites in each direction. Under applied bias, the vacancy will experience an internal electric field, creating a difference in the potential barriers between adjacent sites along the c direction and favouring hopping along the direction of the field. The internal field experienced by the vacancy will be the applied field reduced by a factor of the dielectric constant due to the dielectric screening effect; for a simple calculation I shall use the ‘static’ high frequency dielectric constant $\epsilon_r = 73$ determined from the impedance measurements. For a voltage of 1 V across a 350 nm solar cell, this gives an internal E -field of $3.9 \times 10^4 \text{ V m}^{-1}$. Under an applied field, the forward and backward hopping are given by

$$k_f = f_0 \exp(-(E_a + \Delta E)/k_B T), k_b = f_0 \exp(-(E_a - \Delta E)/(k_B T)), \quad (3.4)$$

where ΔE is the electrostatic energy change between adjacent sites, given by $qE_{\text{ext}}\delta z/\epsilon$. Using the determined material parameters, the ratio of forward to backward hops is therefore given by $\exp(2qE_{\text{ext}}\delta z/\epsilon k_B T) = 1.001$, i.e. the vacancy

will move forward 10 steps for every 20010 hops at room temperature. When the I^- vacancy is at a site with $z = 0$ or 0.5 , it can migrate up or down the c axis to two sites, or in the tetragonal ab plane to four sites. A similar consideration of the relative energies and site ratios gives the relation for the hopping rates $\Gamma_f/\Gamma_{\text{side}} = 1.0005/2$. Therefore when at $z = 0$ or 0.5 , the vacancy will move forward 5 steps for every 20000 hops. In total, for 40010 hops, the vacancy will move forward 15 steps along the c direction, giving a time of 0.034 s to traverse a 350 nm thin film along the c direction.

This is shorter than the timescale of around 1 s observed in fixed voltage switching measurements, however this calculation does not take into account the self-screening of the external field as the ionic polarisation develops, which will rapidly reduce the internal E -field and cause a significant increase in the time taken to establish an equilibrium distribution of vacancies. This calculation should therefore be taken as an order of magnitude estimation of the typical timescales of ionic migration across a thin film device under typical operating conditions. This timescale is much greater than the electron transport timescale, which can be calculated as 3.6 ns under an external bias of 1 V , based on the reported electron mobility [77].

For the dielectric measurements on $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystals, the time taken to traverse a 1.1 mm crystal under a 0.1 V excitation is calculated to be $3.5 \times 10^6\text{ s}$. Clearly, the effect of charge build-up in impedance measurements will only be evident in the sub-mHz frequency range.

3.4.2 Effect of ionic charge accumulation in photovoltaic devices

The accumulation of ionic vacancies near the surface of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ films is expected to alter the internal potential, affecting its charge carrier properties in photovoltaic devices. To consider this in detail, one must consider the spatial

3.4. Implications for conduction in $\text{CH}_3\text{NH}_3\text{PbI}_3$ films

variation of the electron energy bands throughout the film and how these are affected by ionic vacancies.

Figure 3.13(a) shows the vacuum potentials of the FTO and Au metallic contacts, alongside the conduction and valence band energies of $\text{CH}_3\text{NH}_3\text{PbI}_3$. In an operational photovoltaic device, electron- and hole-blocking layers are inserted between the contacts and the $\text{CH}_3\text{NH}_3\text{PbI}_3$, which create a high potential barriers for one charge carrier and therefore give good diode current-voltage characteristics. Here we consider a metal-semiconductor-metal device, as this was the device configuration measured experimentally in the hysteresis measurements. For an intrinsic (undoped) semiconductor, as the metallic contacts are made, the relative energies of the metallic contacts shift in order for the chemical potential to be in equilibrium throughout the device. This leads to a built-in potential across the semiconductor as shown in Figure 3.13(b). This situation is somewhat different to a doped semiconductor, where a depletion region is formed due to the transfer of electrons to the metallic conduction band, leaving behind ionized donor atoms [30]. This creates a Schottky barrier which is sometimes referred to as band bending at the surface (i.e. the internal potential gradient is steeper close to the surface). However, within the central region of the doped semiconductor there is no potential gradient and the bands are flat (there is no potential gradient). In the following discussion an intrinsic semiconductor is considered, as there is not necessarily intrinsic doping in $\text{CH}_3\text{NH}_3\text{PbI}_3$. Figure 3.13(c) shows the effect of ionic drift under the internal potential. A build-up of positive vacancies will occur near the surface of the Au contact, causing a lowering of the electron energy levels. This effect can also be considered as the development of a giant ionic polarisation that creates an internal field opposing the built-in potential; indeed this is the physical implication of the large dielectric constant at low frequency, that the halide perovskite is able to polarise, through ionic motion rather than ferroelectric effects, in order to screen the

3.4. Implications for conduction in $\text{CH}_3\text{NH}_3\text{PbI}_3$ films

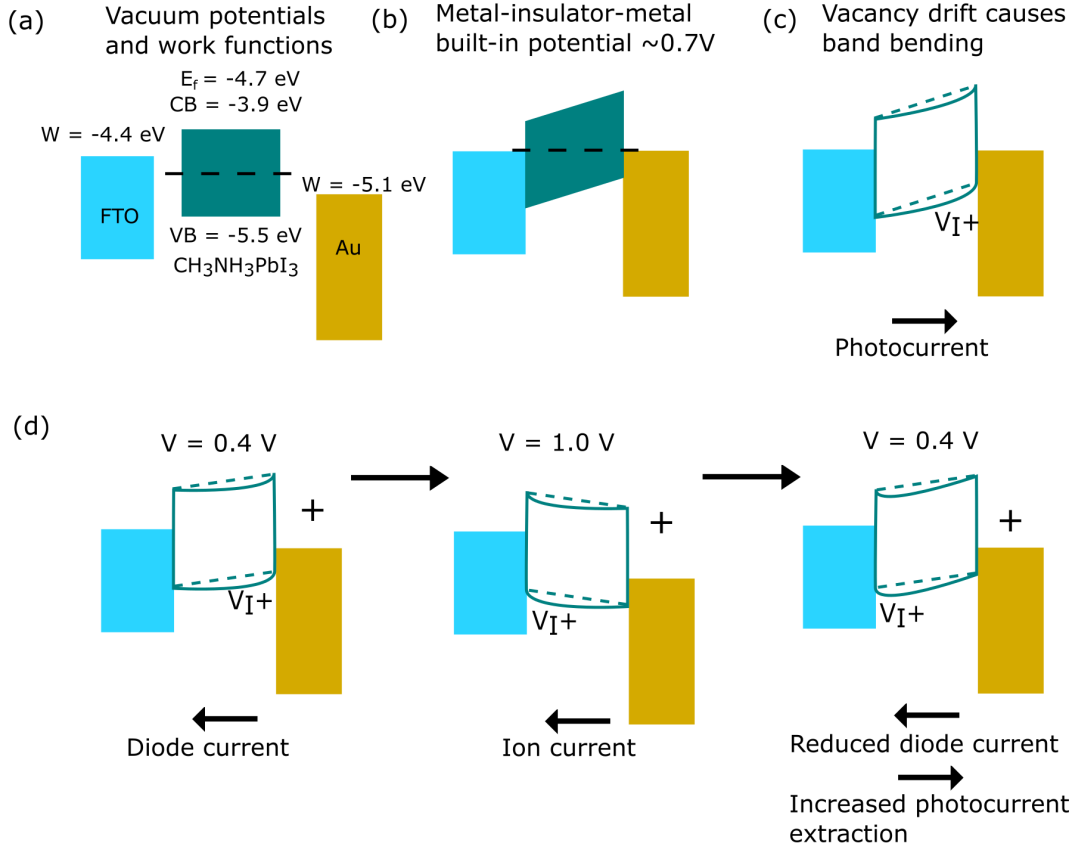


Figure 3.13: Schematic of the spatial variation of electron band energies in a metal-semiconductor-metal device with ionic vacancies. (a) Vacuum work functions of the metallic electrodes and electron energy bands in $\text{CH}_3\text{NH}_3\text{PbI}_3$. (b) Upon contact, the equilibrium condition requires a shift of the energy levels, creating a built-in potential within the semiconductor/insulator. (c) For an undoped semiconductor with ionic vacancies, this potential would cause ionic drift, leading to a lowering of the electron energy levels close to the Au contact. In the diagram, the solid lines represent the spatial variation in the conduction and valence band energies throughout the film, the dashed lines represent the same energies in the absence of ionic drift. (d) Upon application of a positive bias voltage sweep, migration of halide vacancies will occur, causing band bending at the opposite electrode. The change in band bending caused by the ionic redistribution causes a reduction in the diode current and an increase in photocurrent extraction, leading to improved device operation.

3.4. Implications for conduction in $\text{CH}_3\text{NH}_3\text{PbI}_3$ films

external field within the material. This would reduce the photocurrent extraction relative to the case of no ionic drift (dashed lines in Figure 3.13) due to the lower internal field. In the case of multiple ionically conducting species with opposite charges, a band bending effect would occur at both contacts, however the discussion shall be limited to a halide ion migration as there is no evidence of CH_3NH_3 or Pb ion migration on the timescale of hysteresis measurements.

Figure 3.13(d) shows the effect on the electron band energies of applying a voltage sweep to the device. As a positive voltage is applied to the Au contact, the electron bands are lowered. A diode current will start to flow across the device, in the opposite direction to the photocurrent. As the applied voltage increases and overcomes any built-in potential, ion migration will occur across the device, leading to a transient ionic current and electron band bending at the FTO electrode instead of the Au electrode. Once the voltage is reduced, the electron bands are now modified compared to under an equivalent voltage for increasing V . Importantly, the internal field due to the redistribution of ionic charge opposes the external E -field, which reduces the diode current through the device while increasing the likelihood that a photoexcited carrier will be extracted at the desired electrode. This situation will persist until a reverse voltage is applied to induce ion migration, or until the built-in potential causes relaxation to the situation described by Figure 3.13(c).

In terms of the current measured during a positive voltage sweep under no illumination, upon increasing the voltage the transient ionic current will add to the diode current, causing an increased current flow. However, as the vacancy distribution starts to saturate, the internal field created will reduce the internal field, reducing the diode current. This describes the direct and indirect effect on the measured hysteresis; the direct charging due to ionic charge accumulation and the indirect effect this has on reducing the electrical conduction measured during a current-voltage sweep. The fact that this new state is maintained for repeated

sweeps (for example the second up and down pulses in the DWM) implies that the vacancy distribution does not redistribute at zero applied voltage on a timescale of seconds between voltage sweeps.

This mechanism is supported by recent experimental evidence in the literature. A field-switchable photocurrent was observed in $\text{CH}_3\text{NH}_3\text{PbI}_3$ -based devices due to the formation of reversible p-i-n doped structures induced by ion drift [78]. It has also been shown that the light-generated photovoltage causes ionic drift in the same manner as an external electric field, causing ionic migration that increased the conversion efficiency of devices under illumination [98].

3.4.3 Equivalent circuit model for $\text{CH}_3\text{NH}_3\text{PbI}_3$ films

Previous impedance spectroscopy data on thin films in the literature have revealed the presence of a low frequency arc centred at 0.28 Hz [60] or occurring with a characteristic time of several seconds [62]. Several explanation have been proposed for such effects, including molecular dipole ordering and reorientation [60] (despite the fact that molecular dipole reorientation is a high frequency process) and interfacial charge relaxation within the materials [62].

A simple equivalent circuit for a device, including the effect of ionic migration, can be constructed, as shown in Figure 3.14(a). The electronic resistance of the cell R_{elec} , plus the geometrical capacitance due to the dielectric constant and chemical capacitance (C_{tot}) can be modelled by a parallel RC component. The effect of ionic migration can be modelled by the addition of a series RC component in parallel to the electronic processes. Physically, this represents an additional current path through the device that is blocked at the contacts. Under constant voltage V , this would lead to an initial current V/R_{ion} that reduces exponentially to zero as the capacitor saturates, similar to what is observed in the fixed voltage switching measurement. An equivalent ionic capacitance $C_{\text{ion}} = 0.28 \text{ mF}$ can be estimated from the stored charge density of

3.4. Implications for conduction in $\text{CH}_3\text{NH}_3\text{PbI}_3$ films

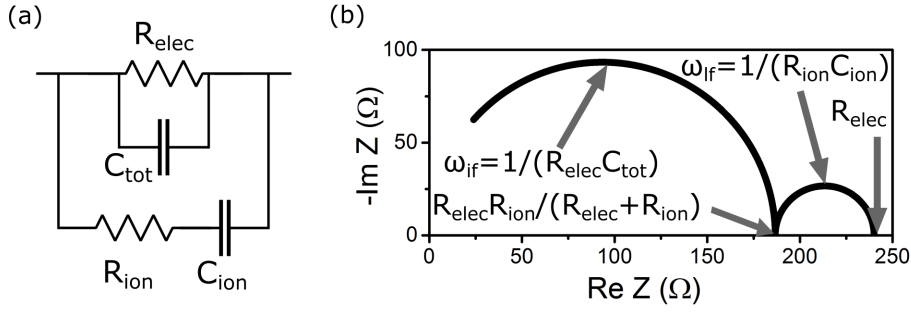


Figure 3.14: (a) Equivalent circuit model for a $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film device. The parallel RC circuit component models the electrical resistance of the device and geometrical capacitance, while the series RC component models the effect of ionic conduction that is blocked at the contacts. (b) The calculated frequency response of the equivalent circuit, plotted as a Nyquist impedance plot, showing an intermediate frequency arc with characteristic frequency $f_{\text{if}} = 15.8 \text{ kHz}$ and a low frequency arc with characteristic frequency $f_{\text{lf}} = 0.68 \text{ Hz}$. The ionic component of the equivalent circuit introduces the additional low frequency arc compared to a simple parallel RC circuit, and the calculated response is in good agreement with experimental observations in the literature [60].

2.5 mC cm^{-2} at 2 V in the DWM measurements (this capacitance includes the indirect effect of ionic migration on the electronic transport). R_{ion} and R_{elec} can be estimated by using an ohmic approximation to the resistance based on the current observed in the DWM measurement. Taking the values of the current at -1 V gives $R_{\text{ion}} = 840 \Omega$ and $R_{\text{elec}} = 240 \Omega$. Considering the dielectric response at frequencies below the molecular dipole resonance frequency, C_{tot} can be estimated as 42 nF . The response of the equivalent circuit is shown in Figure 3.14(b). The addition of the ionic component to the equivalent circuit was found to introduce an additional low frequency arc into the impedance plot, in agreement with reported experimental results but with a characteristic frequency f_{lf} of 0.68 Hz , on the same order of magnitude as reported experimentally [60]. The exact values of the characteristic frequencies are dependent on the geometric dimensions of the film, while the absolute and relative size of the arcs is determined by the magnitudes of R_{ion} and R_{elec} . For example, a film with electron and hole selective contacts would be expected to have a higher R_{elec} , which

would increase the width of the impedance plot and lower the characteristic frequency of the intermediate frequency relaxation.

Based on these considerations, an equivalent circuit that includes the effects of ionic migration provides a good explanation of the low frequency features seen in impedance spectroscopy, and dielectric effects due to ferroelectric/orientational order do not need to be invoked to explain such features.

3.5 Conclusion

In summary, the work presented in this chapter has investigated the issue of current-voltage hysteresis in $\text{CH}_3\text{NH}_3\text{PbI}_3$ devices, ruling out the possibility that this arises from a ferroelectric effect and putting an upper limit on any intrinsic ferroelectric polarisation of $1\text{ }\mu\text{C cm}^{-2}$. Measurements of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$ crystals by dielectric spectroscopy reveal low-frequency dispersion characteristic of hopping conduction, which is attributed to the ionic conduction of halide vacancies by analogy with known lead-halide ionic conductors. The activation energy of ionic conduction is determined to be 0.305 eV and 0.260 eV for $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$ respectively. This is predicted to result in ionic vacancy accumulation on a timescale of $\sim 0.1\text{ s}$ to 1 s under operating conditions in photovoltaic devices, which I propose can explain the current-voltage hysteresis and time dependent currents measured for $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin films.

While the considerations presented here give an overview of the effect of ionic migration on $\text{CH}_3\text{NH}_3\text{PbI}_3$ films, there is clearly a complex interplay between ionic migration, the photogeneration and transport of electronic charges and the surface physics at the interface between the perovskite and electron/hole extraction layers in photovoltaic devices. This creates a significant variation in the reported hysteresis, affected by the film growth and measurement conditions, as well as the

3.5. Conclusion

device history [95]. Despite this fact, consensus is building in the literature that hysteresis does not necessarily inhibit good photovoltaic device performance, as the necessary performance measure is the steady-state stabilised efficiency of the device, which may in fact be enhanced due to the effect of ionic vacancy accumulation on charge carrier extraction. While perovskite devices are still prone to degradation under illumination on long timescales (hours) [58], degradation attributed to ion migration has shown to be reversible over light and dark cycling representative of a day-night cycle [99]. However, any significant amount of vacancy accumulation, even if reversible on a day-night cycle, will in general cause a more unstable crystal structure, which is less than ideal for a photovoltaic device with a desired lifetime of over 20 years. Given the low vacancy migration energies determined in this study, vacancy migration is likely to always occur under photovoltaic operating conditions. Therefore a key challenge will be to manage the perovskite film growth process to minimise the formation of ionic vacancies, if it is found that vacancy migration must be limited to maintain long-term device performance.

Chapter 4

Investigation of structure and dynamics of $\text{CH}_3\text{NH}_3\text{PbI}_3$ through X-ray and neutron scattering

4.1 Introduction

As interest in the lead halide perovskites has intensified, the crystal structure and space group assignment of $\text{CH}_3\text{NH}_3\text{PbI}_3$ has come under renewed scrutiny. Powder X-ray diffraction measurements of the structure of $\text{CH}_3\text{NH}_3\text{PbI}_3$ were first performed in the 1980s by Poglitsch and Weber [65]. This study found that above 327 K, the crystal structure was cubic with $Pm\bar{3}m$ symmetry, between 162 K and 327 K a tetragonal structure is realised, assigned to either $I4/m$ or $I4/mcm$ space group symmetry, while below 162 K the structure is orthorhombic, with assigned space group symmetry $Pna2_1$. Further studies of the crystal structure by single crystal X-ray diffraction were made in 2002 by Kawamura *et al.* [66] In this study, the tetragonal space group was determined to be $I4/mcm$, and the rotation of the PbI_6 octahedra about the tetragonal c axis was identified as the order parameter that drives the cubic-tetragonal

transition.

In a more recent X-ray diffraction study, Baikie *et al.* [100] reported that at room temperature, the tetragonal phase exhibits reflection conditions consistent with the $I4/m$ space group and not $I4/mcm$, however structural refinement was only possible in $I4/mcm$ and not in $I4/m$. Furthermore, the orthorhombic phase was assigned to $Pnma$ rather than $Pna2_1$, in agreement with a previous neutron study on the orthorhombic phase of $\text{CH}_3\text{ND}_3\text{PbBr}_3$ [89]. Other reports by Stoumpos *et al.* [64], and Dang *et al.* [101] determined the tetragonal phase space group to be $I4cm$, however Stoumpos *et al.* state that noncentrosymmetric space group assignment was preferred as the correct choice when ambiguity occurred, due to the noncentrosymmetry introduced to the system by the polar CH_3NH_3 molecule.

One peculiarity of the crystal structure of $\text{CH}_3\text{NH}_3\text{PbI}_3$, as well as other organic halide perovskites such as formamidinium lead iodide ($\text{HC}(\text{NH}_2)_2\text{PbI}_3$), is that the organic molecule is located at a site of higher symmetry than the symmetry of the molecule. In $\text{CH}_3\text{NH}_3\text{PbI}_3$, the site symmetry is $\bar{4}2m$ in the tetragonal phase (assuming $I4/mcm$ space group symmetry) and $m\bar{3}m$ in the cubic phase, whereas the CH_3NH_3 molecule has $3m$ symmetry. Hence the molecule must be disordered in the cubic and tetragonal phases, either statically or dynamically, with ordering only occurring in the orthorhombic phase. This disorder, alongside the fact that the organic molecule contains much lighter elements than the inorganic Pb-I framework, makes a precise determination of the structure difficult for diffraction studies, in particular for X-ray diffraction studies. The orientation of the CH_3NH_3 molecule in the tetragonal phase was determined to align along one of four (111) directions by Kawamura *et al.* [66], however in their study it was not possible to distinguish between C and N, while the H atoms were not included in the refinement.

The timescales of molecular motion have also been investigated by NMR spectroscopy [102], [103] and quasielastic neutron diffraction [104], [105]. This

revealed that the CH_3NH_3 molecule undergoes reorientational motion that becomes increasingly fast as temperature increases, and can be considered as isotropic in the cubic phase.

The issue surrounding the correct structural description has caused significant debate in the literature. Accurate knowledge of the crystal structure and dynamics is essential for understanding how the different elements of the crystal structure contribute to the excellent photovoltaic properties of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and related compounds. For example, one DFT study of the band structure taking into account the rotation of CH_3NH_3 has shown that the lowering of local symmetry when the orientation of the CH_3NH_3 moves from the (111) to (011) direction changes the band gap from direct to indirect [106]. Furthermore, knowledge of the structure and dynamics is crucial to determine whether ferroelectricity in $\text{CH}_3\text{NH}_3\text{PbI}_3$ can contribute to the current-voltage hysteresis. The $I4/mcm$ structure has the non-polar point group $4/mmm$ and as such cannot support a macroscopic ferroelectric polarisation, whereas the $I4cm$ structure has the point group $4mm$ and therefore can allow ferroelectricity. Additionally, the dynamics of the CH_3NH_3 molecule is responsible for the large dielectric constant that will reduce the exciton binding energy, while it will also affect the charge carrier dynamics of free electrons and holes through the interaction with the Pb-I framework. Therefore a detailed understanding of the CH_3NH_3 molecular motion is crucial to understanding the photovoltaic performance of halide perovskite devices.

In this chapter I present X-ray diffraction measurements of single crystals of $\text{CH}_3\text{NH}_3\text{PbI}_3$, at room temperature, in order to investigate the discrepancies reported in the literature. I also present a quasielastic neutron scattering study on single-crystal $\text{CH}_3\text{NH}_3\text{PbI}_3$, a technique that utilises the incoherent scattering of the neutron from the hydrogen atoms to investigate the dynamics of the CH_3NH_3 molecule. This single crystal study enabled a direct measurement of the motion of

the CH_3NH_3 within the crystal and of the anisotropy of motion within different planes, giving key insights that cannot be obtained from the recent quasielastic neutron powder studies in the literature [104], [105].

4.2 Structural investigation by X-ray diffraction.

4.2.1 Crystals grown in the cubic phase

In order to investigate the crystal structure in the tetragonal phase, X-ray diffraction data was taken at 295 K on small ($<100\text{ }\mu\text{m}$) single crystals of $\text{CH}_3\text{NH}_3\text{PbI}_3$, cleaved from larger crystals grown in the cubic phase by a solution growth technique [101]^a. X-ray diffraction measurements were made on an Agilent SuperNova X-ray diffractometer, and the resultant scattering intensities were corrected for absorption by taking into account the crystal shape using the CrysAlis software package. Structural models were refined using the FullProf software suite [107]. The positions of the hydrogen atoms were not included in the refinement due to the low intensity of X-ray scattering from hydrogen and large thermal motions of the CH_3NH_3 molecule. The analysis presented here is representative of a number of measured crystals.

In order to correctly describe the diffraction pattern, one must take into account the effect of symmetry twinning. Crystals of $\text{CH}_3\text{NH}_3\text{PbI}_3$ are grown above the cubic phase transition and upon cooling to room temperature tetragonal phase one expects three types of symmetry twins to form due to the loss of cubic symmetry. The symmetry twins are transformed into one another by the lost threefold axes and are defined by the direction of the fourfold axis, which will lie along one of the three cubic axes. The extent of twinning present will be determined by the crystal size and

^aI am grateful to Dr A. Haghighirad for growing the high-quality $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystals that I used for the X-ray and neutron scattering measurements presented in this chapter.

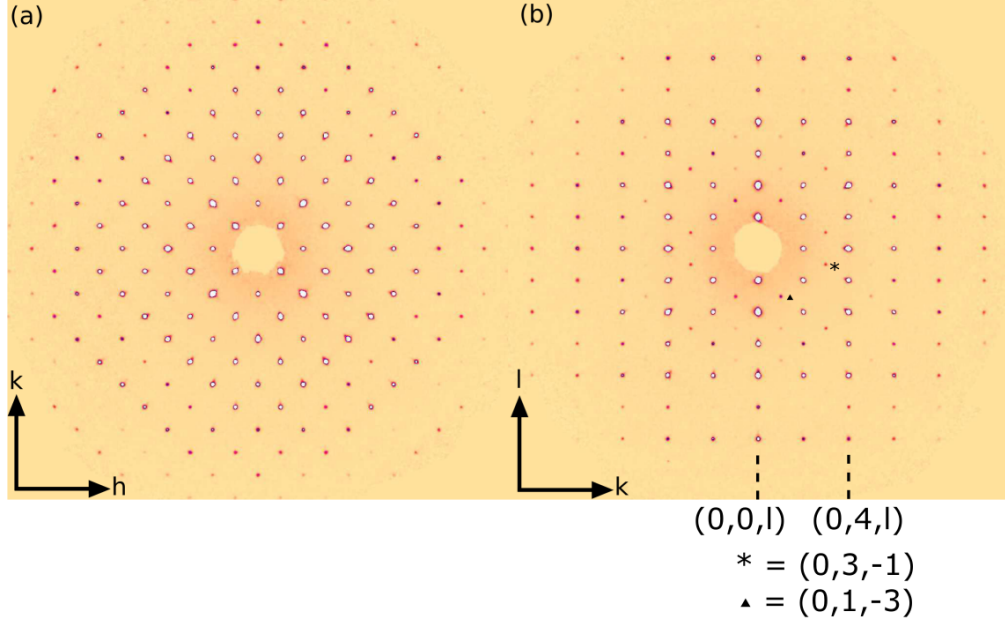


Figure 4.1: X-ray diffraction pattern of $\text{CH}_3\text{NH}_3\text{PbI}_3$ at 295 K in the (a) $(h,k,0)$ and (b) $(0,k,l)$ planes. In the $(0,k,l)$ plane, Bragg peaks are observed at $(0,3,-1)$, $(0,1,-3)$ and $(0,3,-5)$, plus symmetry equivalent positions. These reflections are forbidden in $I4/mcm$ and $I4cm$ but are allowed in lower symmetry space groups such as $I4/m$, as well as in the presence of symmetry twin domains.

may not necessarily be present in a small crystal, depending on the energetics of twin formation and subsequent twin size.

First, a single-twin analysis was performed. The unit cell parameters were determined to be $a = b = 8.8751(1) \text{ \AA}$, $c = 12.6642(3) \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$, in excellent agreement with previous reports [65], [66]. Figure 4.1 shows images of the diffraction pattern in the $(h,k,0)$ plane and $(0,k,l)$ plane. Reflections are observed at a series of positions in the $(0,k,l)$ plane which are forbidden by the $I4/mcm$ and $I4cm$ space groups. For $I4/mcm$ and $I4cm$, the general reflection condition for the $(0,k,l)$ plane is that $k, l = 2n$, whereas for $I4/m$, the general reflection condition for the $(0,k,l)$ plane is that $k + l = 2n$. Therefore a lower symmetry structure for the tetragonal phase would allow for these additional reflections, however one must also take into account the potential for symmetry twins to account for these reflections;

4.2. Structural investigation by X-ray diffraction.

Table 4.1: Atomic parameters at 295 K, based on refinement of single-crystal diffraction data into the $I4/m$ space group. Standard errors are given in parentheses for all independent parameters.

Space group $I4/m$				
	x	y	z	$U_{eq}(\text{\AA}^2)$
Pb(1)	0.0	0.0	0.0	0.033(1)
Pb(2)	0.0	0.0	0.5	0.033(1)
I(1)	0.2163(3)	0.2851(4)	0.0	0.088(3)
I(2)	0.0	0.0	0.2489(4)	0.086(2)
C	0.479(44)	-0.050(24)	0.286(18)	0.11(1)
N	0.462(17)	0.080(15)	0.271(16)	0.07(1)
	$U_{11}(\text{\AA}^2)$	$U_{22}(\text{\AA}^2)$	$U_{33}(\text{\AA}^2)$	$U_{12}(\text{\AA}^2)$
Pb(1)	0.032(1)	0.032	0.034(2)	0.0
Pb(2)	0.033(1)	0.033	0.032(1)	0.0
I(1)	0.078(3)	0.064(3)	0.121(2)	-0.046(2)
I(2)	0.117(2)	0.117(2)	0.024(1)	0.0
Number of independent reflections = 449, $R_{\text{int}} = 5.35\%$, $R(F^2) = 3.84\%$, number of fitted parameters = 23				

i.e. can these peaks be successfully indexed in the reference frame of a symmetry twin.

In order to test the lower symmetry description of the crystal structure, the diffraction data was refined in the $I4/m$ space group. A structural model was successfully refined in $I4/m$, with an R -int of 5.14 and an $R(F^2)$ of 3.84, suggesting a good fit; the structural parameters are shown in Table 4.1. However upon closer inspection of the observed and calculated intensities it can be seen that an $I4/m$ structure does not account for the intensity of the additional reflections. Figure 4.2 shows the observed and calculated intensities for the lower symmetry $I4/m$ structure, split into the reflections that are allowed and forbidden by the reflection conditions of $I4/mcm$. As can be seen from Figure 4.2(b), the most intense reflections that are only allowed in $I4/m$ are over an order of magnitude more intense than calculated based on the structural model. Therefore, a structure with $I4/m$ symmetry is not sufficient to describe the additional reflections and symmetry

4.2. Structural investigation by X-ray diffraction.

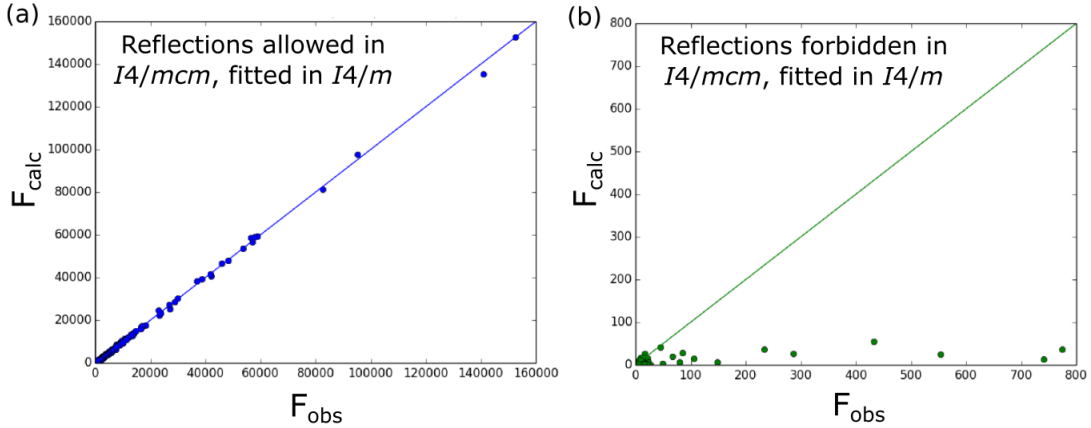


Figure 4.2: Observed and calculated intensities for the diffraction data based on a lower symmetry $I4/m$ structure. The observed reflection intensities are split into two groups, those that are allowed (a) and forbidden (b) by the reflection conditions of $I4/mcm$. As can be seen from plot (b), the most intense reflections that are only allowed in $I4/m$ are an over an order of magnitude more intense than calculated based on the structural model, hence a structure with $I4/m$ symmetry is not sufficient to describe the additional reflections.

twin domains must be considered to account for these additional reflections.

To consider the effect of symmetry twin domains, a refinement was performed including the existence of three domains related by the cubic threefold axis. A successful refinement was achieved in the space group $I4/mcm$, and the results of the structural and domain refinement are shown in Table 4.2. The refinement gave an improved $R(F^2)$ factor of 3.23%, compared to 3.84% for the $I4/m$ structure. The obtained structure is similar to that previously reported by Kawamura *et al.* [66], however the position of the C and N atoms could not be determined with high accuracy, as evidenced by the large thermal displacement parameters obtained. Interestingly, the I atoms also displayed large anisotropic thermal motions perpendicular to the direction of the Pb-I-Pb bonds. The domain fractions in this crystal were determined to be 0.92(1), 0.04(1) and 0.04(1), indicating the presence of symmetry twinning within the crystal. Importantly, the additional reflections could all be indexed as allowed peaks of the two twin domains. Therefore the

4.2. Structural investigation by X-ray diffraction.

Table 4.2: Atomic parameters at 295 K, based on refinement of single-crystal diffraction data into the $I4/mcm$ and $I4cm$ space groups. Standard errors are given in parentheses for all independent parameters.

Space group $I4/mcm$				
	x	y	z	$U_{eq}(\text{\AA}^2)$
Pb	0.0	0.0	0.0	0.033(1)
I(1)	0.2144(4)	0.2856	0.0	0.085(1)
I(2)	0.0	0.0	0.25	0.082(1)
C	0.529(18)	-0.029	0.279(15)	0.11(1)
N	0.435(10)	0.065	0.219(12)	0.08(1)
	$U_{11} = U_{22}(\text{\AA}^2)$	$U_{33}(\text{\AA}^2)$	$U_{12}(\text{\AA}^2)$	
Pb	0.033(1)	0.033(1)	0.0	
I(1)	0.070(1)	0.116(3)	-0.044(2)	
I(2)	0.111(3)	0.023(1)	0.0	
Number of independent reflections = 407, $R_{\text{int}} = 5.10\%$, $R(F^2) = 3.23\%$, number of fitted parameters = 18. Refined domain fractions; 0.92(1), 0.04(1), 0.04.				
Space group $I4cm$				
	x	y	z	$U_{eq}(\text{\AA}^2)$
Pb	0.0	0.0	0.0	0.033(1)
I(1)	0.2143(3)	0.2857	0.0004(10)	0.086(1)
I(2)	0.0	0.0	0.2496(7)	0.082(1)
C	0.527(19)	-0.026	0.277(12)	0.13(1)
N	0.435(8)	0.065	0.220(8)	0.09(1)
	$U_{11} = U_{22}$	U_{33}	U_{12}	
Pb	0.033(1)	0.033(1)	0.0	
I(1)	0.071(1)	0.116(2)	-0.044(1)	
I(2)	0.111(2)	0.023(1)	0.0	
Number of independent reflections = 762, $R_{\text{int}} = 5.05\%$, $R(F^2) = 3.42\%$, number of parameters = 20. Refined domain fractions; 0.915(9), 0.042(7), 0.043.				

4.2. Structural investigation by X-ray diffraction.

presence of $I4/mcm$ symmetry twins provides a natural explanation of previous reports in the literature of an $I4/m$ space group [100].

In order to investigate the potential for a ferroelectric displacement of the I atoms, the structure was also refined into the $I4cm$ space group. The $I4cm$ space group allows a shift of the I atoms along the z direction and the CH_3NH_3 site symmetry is reduced to m ; as such the CH_3NH_3 is disordered but occupies one of two orientations, both of which have a dipole moment along the $+c$ direction. It was found that the $R(F^2)$ for $I4cm$ was slightly worse at 3.42%. Importantly, the I atoms were not shifted, within error, from their positions in the higher symmetry $I4/mcm$ space group, while the reduction in site symmetry for the C-N molecule from fourfold to twofold does not result in an improved fit. This comparative study therefore shows that there is no evidence that the crystal adopts a lower symmetry space group than $I4/mcm$.

4.2.2 Crystals grown below the cubic phase transition

For the quasielastic neutron scattering measurements presented later in this chapter, it was desirable to minimise the amount of twinning in crystals of $\text{CH}_3\text{NH}_3\text{PbI}_3$. One means to circumvent the issue of symmetry twinning is to grow crystals below the cubic-tetragonal phase transition. However this is experimentally challenging, as lower temperatures are not optimal for the formation of large single crystals from solution growth processes, and only smaller single crystals were formed of a typical maximum size of $1\text{ mm} \times 1\text{ mm} \times 1\text{ mm}$. To investigate whether a low temperature growth process can eliminate symmetry twinning, X-ray diffraction measurements were performed on these smaller crystals grown below the cubic-tetragonal phase transition.

Crystals grown below the phase transition were found to show significantly less symmetry twinning for crystals of comparable size. Data was taken on small ($< 100\text{ }\mu\text{m}$) single crystals of $\text{CH}_3\text{NH}_3\text{PbI}_3$. Results of a structural refinement of the

4.2. Structural investigation by X-ray diffraction.

crystal structure into the $I4/mcm$ space group for a typical crystal is shown in Table 4.3. The R factors were slightly higher at $R_{\text{int}}=5.96\%$ and $R(F^2) = 4.26\%$, and the refinement gave similar atomic parameters to the crystals grown in the cubic phase. A refinement was also attempted in $I4cm$. This also gave an internal R -factor of 5.96% and a slightly worse $R(F^2)$ of 4.31% . The positions of the I atoms were found to be the same within error as the $I4/mcm$ structure (I(1); $z = -0.0003(9)$, I(2); $z = 0.2500(7)$), giving no indication of a polar Pb-I framework.

The domain fraction of the largest domain was determined to be $98.6(6)\%$, significantly higher than the $92(1)\%$ found for the crystal grown above the cubic transition, however weak diffraction peaks were still observed at the forbidden reflections, due to the tetragonal symmetry twins. The existence of a very small twin fraction could be due to growth twins, where crystal twins grow with different orientations but share a common plane of atoms: one may expect the nucleation of some growth twins due to the close matching of the twin lattices, particularly for the slower growth in the tetragonal phase. Furthermore, the cubic to tetragonal phase transition has been shown to be broad and exhibit phase coexistence [108], and as such it is possible that phase coexistence may be present during growth leading to a reduced but non-zero level of twinning.

4.2.3 Discussion

The findings of this analysis are consistent with subsequent neutron diffraction studies in the literature, which have since sought to address the issues surrounding the crystal structure. Weller *et al.* [63] performed a neutron powder diffraction study, where the orthorhombic phase at 100 K was determined to have $Pnma$ symmetry (in agreement with an earlier neutron powder diffraction study [89]), an $I4/mcm$ structure in the tetragonal phase at 180 K and a $Pm\bar{3}m$ cubic structure at 352 K. Furthermore, the data indicated orientational disorder in the tetragonal

4.2. Structural investigation by X-ray diffraction.

Table 4.3: Atomic parameters at 295 K, based on refinement of single-crystal diffraction data into the $I4/mcm$ space group. Errors are given in parentheses for all independent parameters.

Space group $I4/mcm$				
	x	y	z	$U_{eq}(\text{\AA}^2)$
Pb	0.0	0.0	0.0	0.033(1)
I(1)	0.2134(3)	0.2866	0.0	0.0854
I(2)	0.0	0.0	0.25	0.0816
C	0.528(13)	-0.028	0.276(10)	0.11(1)
N	0.433(7)	0.067	0.218(8)	0.08(1)
	$U_{11} = U_{22}$	U_{33}	U_{12}	
Pb	0.035(1)	0.034(1)	0.0	
I(1)	0.071(1)	0.116(2)	-0.043(1)	
I(2)	0.108(3)	0.026(1)	0.0	
Number of independent reflections = 397, $R_{\text{int}} = 5.96\%$, $R(F^2) = 4.26\%$, number of fitted parameters = 18. Refined domain fractions; 0.986(6), 0.005(5), 0.009.				

phase, which was refined as a fourfold orientational disorder, with increasingly large thermal displacement parameters upon increasing temperature. Another study was performed by Whitfield *et al.* [108], who investigated the structure of deuterated and hydrogenous $\text{CH}_3\text{NH}_3\text{PbI}_3$ by neutron and synchrotron X-ray diffraction. This study also found that the orthorhombic phase is described by the $Pnma$ structure, with the tetragonal structure being of $I4/mcm$ symmetry. In the tetragonal phase, both fourfold and eightfold disorder (where the C/N atoms can be interchanged) were considered, however an unambiguous determination between the two was not possible [108]. Furthermore, a high level of disorder was found in the cubic phase, with the CH_3NH_3 molecule occupying one of 24 equivalent orientations.

4.3 Rotational dynamics of CH_3NH_3 investigated by quasielastic neutron scattering

Quasielastic incoherent neutron scattering has the potential to resolve some of the issues regarding the cation orientation and motion that pose challenges for refinement of Bragg diffraction data. As described in Chapter 2, incoherent quasielastic scattering measures the self-correlation of a particle as a function of time. This, combined with the directional information contained within the scattering wavevector, enables determination of the molecular motions in different spatial directions within the crystal. Incoherent scattering techniques are particularly well suited to studying the dynamics of the CH_3NH_3 molecule as the large incoherent cross section of hydrogen will dominate over all other elements in the material.

There have been two recent reports in the literature of quasielastic neutron scattering studies [104] [105], however both studies were performed on powder samples and thus only contain information on the spherically averaged properties. Chen *et al.* [104] measured the quasielastic scattering as a function of temperature to determine timescales of rotation, and fitted rotational models to describe the q -dependence of quasielastic scattering. Another study was performed by Leguy *et al.* [105], who also investigated the rotational timescales and q -dependence of quasielastic scattering. The data was interpreted in terms of the stabilisation of ferroelectric or antiferroelectric domains, however the deduced timescales were inconsistent with previous studies [65, 102, 103]. As these studies were performed on powder samples, unambiguous determination of the CH_3NH_3 reorientational motion was not possible; Leguy *et al.* [105] found several reorientational motions consistent with the data, while Chen *et al.* [104] found that an isotropic and fourfold model give similar results at 300 K.

4.3. Rotational dynamics of CH₃NH₃ investigated by quasielastic neutron scattering

In this section I present temperature dependent measurements on a large cubic crystal, to investigate the changing rotational and reorientational timescales over the three phases. I also present a study on an array of tetragonal single crystals, in order to investigate scattering in different crystallographic planes, revealing how the molecular dynamics change between the orthorhombic and tetragonal phase up to room temperature.

4.3.1 Calculated incoherent neutron scattering functions

As a prelude to the experimental results, it is insightful to consider the expected forms of scattering due to the particular molecular motions. In this section I shall use the symmetry formalism applied to jump models as described in Chapter 2 to calculate the expected forms of scattering.

4.3.1.1 Form of $S(\mathbf{Q}, \Delta E)$ for a threefold jump model in the orthorhombic phase

Figure 4.3 shows the orthorhombic structure viewed along the orthorhombic b axis (the tetragonal c axis), based on the recently reported $Pnma$ structure [63]. The CH₃NH₃ molecule is located on a site of symmetry $1m1$, however the mirror operation does not correspond to a physical rotation of the molecule. Therefore, the rotational dynamics are purely described by the molecular point symmetry 3. Therefore, as described in Chapter 2, the expressions for the characteristic timescales and amplitudes of scattering for a jump rotations are given by

$$A_\mu(\mathbf{Q}) = \frac{\chi_\mu^E}{g} \sum_\nu \chi_\mu^\nu \sum_{C_\nu} \exp\{i\mathbf{Q} \cdot (\mathbf{R} - C_\nu \mathbf{R})\}, \quad (4.1)$$

$$\frac{1}{\tau_\mu} = \sum_\nu \frac{n_\nu}{\tau_\nu} \left(1 - \frac{\chi_\mu^\nu}{\chi_\mu^E}\right), \quad (4.2)$$

where ν labels the classes of C and μ labels the irreducible representations of Γ .

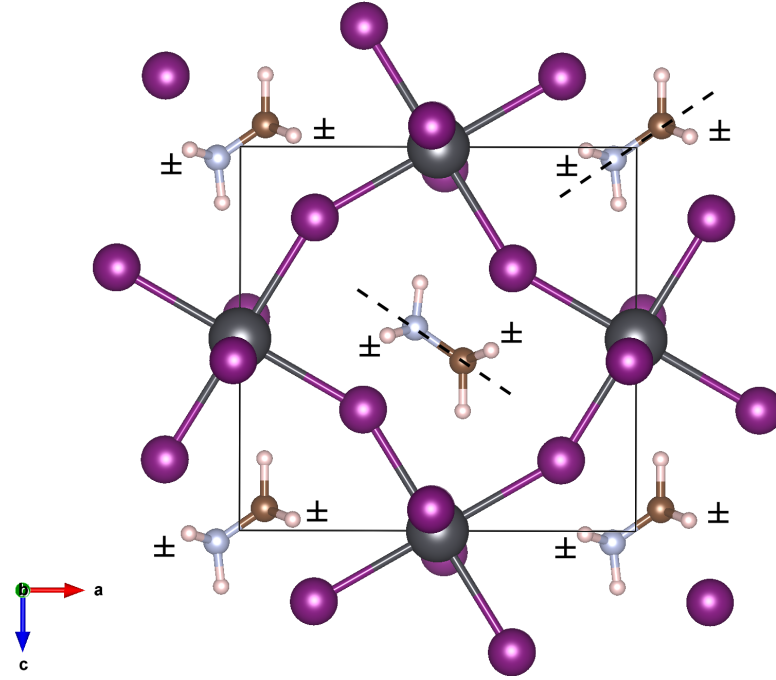


Figure 4.3: $Pnma$ orthorhombic crystal structure reported in Ref. [63], projected along the orthorhombic b axis (tetragonal c axis), showing the staggered orientation of the two crystallographically equivalent CH_3NH_3 molecules at $y = 0.75$. $\pm$ indicates the existence of hydrogen atoms above and below the $y = 0.75$ plane where the lower is obscured from view. For threefold rotational motion about the C-N axis (dashed line), the strongest quasielastic scattering is expected in the plane normal to the C-N axis, therefore the sum of the scattering from the two molecular orientations is strongest along the tetragonal c direction.

The point group 3 has two real irreducible representations, the totally symmetric representation A, and the two-dimensional representation E^b. Applying the relation of Equation 4.2 to the character table of the point group 3 leads to the inverse timescales $1/\tau_\mu = 0$ and $1/\tau_\mu = 3/\tau_3$ for the A and E irreducible representations respectively, where τ_3 is the timescale on which molecule undergoes a threefold rotation about the C-N axis. Therefore the A mode corresponds to purely elastic scattering, while the E mode corresponds to quasielastic scattering with an

^bThe two-dimensional representation E can be further reduced to two one-dimensional complex representations that are complex conjugates of each other. However, in dealing with physical properties such as rotational timescales, one must take the sum of the characters of these two complex representations to determine the characters of the real representation E.

4.3. Rotational dynamics of CH_3NH_3 investigated by quasielastic neutron scattering

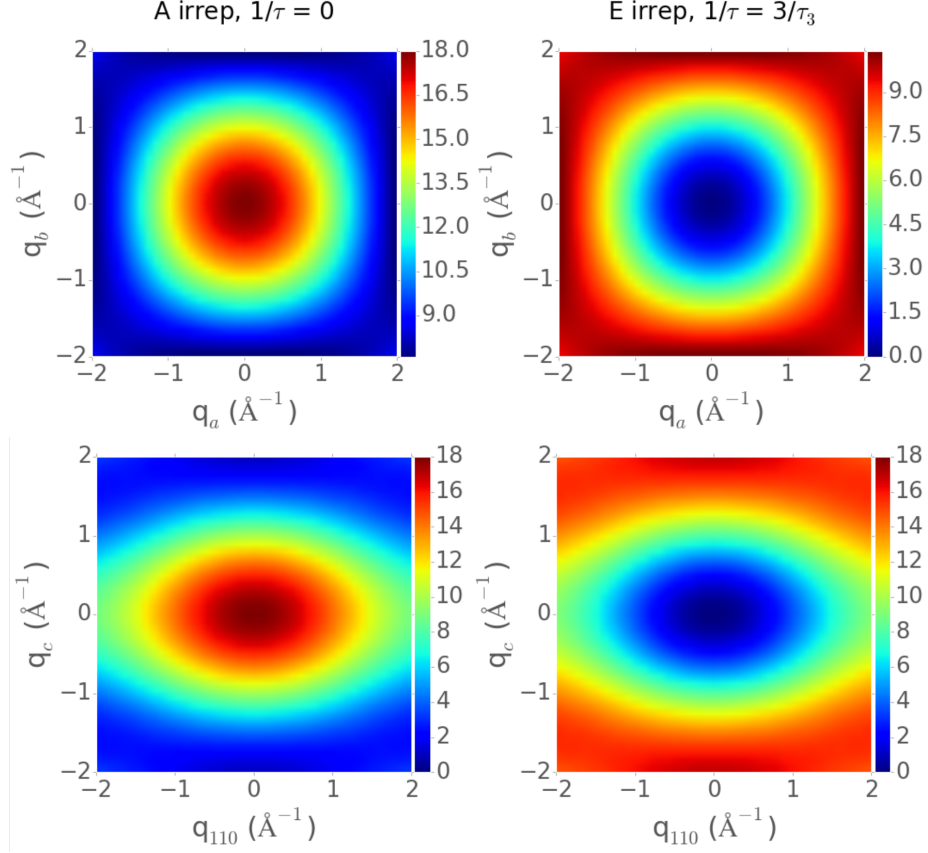


Figure 4.4: Calculated total (energy-integrated) contributions to incoherent scattering in the orthorhombic phase from the A and E modes, in the q_a - q_b and q_{110} - q_c planes. The tetragonal setting of reciprocal space is used to enable comparison between temperatures. The calculation assumed an equal fraction of orthorhombic twins (with no $\langle u^2 \rangle$ value). The energy distribution at each q -point is given by a delta function for the A mode, and a Lorentzian with half-width $3/\tau_3$ for the E mode. As the CH_3NH_3 molecular axes lie in the tetragonal ab plane with a staggered orientation, the threefold rotation of the CH_3NH_3 molecules gives the highest intensity of scattering along the tetragonal c direction.

energy-transfer distribution characterised by a Lorentzian with half-width $3/\tau_3$. In determining the expected $\mathbf{q}$ -dependence of the quasielastic scattering $A_\mu(\mathbf{q})$ from Equation 4.1, one must take the effect of orthorhombic twinning into account, as the dot product between scattering vector and atomic positions will be different for orthorhombic symmetry twins. The orthorhombic symmetry twins arise due to the loss of the tetragonal fourfold symmetry, which leads to a non-unique choice of the

4.3. Rotational dynamics of CH₃NH₃ investigated by quasielastic neutron scattering

orthorhombic a axis from the tetragonal a or b axis. In this analysis, an equal population of the two orthorhombic twins is assumed, as in the experiment there is no reason that one twin should be favoured over the other, while the large number of crystals means that close to a 50:50 domain distribution should be obtained if each crystal forms only one orthorhombic domain.

The amplitudes were calculated from Equation 4.1 for the two modes in the q_a - q_b and q_{110} - q_c planes, assuming an equal fraction of orthorhombic twins, and are shown in Figure 4.4. In all calculations and fits presented in this Chapter, only the hydrogen atoms are considered to contribute to the scattering, as the incoherent cross section of hydrogen is over 160 times larger than any of the other elements in CH₃NH₃PbI₃. The tetragonal setting of reciprocal space is used, to enable comparison between all temperatures investigated. The molecular threefold rotations in the $Pnma$ structure produce the highest scattering intensity along the tetragonal c axis, while the scattering intensity in the ab plane is almost isotropic. The high level of isotropy within the ab plane is due to the symmetry twinning introduced, however the scattering in the q_{110} - q_c plane is unaffected by the orthorhombic twin fraction. Physically, the highest intensity of scattering along the c direction is due to the staggered orientation of the CH₃NH₃ molecules in the ab plane. The strongest quasielastic scattering from each molecule will occur in the plane normal to the C-N rotational axis. Therefore the maxima of scattering from the two molecular orientations sum directly along the tetragonal c direction, but are along different direction in the ab plane, causing anisotropic scattering intensity in the $q_{110} - q_c$ plane.

4.3.1.2 Form of $S(\mathbf{Q}, \Delta E)$ for a combined threefold-fourfold jump model in the tetragonal phase.

As consensus in the literature grows around a tetragonal structure with $I4/mcm$ symmetry, a model based on the published tetragonal structure becomes a natural starting point for analysis of quasielastic scattering data. Figure 4.5 shows the tetragonal structure at 180 K determined by Weller *et al.* [63], in which the CH₃NH₃ can occupy one of four symmetry equivalent orientations (the site symmetry is $\bar{4}2m$). The hydrogen atomic positions determined in this study were used for the calculations of predicted quasielastic scattering intensity. In the tetragonal phase, one must also consider the effect of rotations about the molecular threefold axis. As such, we can apply the combined jump model group theoretical result to the product group of the rotations about crystal and molecular axes, as discussed in Chapter 2. This gives the following expression for the characteristic timescales and amplitudes of scattering;

$$A_\mu(\mathbf{Q}) = \frac{\chi_\mu^{Ee}}{g} \sum_\nu \sum_\eta \chi_\mu^{\nu\eta} \sum_{C_\nu} \sum_{M_\eta} \exp\{i\mathbf{Q} \cdot (\mathbf{R} - C_\nu M_\eta \mathbf{R})\}, \quad (4.3)$$

$$\frac{1}{\tau_\mu} = \sum_\nu \frac{n_\nu}{\tau_\nu} \left(1 - \frac{\chi_\mu^{\nu e}}{\chi_\mu^{Ee}}\right) + \sum_\eta \frac{n_\eta}{\tau_\eta} \left(1 - \frac{\chi_\mu^{E\eta}}{\chi_\mu^{Ee}}\right). \quad (4.4)$$

While the crystal site symmetry of the centre of the CH₃NH₃ molecule is $\bar{4}2m$, the mirror operations of $\bar{4}2m$ do not correspond to physical reorientations of the molecule, whilst the 2_x operations result in the same physical transformations as the $\bar{4}$ operations. Therefore to fully describe the rotations of the molecule in the crystal, it is sufficient to use a crystal point group $\bar{4}$ and a molecular point group 3. The $\bar{4}$ point group contains two fourfold roto-inversion operators as well as a twofold rotation, to which are ascribed characteristic timescales τ_4 and τ_2 , as shown in Figure 4.5.

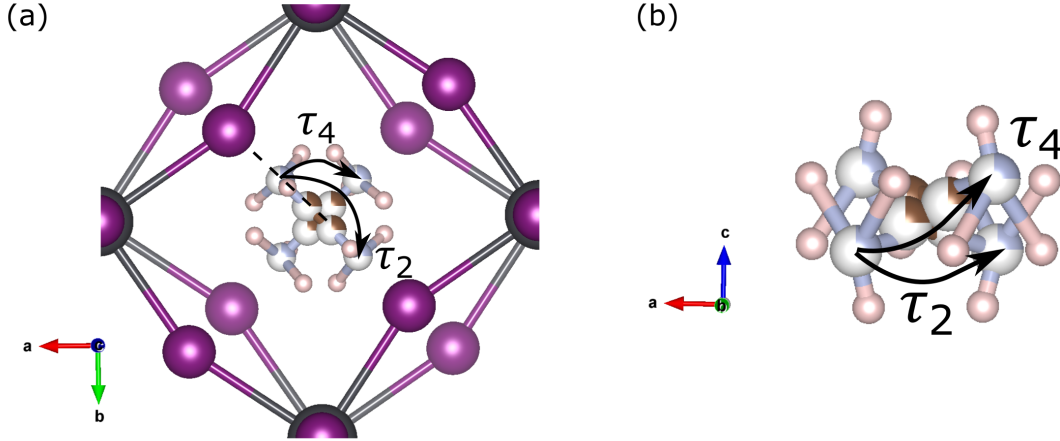


Figure 4.5: Rotational motions of the CH_3 end of the CH_3NH_3 molecule, based on the $I4/mcm$ crystal structure at 180 K. τ_2 and τ_4 are twofold and fourfold reorientations of the molecule about the c axis, whereas τ_3 is a threefold rotation about the molecule's own axis and does not give reorientation of the C-N molecular axis.

The product group $\Gamma = 3 \times \bar{4}$ has six real irreducible representations ^c. The rotational timescales were calculated from Equation 4.4 for each irreducible representation, and are listed in Table 4.4. The amplitudes for the tetragonal phase were calculated using Equation 4.3 and the literature atomic coordinates for the $I4/mcm$ phase at 180 K [63]; the amplitudes for each irreducible representation are shown in Figure 4.6. In this figure, the q -planes plotted correspond to the q -planes measured experimentally in this Chapter and the intensities correspond to the integrated intensities across all energy transfers ΔE at a given q -point. The $\Gamma_\mu = A \times A$ irreducible representation corresponds to elastic scattering (as $1/\tau_\mu = 0$) and gives the largest contribution to scattering at low $|q|$. The other five modes have energy distributions described by the Lorentzian functions $L(\Delta E, \tau_\mu)$. As it is expected that the τ_3 rotational motion happens on a much faster timescale than the τ_4 and τ_2 reorientational motions, the five quasielastic contributions can be further

^cAs is the case for the point group 3, the E representation of $\bar{4}$ is also a 2D real representation that can be reduced to two 1D complex irreducible representations. As such the six representations of Γ can be further reduced into lower-dimensional complex representations.

4.3. Rotational dynamics of CH₃NH₃ investigated by quasielastic neutron scattering

μ	Γ_μ	$1/\tau_\mu$
0	A $\times$ A	0
1	B $\times$ A	$4/\tau_4$
2	E $\times$ A	$2/\tau_4 + 2/\tau_2$
3	A $\times$ E	$3/\tau_3$
4	B $\times$ E	$4/\tau_4 + 3/\tau_3$
5	E $\times$ E	$2/\tau_4 + 2/\tau_2 + 3/\tau_3$

Table 4.4: Timescales associated with each irreducible representation of the product group $\Gamma = S_4 \times C_3$.

divided as follows. The timescales of the $B \times A$ and $E \times A$ modes will be much longer than the other three quasielastic modes, which have timescales dominated by τ_3 . Therefore the intensity of the $B \times A$ and $E \times A$ modes is expected to be dominant at low energy transfers, while the remaining three modes will dominate at higher energy transfer. Figures 4.7(a) and (b) show the modes summed into three groups for scattering in the $q_a - q_b$ and $q_{110} - q_c$ planes: the elastic mode and the modes which are expected to dominate at low and high energy transfer. This reveals that the scattering at low energy transfer is expected to be fairly isotropic in the $q_a - q_b$ plane but weaker along the q_c direction. However the scattering at high energy transfer will be fairly isotropic in the $q_a - q_b$ plane but stronger along the c direction. This is consistent with what one expects from a CH₃NH₃ molecular axis reorienting predominantly in the ab plane, giving higher scattering in the ab plane on longer timescales (low energy transfers), combined with faster threefold rotations about the C-N axis giving higher scattering along the c axis on shorter timescales (high energy transfers). As discussed in the following section, twinning was present in the measured crystals. Figures 4.7(c) and (d) show the same summed modes for the twin fractions that were determined experimentally. The angular dependence of scattering within the $q_{110} - q_c$ plane is less anisotropic, however a clear contrast is still visible between the c and (110) directions. In the $q_a - q_b$ plane, the angular dependence within the plane is essentially isotropic.

4.3. Rotational dynamics of CH₃NH₃ investigated by quasielastic neutron scattering

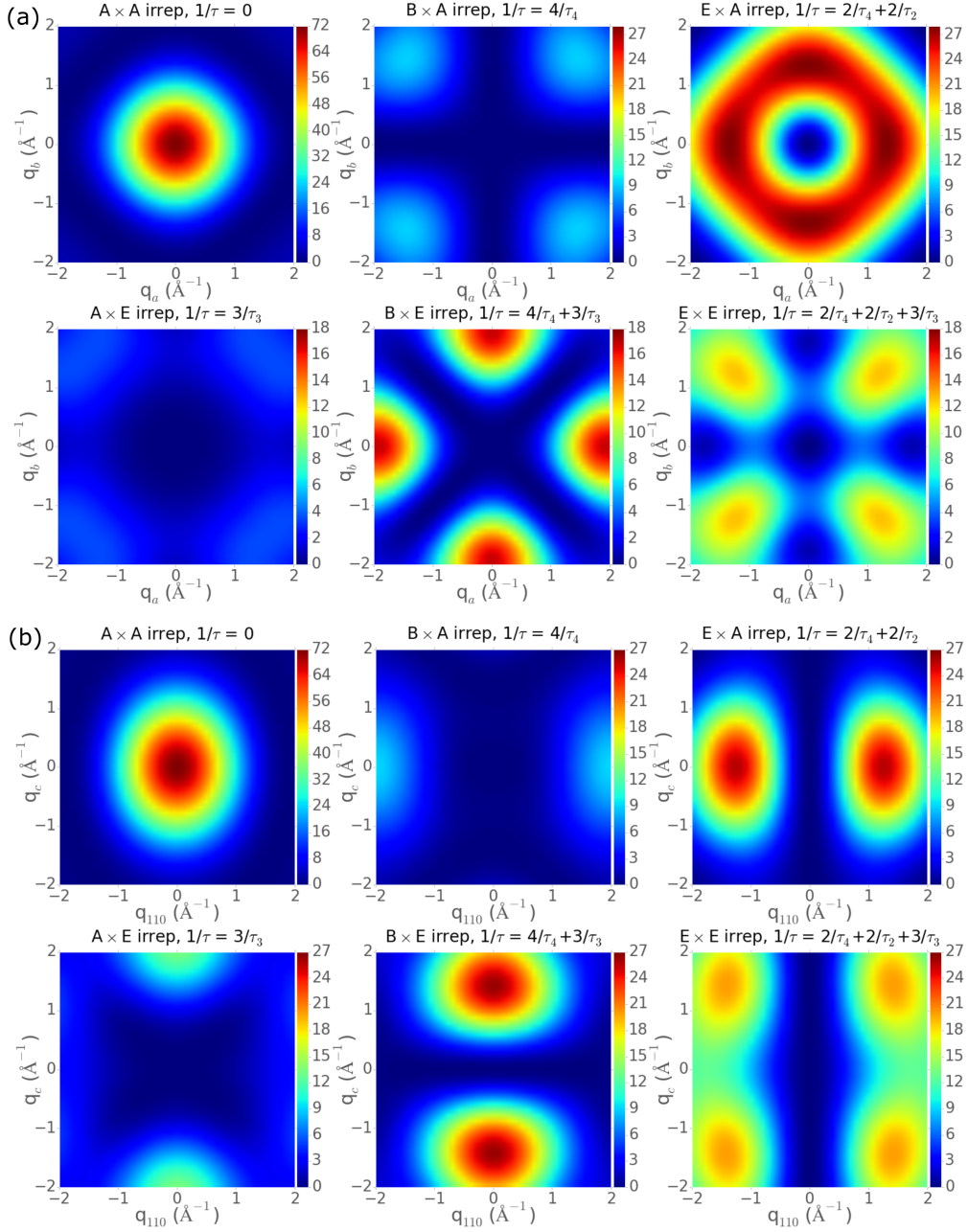


Figure 4.6: Calculated amplitudes (energy-integrated) of incoherent scattering in the tetragonal phase in the (a) q_a - q_b plane and (b) q_{110} - q_c plane from the six irreducible representations of the point group $\Gamma = S_4 \times C_3$. The calculation included an isotropic $\langle u^2 \rangle$ value of $0.16 \text{ \AA}^2$ to enable comparison to the experimental data. The $\Gamma_\mu = A \times A$ mode gives a purely elastic contribution, while the energy distribution for the other five modes is described by the Lorentzians $L(\Delta E, \tau_\mu)$.

4.3. Rotational dynamics of CH_3NH_3 investigated by quasielastic neutron scattering

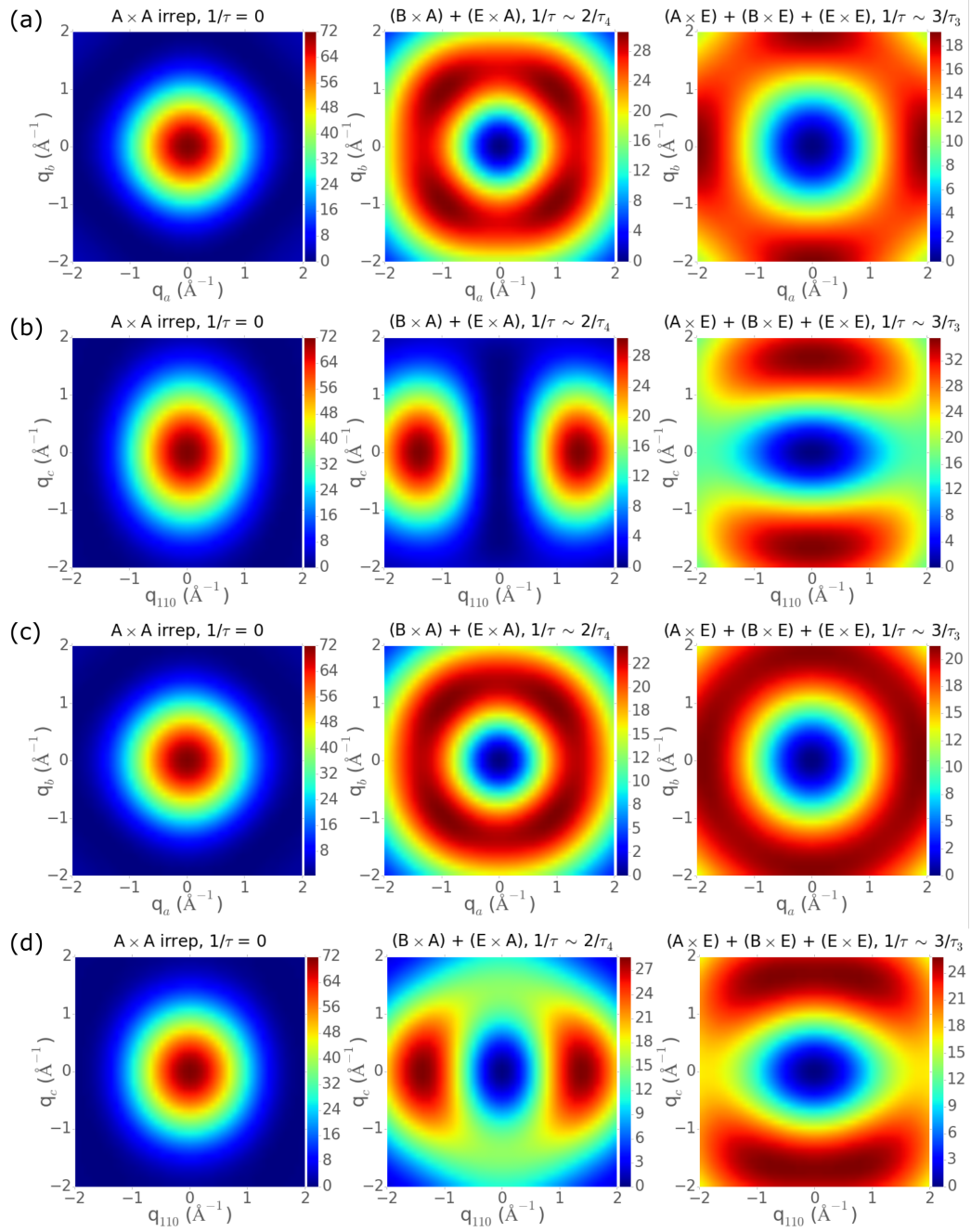


Figure 4.7: Calculated amplitudes summed into three groups based on the expected energy-transfer distributions: the elastic, low-energy transfer and high-energy transfer components. For the (a) q_a - q_b plane and (b) q_{110} - q_c plane (assuming $\langle u^2 \rangle = 0.16 \text{ \AA}^2$). (c) and (d) show the expected scattering for the extent of twinning determined in the experiment, as discussed in Section 4.3.2.

4.3.2 Experimental details

4.3.2.1 Measurements on a large cubic crystal

Temperature dependent measurements were first made on a large crystal ($\sim 6\text{ mm} \times 10\text{ mm} \times 3\text{ mm}$) grown in the cubic phase. The crystal was mounted onto an aluminium finger and secured in place with aluminium foil. The crystal was mounted such that one of the cubic fourfold axes was along the axis of rotation ϕ_{rot} and as such scattering was measured in the cubic ab plane.

Measurement of Bragg reflections on OSIRIS revealed significant symmetry twinning in the tetragonal phase. The crystal was grown in the cubic phase in order to achieve the sample mass needed to obtain a high scattering intensity, however this introduced significant symmetry twinning. Furthermore, the size of the crystal meant that multiple-scattering events became significant, inhibiting accurate determination of twin fractions and preventing an accurate investigation of molecular rotation models from the $\mathbf{q}$ -dependence of scattering. For this reason, investigation of rotational models was only performed on an array of smaller single crystals grown below the cubic-tetragonal phase transition. The smaller size of these crystals meant that multiple scattering effects could be significantly reduced, twinning could be well characterised and a larger contrast could be achieved between twin domains, however this resulted in the need for significantly longer counting times to obtain sufficient statistics.

4.3.2.2 Measurements on an array of tetragonal crystals

To investigate the $\mathbf{q}$ -dependence of scattering, it is desirable to perform measurements on single crystals with minimal levels of symmetry twinning, to achieve the highest intensity contrast for scattering in different crystal planes. Cuboid-shaped crystals grown below the cubic-tetragonal phase transition were screened by X-ray diffraction

4.3. Rotational dynamics of CH_3NH_3 investigated by quasielastic neutron scattering

on an Agilent SuperNova diffractometer (Molybdenum source). Data was collected for scattering into a large volume in reciprocal space, to check for the existence or absence of twin reflections. Crystals with minimal levels of twinning were selected and the c and (110) faces were determined. However, the absorption length for $\text{CH}_3\text{NH}_3\text{PbI}_3$ at the Mo X-ray wavelength ($0.7107 \text{ \AA}$) is 26 mm^{-1} , and as such the measurement was only sensitive to the volume of each crystal within $\sim 0.1 \text{ mm}$ of the surface. Therefore the alignment procedure attempted to determine the dominant twin of each crystal. In the remainder of this chapter, the crystal array will be labelled by the dominant twin domain.

The crystals were mounted onto an aluminium plate with Fomblin grease (perfluoropolyether) and manually co-aligned under a microscope, using the orthogonal edges of the cuboid crystals for reference. Fomblin grease was used to minimise background scattering as it contains no hydrogen. A background measurement of an equal amount of Fomblin grease on an aluminium plate was subtracted from each dataset to correct for background scattering. The crystals were co-aligned such that the common c and (110) directions were known (of the dominant twin of each crystal), to within an alignment error of approximately $\pm 2^\circ$. This was later confirmed by measuring a rocking-curve scan of the (220) and (004) reflections on OSIRIS.

Scattering data was taken on an array of 20 co-aligned crystals, of typical dimension $\sim 1 \text{ mm} \times 1 \text{ mm} \times 1 \text{ mm}$. A photograph of the crystal array is shown in Figure 4.8(a). The size and position of the crystals was measured with a microscope and an absorption correction to all datasets was performed using the Mantid software package [109] after calibration for detector efficiencies and subtraction of the background scattering dataset. Measurement of Bragg reflections on OSIRIS revealed that the crystal array did indeed have a common dominant tetragonal symmetry twin, however substantial twinning was still present. Measurement of the

4.3. Rotational dynamics of CH_3NH_3 investigated by quasielastic neutron scattering

Bragg reflections while performing a 2 mm-wide raster scan across the array revealed an area of high twinning at the top of the array (indicated in Figure 4.8(a)). These crystals were screened from the set of measurements of the q_a - q_b plane by lowering the beam blocking jaws that control the aperture of the incoming neutrons and were removed before measurement of the $q_{110} - q_c$ plane, to try to create a comparable level of twinning in both sets of measurements.

To accurately determine the twin fractions, a measurement of the (220) and (004) reflections was taken at two sample rotation angles ϕ_{rot} that were 90° apart. At each rotation angle, two twins produce a (220) reflection while the third produces an (004) reflection. The intensities of both reflections were calculated from the published tetragonal crystal structure [63] using the Vesta software package [110], and measurement of integrated peak intensity at both angles allowed the twin fractions to be determined (see Figure 4.8(b),(c)). For the q_a - q_b plane measurements, the twin fractions were determined to be 63.0% (for the dominant q_a - q_b twin), 18.8% and 18.2% (for the q_{110} - q_c and q_c - q_{110} twins). For the q_{110} - q_c plane measurement, the twin fractions were determined to be 50.5% (for the dominant q_{110} - q_c twin), 43.3% and 6.2% (for the q_a - q_b and q_{110} - q_c twins). When fitting the experimental quasielastic scattering data, the twin fractions were fixed to these values. In all plots of the experimental data, the axes refer to the axes of the dominant twin. While a completely untwinned set of crystals would have been preferable, the calculated scattering patterns show that there is enough of the dominant twin in each case to provide measurable contrast in scattering along different reciprocal space directions. The discrepancy between the determined twin fractions in the two measurements is likely due to the fact that a slightly different area of the array was measured in each measurement. In each case, the edge of the beam blocking jaws may block a different area of the sample, while some of the five crystals that were removed may have been contributing to the signal in the first

4.3. Rotational dynamics of CH_3NH_3 investigated by quasielastic neutron scattering

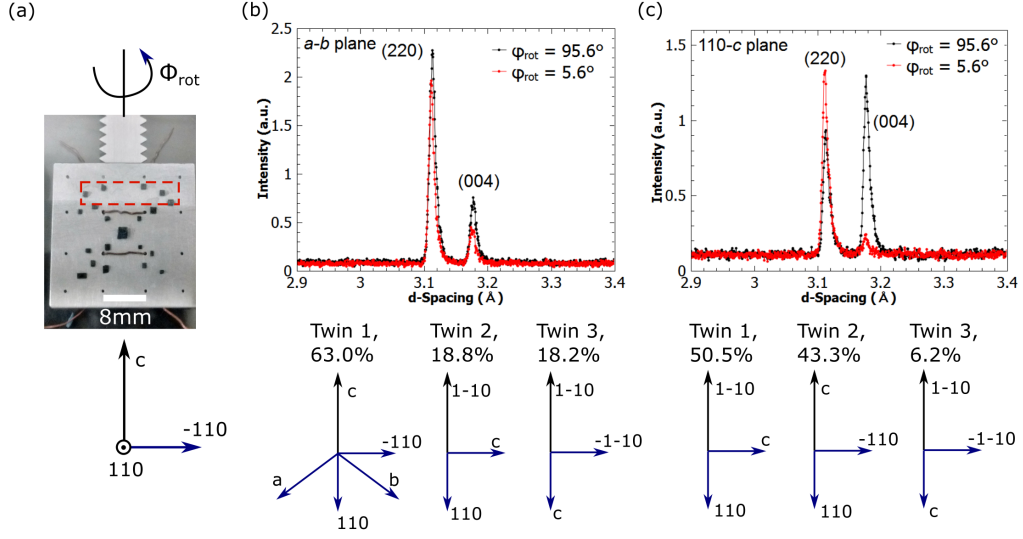


Figure 4.8: (a) Array of 20 co-aligned crystals used in the quasielastic scattering measurements, shown in the orientation for measurements of the q_a - q_b plane. For measurements of the q_{110} - q_c plane, the aluminium plate was rotated by 90° about (110) after completing all measurements of the q_a - q_b plane (the 5 crystals within the red box were also removed, as these had been screened from the q_a - q_b plane measurements). (b), (c) Volume fractions of the three tetragonal twins were determined by integrating the intensity of the (220) and (004) peaks, measured in the backscattering diffraction detector on OSIRIS, for the q_a - q_b and q_{110} - q_c planes. For each angle of crystal array rotation ϕ_{rot} , two twins contribute to the (220) reflection while the third twin produces the (004) reflection, allowing the volume fractions to be determined.

measurement.

At each temperature, data was measured at a set of rotation angles 15° apart. In the q_a - q_b plane, data was measured at four angles (five in the orthorhombic phase), whilst in the q_{110} - q_c plane data was measured at eight angles. The set of angles was chosen to cover the minimum symmetry inequivalent areas in both planes of the tetragonal phase. During data analysis the quasielastic scattering data was binned into energy bins of 0.05 meV width between -0.2 meV and 0.5 meV for the orthorhombic phase, and between -0.2 meV and 1.0 meV for the tetragonal phase. Furthermore, data was binned into q -bins of width $0.15 \text{ \AA}^{-1}$ between $0.4 \text{ \AA}^{-1}$ and $1.75 \text{ \AA}^{-1}$, using the $S(q, \omega)$ routine in Mantid. Bragg peaks were detected in the spectrometer detectors at a few measurement angles: these were removed from the

4.3. Rotational dynamics of CH₃NH₃ investigated by quasielastic neutron scattering

dataset by removing certain detectors during the analysis in Mantid, while a few detectors were also excluded due to detector malfunction which caused a saturated signal. As several detectors are grouped into each q -bin to determine a mean value, the removal of these detectors did not significantly effect the dataset. To fit the data, a least squares algorithm was used to minimise the residuals of the dataset and simulated scattering. A normalised chi-square (χ^2) goodness of fit measure was used: a χ^2 value of 1.0 is the mean value that one would expect for a dataset described by the model with normally distributed random errors.

Fits were attempted across the whole energy transfer range including the elastic scattering, however it was found that scattering models based solely on the molecular motion of the CH₃NH₃ could not sufficiently account for the magnitude and $\mathbf{q}$ -dependence of the experimental elastic scattering. In particular, the fact that the elastic intensity is over an order of magnitude larger than the quasielastic intensity meant that a fitting routine that minimises a goodness of fit measure such as χ^2 was dominated by the elastic residuals as opposed to the quasielastic scattering under investigation. Therefore, the energy transfer window -0.05 meV to 0.05 meV was excluded from the fitting range, to remove the majority of the contribution due to the elastic scattering and instrument resolution (full width at half maximum (FWHM) of 0.025 meV). When fitting the simulated scattering, the form of the instrument resolution function (determined from a measurement of a vanadium standard) was used to calculate the contribution of elastic scattering into the lowest energy transfer bins, which was only found to be significant at low- q .

In the case where there is no thermal motion of the atoms, except for the jump rotations between discrete sites, the sum of the elastic and quasielastic intensities should give a constant q -independent scattering intensity. In reality, the higher frequency thermal motions of the crystal, including vibrations, librations and bending modes, will give a Debye-Waller factor of the form $\exp(-\langle(\mathbf{u} \cdot \mathbf{q})^2\rangle)$ in the

4.3. Rotational dynamics of CH₃NH₃ investigated by quasielastic neutron scattering

harmonic approximation, where $\mathbf{u}$ is the displacement vector of the scatterer due to these higher frequency modes [111]. The effect of these higher frequency motions causes a reduction in scattering for increasing q . In order to account for these higher frequency vibrations, one of two approaches can be made. First, the experimental elastic and quasielastic intensity can be energy-integrated at each $\mathbf{q}$ -point. The $\mathbf{q}$ -dependence of the energy-integrated scattering intensity should then be constant, except for the Debye-Waller factor due to higher-frequency motions and the sum therefore gives a direct measure of this Debye-Waller factor, which is not necessarily isotropic or of the form given by the harmonic approximation. The experimental data can be divided by this measured Debye-Waller factor to give the $\mathbf{q}$ -dependence of quasielastic scattering solely due to the geometry and timescales of the jump motions. The second approach is to include an anisotropic Debye-Waller factor as a fitting parameter when fitting the quasielastic data. The first method is in general preferable, as it takes into account the elastic scattering intensity relative to the quasielastic intensity, even if this is not directly fitted. It also removes the need to fit Debye-Waller factors, which can only approximate the effect of the higher frequency motions. However, the first approach requires one to be able to integrate the total quasielastic scattering from the motion under investigation. This becomes problematic for the fast threefold motion in the tetragonal phase which extends beyond the energy window measured; this would cause an undercalculation of the total scattering intensity at high q when attempting to determine the Debye-Waller factor. The energy-integrated intensity will be discussed at each temperature in Section 4.3.4. The first method will be used to experimentally determine the Debye-Waller factor in the orthorhombic phase, however in the tetragonal phase the Debye-Waller factors will be included as fit parameters, due to the fact that a significant amount of quasielastic intensity is outside the measurable energy range.

4.3.3 Study of the temperature dependence of rotational dynamics

The quasielastic neutron scattering from a large cubic crystal of $\text{CH}_3\text{NH}_3\text{PbI}_3$ was measured on the OSIRIS spectrometer at the ISIS neutron facility at the Rutherford Appleton Laboratories. Measurements were taken of scattering in the cubic phase at 350 K, in the tetragonal phase at 320 K, 300 K, 280 K, 175 K, and in the orthorhombic phase at 155 K. At all temperatures, measurements were taken at two angles of rotation, an absorption correction and detector calibration were applied, and the detectors were grouped into 6 q -groups to improve statistics. The instrument resolution function was also determined by taking a measurement of the elastic scattering at 6 K at the same two angles of rotation. Fits were performed to the data over the energy transfer range -0.5 meV to 1.8 meV using the ConvFit routine in Mantid. In this routine, the instrument resolution function is convoluted with one or two Lorentzians to describe the quasielastic scattering plus a delta function to describe the elastic scattering, to fit the data for each detector group. It was found that consistent values for the Lorentzian FWHM parameters could only be obtained for the four detector groups at highest q ($0.9 < q < 1.8$), where the quasielastic scattering is strongest. The best estimates for the FWHM values at each temperature were determined by taking an average of the fitted values for the four highest q -groups for the two crystal rotation angles. The error on the FWHM was taken as the maximum-minimum range of FWHM values obtained from the fits.

Fits to the experimental data at a series of characteristic temperatures for the $q = 1.59\text{ \AA}^{-1}$ detector group is shown in Figure 4.9. In the orthorhombic phase at 155 K, the data is well characterised by a single Lorentzian distribution, corresponding to rotation about the C-N threefold axis. In the tetragonal phase, significant scattering is observed at energy transfers above 0.5 meV , which gradually reduces in intensity for increasing energy transfer, while a narrow Lorentzian distribution is also evident.

4.3. Rotational dynamics of CH_3NH_3 investigated by quasielastic neutron scattering

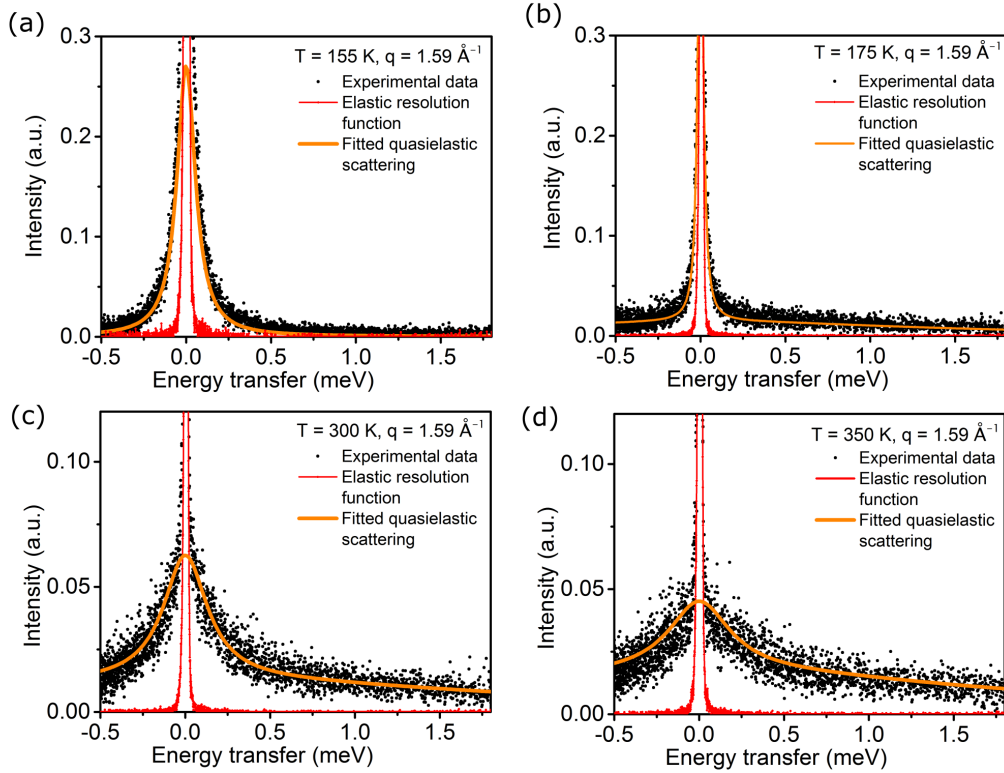


Figure 4.9: Experimental data and fits to the quasielastic scattering intensity at 155 K (a), 175 K (b), 300 K (c) and 350 K (d). Two intensity scales are used to allow comparison across the orthorhombic-tetragonal transition and tetragonal-cubic transition. At 155 K the data is fitted with a single Lorentzian, whereas two Lorentzians are needed to fit the data in the tetragonal and cubic phases. Between 175 K and 350 K, the broad Lorentzian describing the threefold rotation is largely unchanged, whereas the narrow Lorentzian describing the reorientational motion broadens significantly between 175 K and 300 K.

A good fit to the data was achieved with two Lorentzian functions; the broad and narrow Lorentzians ascribed respectively to a fast rotational motion about the C-N axis and a slow reorientational motion of the CH_3NH_3 molecule. In the cubic phase, the scattering is qualitatively similar to the tetragonal phase at 300 K, however the narrow Lorentzian has broadened further, corresponding to reorientational motion on a shorter timescale.

In order to relate the Lorentzian widths to rotational timescales, one must consider

4.3. Rotational dynamics of CH₃NH₃ investigated by quasielastic neutron scattering

the form of scattering given by the appropriate jump model. In the orthorhombic phase, the threefold jump model gives a single quasielastic scattering mode with an energy transfer described by a single Lorentzian distribution with half width $\Delta = 3/\tau_3$. The fitted FWHM therefore corresponds to a rotational timescale τ_3 of 30(2) ps. In the tetragonal phase, the fourfold jump model based on $I4/mcm$ symmetry has five quasielastic modes with energy transfer distributions described by five different timescale parameters, as shown previously in Table 4.4. However, an approximation can be made given the large difference in energy widths of the fitted Lorentzians, which reduces the five distributions to the sum of two Lorentzian lineshapes to a good approximation. Each distribution will be dominated by the shortest timescale, therefore the $B \times A$ and $E \times A$ will contribute to the narrow Lorentzian, while the other three modes will contribute to the broad Lorentzian. Calculations show that the spherically averaged contribution from the $E \times A$ mode is much larger than the $B \times A$ mode, while no evidence is seen in the measurements for the τ_2 motion on timescales within the measurable energy transfer range; therefore the narrow Lorentzian half width at half maximum (HWHM, Δ) can be approximated as $\Delta_1 \approx 2/\tau_4$. For the slower motion, the approximation $\Delta_2 \approx 3/\tau_3$ is used, as at all temperatures the τ_4 terms in $B \times E$ and $E \times E$ will only give a small correction to the determined τ_3 . Using this approximation, at 175 K the timescales are calculated to be $\tau_4 = 82$ ps, $\tau_3 = 1.25$ ps. The timescale parameters calculated from the FWHM values at all measured temperatures are shown in Table 4.5. At temperatures between 280 K and 320 K, the τ_3 parameter is almost unchanged compared to at 175 K, while the τ_4 parameter has reduced by an order of magnitude to 7.6 ps at 320 K. As the HWHM of the broad Lorentzian (~ 1.5 meV to 2.5 meV) is of comparable size of the energy window measured, it was not possible to determine this parameter with high accuracy, and the result is also consistent with an unchanged τ_3 across the tetragonal phase. In the cubic phase at 350 K, the molecule is expected to undergo reorientations between

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T (K)	τ_3 (ps)	τ_3 range (ps)	τ_4 (ps)	τ_4 range (ps)
350	1.09	0.96-1.32	6.82	6.02-8.54
320	1.02	0.93-1.13	7.60	8.65-8.11
300	0.86	0.78-0.93	8.65	8.12-9.39
280	0.86	0.78-1.05	11.08	9.92-13.19
175	1.25	1.10-1.42	82.42	73.67-104.25
155	30.36	28.46-31.91	-	-

Table 4.5: Mean values for the rotational timescales based on fits to the experimental data, alongside the minimum to maximum range of values obtained from the fits. The timescales were obtained from the relations $\tau_4 = 2\hbar/\Delta_1$, $\tau_3 = 3\hbar/\Delta_2$, where Δ_1 , Δ_2 are the half width half maxima of the narrow and broad Lorentzians describing the energy-transfer data.

many symmetry-equivalent orientations and for a full description of the motion one must consider threefold, fourfold and twofold rotations of $m\bar{3}m$. For simplicity and to aid comparison between the cubic and tetragonal phase, the same definition of the rotational timescales is used as the tetragonal phase. In the cubic phase, the reorientational timescale continues to reduce, while the τ_3 parameter is unchanged within experimental uncertainty.

The derived timescales are plotted as a function of $1/T$ in Figure 4.10, which reveals the thermally activated behaviour of the reorientational motion. The thermally activated motion can be described by the Arrhenius relation

$$\tau = \tau_0 \exp(-E_a/k_B T). \quad (4.5)$$

A linear fit was made to $\ln(\tau)$ against $1/T$ to determine the activation energies between 350 K and 175 K. The activation energy for reorientation was found to be 79(4) meV, while the C-N threefold axial rotation could also be described by a small thermal activation energy of 9(5) meV.

The thermally activated behaviour observed is somewhat consistent with a previous quasielastic neutron scattering study on a powder sample [104], however

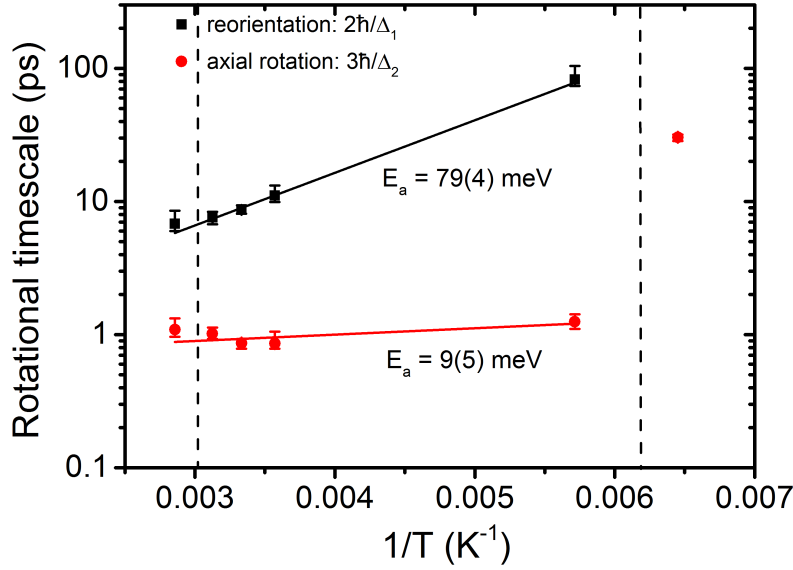


Figure 4.10: Logarithmic plot of the rotational timescales as a function of inverse temperature, revealing thermally activated behaviour of the reorientational motion across the cubic and tetragonal phases with an activation energy of 79(4) meV. The threefold rotational motion shows weak thermal activation with an activation energy of 9(5) meV.

this study reported a step change in the rotational timescales between 260 K and 300 K with different activation energies either side of this temperature range; behaviour which we do not see evidence for in these measurements. Thermally activated behaviour with a single activation energy between 350 K and 175 K is also consistent with the dielectric data on $\text{CH}_3\text{NH}_3\text{PbI}_3$ shown in Chapter 3, which does not show any transitional features in this temperature range. Furthermore, the quasielastic scattering data shows the freezing of the reorientational motion at the tetragonal-orthorhombic phase transition, a finding consistent with the dielectric data and the published crystal structures. Nevertheless, while the rotational timescales can be accurately determined from the energy-transfer dependence of scattering, the timescales cannot be unambiguously assigned to particular reorientational motions without direct observation of the $\mathbf{q}$ -dependence of

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scattering. A direct measurement of the $\mathbf{q}$ -dependence of scattering is the focus of the next section.

4.3.4 Quasielastic scattering resolved in q -space

4.3.4.1 Qualitative discussion of the temperature-dependent scattering

Quasielastic neutron scattering was measured on an array of tetragonal single crystals, at temperatures of 150 K, 175 K and 290 K, to investigate the $\mathbf{q}$ -dependence of scattering. Figure 4.11 shows the measured scattering intensity in the $q_a - q_b$ and $q_{110} - q_c$ planes at 150 K, 175 K and 290 K. No correction for the Debye-Waller factor has been applied to these plots. Figure 4.12 shows the energy transfer dependence and $|q|$ for two crystal rotation angles in the $q_{110} - q_c$ plane corresponding to scattering predominantly along q_c and q_{110} . The 2D plots in Figure 4.11 were created by integrating different ranges of energy transfer, in order to select the regions of energy transfer dominated by each rotational motion. Qualitatively, the short-timescale ‘ τ_3 ’ rotational motion shows slightly increased intensity along the c direction in the orthorhombic phase, suggesting a preferential orientation of the C-N axis in the ab plane. Plotting the angular dependence of intensity reveals a difference of approximately 20% at high q -values between the c and (110) directions. At 175 K, a similar level of anisotropy is still observed, again with an intensity difference of approximately 20%, however at 290 K the intensity is isotropic within error. Within the q_a - q_b plane, the τ_3 motion is expected to cause near isotropic scattering, and there are no distinct trends observable in the angular dependence of the data at high q .

Interestingly, the low energy transfer data appears highly isotropic at both 175 K and 290 K, in both the q_a - q_b and q_{110} - q_c planes. This implies that over the longer timescales associated with this motion (~ 80 ps and ~ 10 ps respectively), the position of a hydrogen atom is uncorrelated to its initial position, in any direction in

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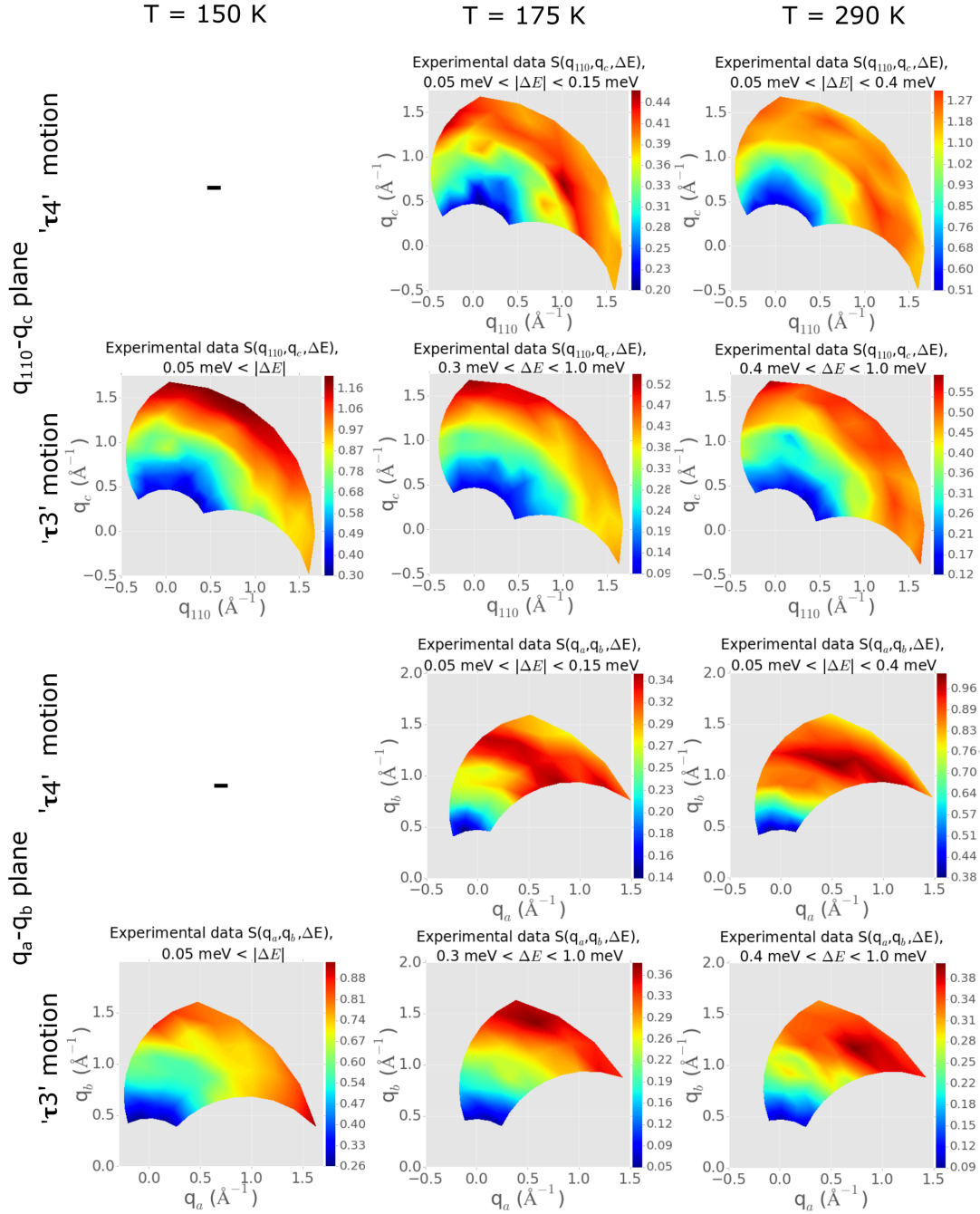


Figure 4.11: Evolution of scattering intensity as a function of temperature, in the $q_{110} - q_c$ and $q_a - q_b$ planes. In the tetragonal phase, the upper and lower plots show the integrated intensity for energy ranges corresponding to dominant ranges of the narrow and broad Lorentzian lineshapes, corresponding to the ' τ_4 ' reorientational motion and the ' τ_3 ' axial rotation. At 150 K, only the threefold motion is present (lower plot).

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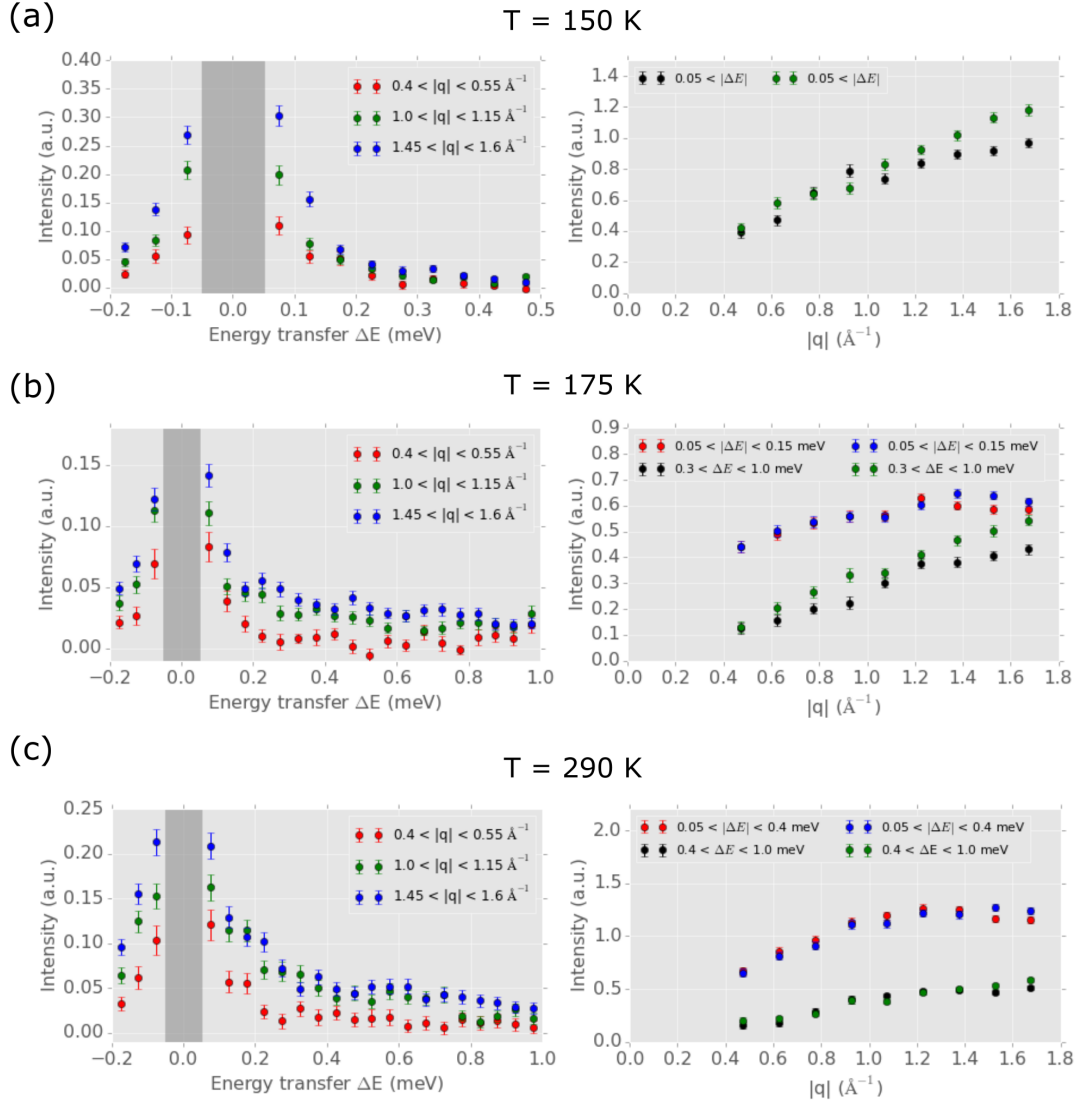


Figure 4.12: Evolution of scattering intensity as a function of temperature in the $q_{110} - q_c$ plane as a function of energy transfer and $|q|$. For the $|q|$ dependence, the experimental values are shown at two rotation angles corresponding to scattering predominantly along q_c (blue & green) and q_{110} (red & black). At 175 K, the $0.05 \text{ meV} < \Delta E < 0.15 \text{ meV}$ data is offset by 0.2 meV for clarity.

space. This is unexpected, as the fourfold jump rotations in the $I4/mcm$ structure are predominantly rotations in the ab plane, which implies that over long timescales the position will become uncorrelated in the ab plane but not in the c -direction. Indeed, this appears at first to be inconsistent with the higher energy transfer

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scattering at 175 K which implies that the molecule prefers to lie in the *ab* plane at this temperature. These two observations will be reconciled by investigating the Debye-Waller factor from the energy-integrated scattering at 175 K, which shows that the higher-frequency motions are greater in the (110) direction at high-*q*, giving rise to the observed anisotropy. At 290 K, the isotropy of both the low and high energy transfer data implies that the CH₃NH₃ molecule undergoes free isotropic rotation.

The $|q|$ dependence of scattering also shows some variation with temperature. There is a shift to lower $|q|$ of the maximum intensity in the low energy transfer window as temperature increases. This demonstrates the increasing thermal motion of the molecule i.e. a larger value of $\langle u^2 \rangle$, or rotational motion on a larger radius of rotation. For the high energy transfer data, the scattering continues to increase with $|q|$ throughout the measured *q*-range at 150 K/175 K, indicating rotation with a smaller radius compared to the long-timescale motion. At 290 K the scattering has levelled off at high $|q|$, however this may be due to the inclusion of the tails of the narrower Lorentzian distribution which show this dependence. For the energy transfer dependence, one Lorentzian lineshape is clearly seen in the orthorhombic phase, while one broad and one narrower Lorentzian can be seen in the tetragonal phase, in good agreement with the measurements on the large cubic crystal.

In the following sections the data will be fitted with different scattering models, in order to determine which models best describe the data at each temperature and test the validity of these qualitative observations.

4.3.4.2 *q*-dependent scattering at 150 K

First, the total energy-integrated scattering was investigated to determine the form of the Debye-Waller correction due to higher frequency motions. Figure 4.13 shows the **q**-dependence of the total energy-integrated scattering (only positive energy transfers

4.3. Rotational dynamics of CH₃NH₃ investigated by quasielastic neutron scattering

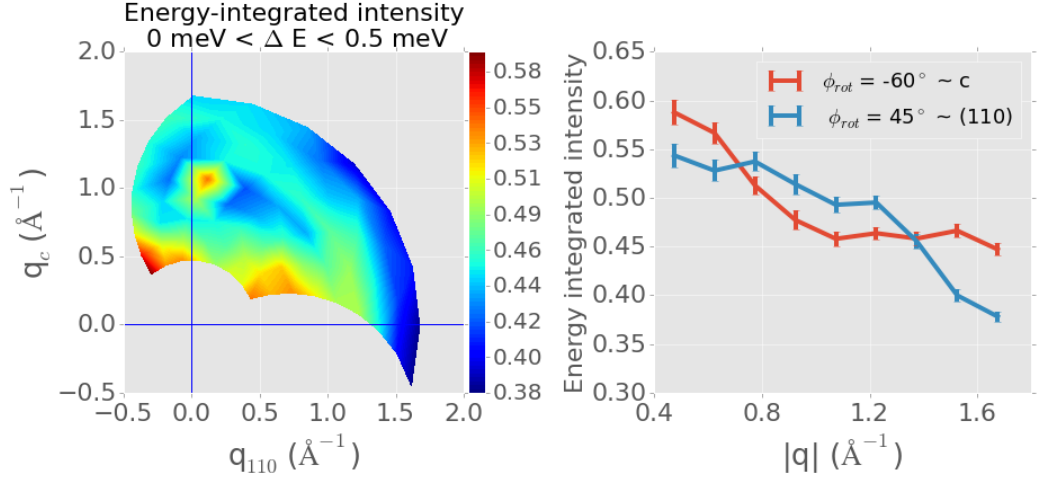


Figure 4.13: Total energy-integrated scattering (elastic + quasielastic for $\Delta E > 0$) in the $q_{110} - q_c$ plane at 150 K. The $\mathbf{q}$ -dependent form is given by the Debye-Waller factor due to higher frequency motions. There is a clear anisotropy in the data, with a greater intensity along the c direction at high q , however at medium q -values the intensity is greater along the 110 direction. When dividing out by this factor, it is revealed that the anisotropy of the higher-frequency motions was the cause of the increased quasielastic scattering along c , which is no longer present.

were integrated, as not all of the quasielastic scattering is within the measured energy range for $\Delta E < 0$). The total energy-integrated scattering shows anisotropy within the $q_{110}-q_c$ plane; at large q -values, the total scattering is greater along the q_c direction, while for $|q| \sim 1$ Å⁻¹, the total scattering is greater along the q_{110} direction. This reveals that the largest motions of the CH₃NH₃ molecule about its centre of mass due to higher frequency vibrations occur mainly in the ab plane.

In order to correctly account for this anisotropic Debye-Waller factor, the quasielastic scattering data was divided by the total energy-integrated scattering at each $\mathbf{q}$ -point. The effect of this is to transform the absolute quasielastic scattering intensity into a quasielastic scattering intensity relative to the total energy-integrated scattering. This effectively shows where the quasielastic scattering is greater relative to the elastic intensity and enables one to definitively determine the nature of the molecular motion through how the scattering intensity is

4.3. Rotational dynamics of CH_3NH_3 investigated by quasielastic neutron scattering

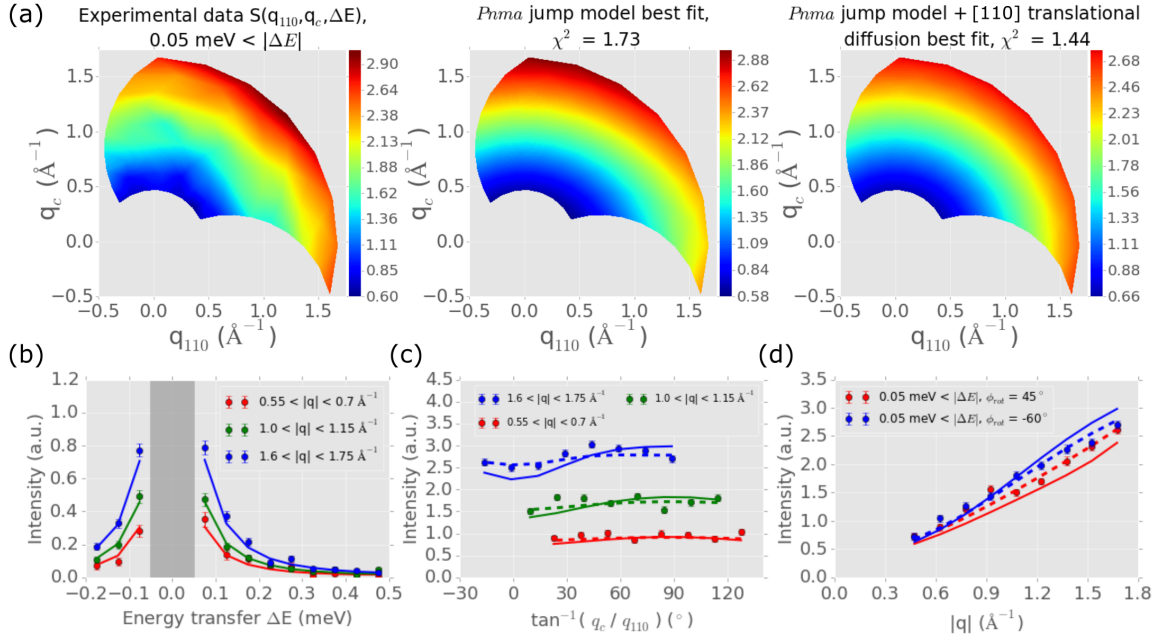


Figure 4.14: (a) Experimental data for scattering in the $q_{110} - q_c$ plane at 150 K, integrated over the quasielastic energy transfer range $|\Delta E| < 0.05$ meV, alongside the best fit for a jump model based on the published $Pnma$ structure and a the same jump model with additional bound translational diffusion along the $[1\ 1\ 0]$ direction. The data is plotted in the reference frame of the largest tetragonal domain. (b) Intensity dependence on energy transfer, in addition to the angle dependence (c) and $|q|$ dependence (d). Solid lines show the best fit for the $Pnma$ jump model ($\chi^2 = 1.73$) and dashed lines (in (c) & (d)) show the best fit for the model including bound translational diffusion ($\chi^2 = 1.44$). In (d), values are shown at two rotation angles corresponding to scattering predominantly along q_c (blue) and q_{110} (red).

distributed between the elastic and quasielastic scattering amplitudes.

Figure 4.14 shows the quasielastic scattering intensity in the $q_{110} - q_c$ plane after dividing by the Debye-Waller factor, alongside the best fits for two models and cuts of the scattering intensity along energy transfer, angle in the plane and $|q|$. The anisotropy between the q_c and q_{110} directions has been significantly reduced by correcting for the Debye-Waller factor. This shows that the anisotropy between the q_c and q_{110} direction discussed previously was largely due to the effect of anisotropic higher frequency motions of the molecule. Nevertheless, there is still some variation with angle in the plane at high- q , with a maxima at $\sim 45^\circ$. Figure 4.15 shows the

4.3. Rotational dynamics of CH₃NH₃ investigated by quasielastic neutron scattering

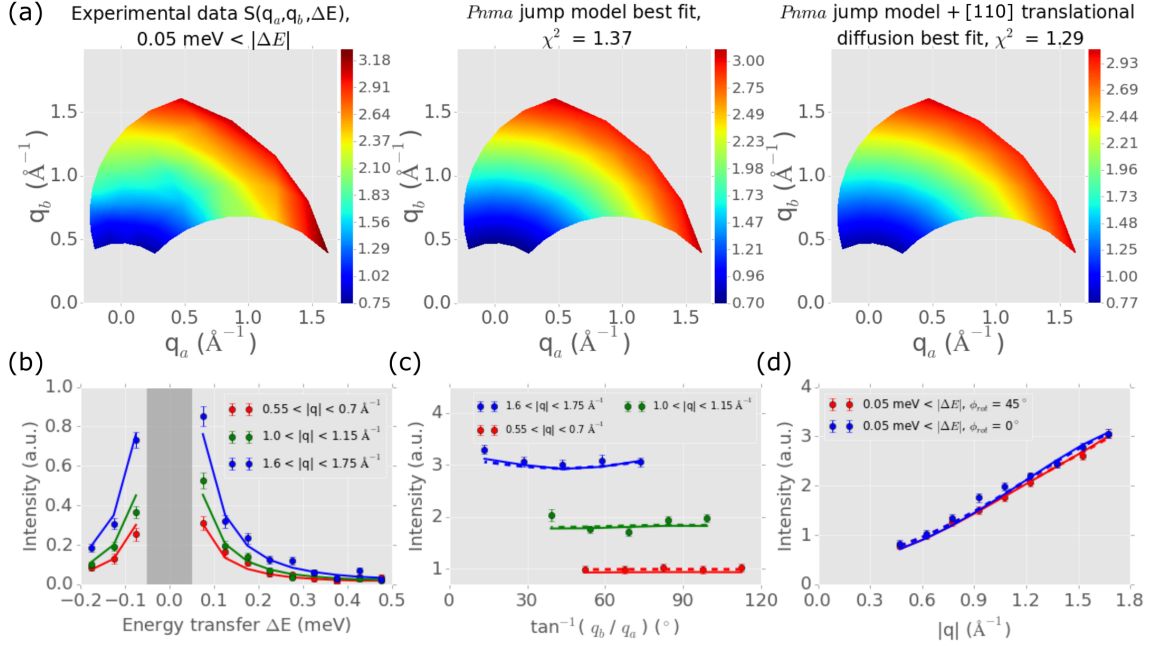


Figure 4.15: (a) Experimental data for scattering in the $q_a - q_b$ plane at 150 K, integrated over the quasielastic energy transfer range $|\Delta E| < 0.05 \text{ meV}$, alongside the best fit for a jump model based on the published $Pnma$ structure and the same jump model with additional bound translational diffusion along the $[1\ 1\ 0]$ direction. The data is plotted in the reference frame of the largest tetragonal domain. (b) Intensity dependence on energy transfer, in addition to the angle dependence (c) and $|q|$ dependence (d). Solid lines show the best fit for the $Pnma$ jump model ($\chi^2 = 1.37$) and dashed lines (in (c) & (d)) show the best fit for the model including bound translational diffusion ($\chi^2 = 1.29$). In (d), values are shown at two rotation angles corresponding to scattering predominantly along q_b (blue) and q_{110} (red).

scattering in the $q_a - q_b$ plane after the Debye-Waller correction, which is still predominantly isotropic.

The first model tested was the threefold rotational model based on the published $Pnma$ structure [63]. A global fit was performed to each of the corrected datasets over the intervals $-0.2 \text{ meV} < \Delta E < -0.05 \text{ meV}$ and $0.05 \text{ meV} < \Delta E < 0.5 \text{ meV}$, with free parameters τ_3 and a global scale parameter A . The resultant parameters obtained from the fits to different models for the orthorhombic phase are summarised in Table 4.6. The fit to the $q_{110} - q_c$ data gave a χ^2 value of 1.73, with parameters $\tau_3 = 36(1) \text{ ps}$ and $A = 0.305(4)$. The scattering dependence on energy

4.3. Rotational dynamics of CH₃NH₃ investigated by quasielastic neutron scattering

transfer was found to be well described by a single Lorentzian function, corresponding to the τ_3 rotational motion. However, with regards to the q -vector variation in scattering intensity, significant discrepancy is seen between the model and experimental data. The jump model predicts a significant anisotropy at high- q between the q_c and q_{110} directions, which is not evident in the data, and gives an overestimation of the intensity along q_c and an underestimation along q_{110} . The best fit to the $q_a - q_b$ data with the $Pnma$ model gave a χ^2 of 1.37, and parameters $\tau_3 = 35(1)$ ps and $A = 0.361(5)$. Both the experimental data and fit show little variation in the plane as a function of angle, while the form of the q -dependence of scattering is well described by the fitted function. Nevertheless, the χ^2 values of the fits imply that further improvements could be made in the model, particularly for describing the $q_{110} - q_c$ data.

In order to investigate alternative descriptions of the CH₃NH₃ ordering in the orthorhombic phase, fits were made to a number of models. One alternative model is the model of uniaxial diffusion around a ring, as described in Chapter 2. Based on the reported crystal structures obtained from neutron scattering studies [63], the

plane	Model	χ^2	Fitted parameters	
$q_{110} - q_c$	$Pnma$ jump	1.73	$\tau_3 = 36(1)$ ps	$A = 0.305(4)$ a.u.
	Uniaxial rotation	1.65	$\tau_{\text{uni}} = 15.3(6)$ ps	$A = 11.8(2)$ a.u.
	Isotropic rotation	1.58	$r_{\text{iso}} = 0.60(2)$ Å $A = 19.9(7)$ a.u.	$\tau_{\text{iso}} = 12.2(4)$ ps
	$Pnma$ jump + [1 1 0]-translation	1.44	$\tau_3 = 61(4)$ ps $\tau_{\text{trans}} = 45(3)$ ps	$A = 0.36(1)$ a.u. $L_{[110]} = 0.98(4)$ Å
	$P1$ jump	1.78	$\tau_3 = 35(1)$ ps	$A = 20.9(9)$ a.u.
$q_a - q_b$	$Pnma$ jump	1.37	$\tau_3 = 35(1)$ ps	$A = 0.361(5)$ a.u.
	Isotropic rotation	1.35	$r_{\text{iso}} = 0.62(2)$ Å $A = 20.9(9)$ a.u.	$\tau_{\text{iso}} = 12.2(5)$ ps
	$Pnma$ jump + [1 1 0]-translation	1.29	$\tau_3 = 65(14)$ ps $\tau_{\text{trans}} = 43(4)$ ps	$A = 0.42(3)$ a.u. $L_{[110]} = 0.99(13)$ Å

Table 4.6: χ^2 goodness of fit values and fitted parameters for the models used to investigate the data at 150 K.

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hydrogen atoms were assumed to move on rings of radii 0.9 Å and 1.1 Å for the NH₃ and CH₃ ends of the molecule, where the orientation of the rings coincide with the three H positions at each end of the molecule in the *Pnma* structure. A fit to the data of this uniaxial diffusion model gave a χ^2 value of 1.65 for the $q_{110} - q_c$ plane, signalling a slightly better fit than for the *Pnma* jump model due to a slight reduction in the planar anisotropy. A fit was also made to the isotropic rotational diffusion model (Equation 2.13). This gave a fit with a χ^2 of 1.58 for the $q_{110} - q_c$ plane and 1.35 for the $q_a - q_b$ plane, however the fit gave unphysically low r_{iso} parameters of 0.60(2) Å and 0.62(2) Å and cannot account for the angular dependence of scattering at high- q in the $q_{110} - q_c$ plane. Furthermore, the model of spherical isotropic rotation is inconsistent with the dielectric data presented in Chapter 3, which indicates a freezing of each CH₃NH₃ dipole in a given direction. A recent *ab initio* study of the cation dynamics in the orthorhombic phase suggested that experimental inelastic neutron scattering data can only be well described by a low symmetry structure, with the best agreement found for a structure with *P1* symmetry [112]. This *P1* model was used to fit the $q_{110} - q_c$ plane data, giving a χ^2 value of 1.78. In the *P1* structure described in the study, half of the CH₃NH₃ molecules lie out of the tetragonal *ab* plane, with the C-N axis pointing predominantly along the tetragonal *c* axis, with the other half of the molecules lying in the tetragonal *ab* plane as in the *Pnma* structure. However, for the threefold rotations about the *c* axis, the largest scattering signal would be in the tetragonal *ab* plane, and as such the *P1* model gives a slightly higher level of scattering in the (110) direction than in the *c* direction, in contrast to the experimental data.

As the *Pnma* model has been found to be the best structural description in the literature from neutron diffraction studies [63], modifications to this model were considered in order to give a better fit to the data. A type of motion that can give increased quasielastic scattering along a given direction is bound translational diffusion, i.e. the center of mass of the scatterer can diffuse between two hard barriers

4.3. Rotational dynamics of CH_3NH_3 investigated by quasielastic neutron scattering

separated by a distance L . Therefore, a model consisting of a convolution of bound translational diffusion along $[1\ 1\ 0]$ and the threefold jump rotations of the $Pnma$ structure was also considered. The best fit to the data is shown in Figures 4.14 and 4.15. For the $q_{110} - q_c$ plane data, this gave a significantly improved fit with a χ^2 of 1.44, while the fit in the $q_a - q_b$ plane was also slightly improved with a χ^2 of 1.29. The bounding-box length $L_{[110]}$ was fitted as $0.98(4)\text{ \AA} / 0.99(13)\text{ \AA}$, and the timescales of diffusion and jump rotation were of a similar magnitude, at around 45 ps and 60 ps respectively. Given the similar magnitude of the timescales of motion, it is possible that the two motions are coupled, such that on the timescale of a rotation, the molecule also undergoes translational motion. While the size of L_z is fairly large at $\sim 1\text{ \AA}$ (implying translational motion of $\pm 0.5\text{ \AA}$ from the centre of mass), the size of the ionic ‘cage’ that the CH_3NH_3 molecule is located in is significantly distorted relative to the cubic phase (see Figure 4.3). The distance between I atoms defining the length of the ionic cage along $[1\ 1\ 0]$ is $7.7\text{ \AA}$ in the orthorhombic phase, whereas this distance in the cubic phase is only $6.3\text{ \AA}$, suggesting that in the orthorhombic phase there is additional space of up to $1.4\text{ \AA}$ along the $[1\ 1\ 0]$ direction that the molecule could potentially explore. Furthermore, it is unclear which I atoms the CH_3NH_3 molecule will bond with and as such there may be significant translational motion if, as the molecule rotates, H-I bonds are formed with a number of different I atoms that form the ionic cage.

These findings suggest that the best description of the orthorhombic structure is one where the CH_3NH_3 molecule is predominantly oriented in the tetragonal ab plane, but is able to undergo significant translational motion along the $[1\ 1\ 0]$ direction. This reconciles the fact that the CH_3NH_3 molecule is known to order from the dielectric data with the fact that the scattering observed is less anisotropic than expected based purely on threefold jumps of the CH_3NH_3 molecule.

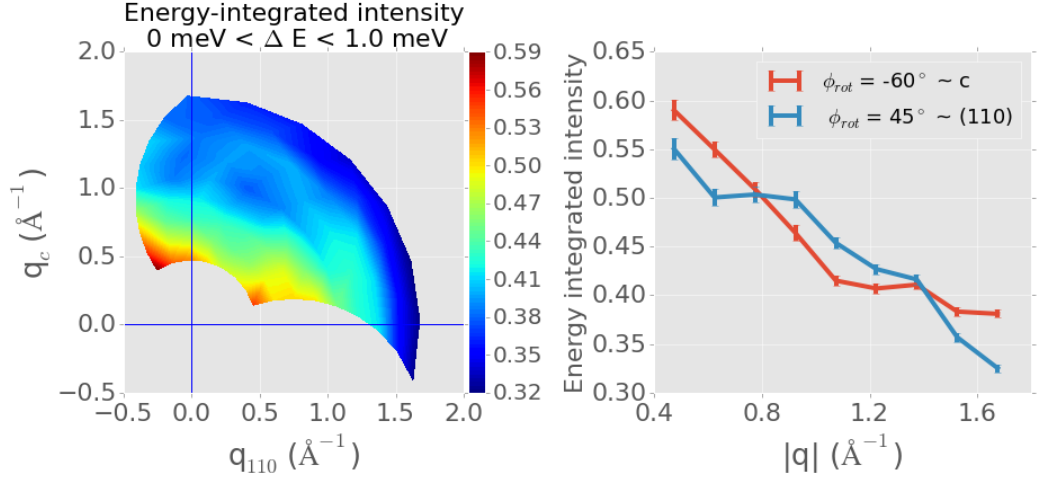


Figure 4.16: Total energy-integrated scattering (elastic + quasielastic for $\Delta E > 0$) in the $q_{110} - q_c$ plane at 175 K. The data shows some anisotropy at high q , however this is reduced compared to at 150 K. Furthermore, there is a greater reduction in the total scattering as a function of q due to the fact that a large fraction of the broad quasielastic mode is not contained within the energy range of the experiment.

4.3.4.3 q -dependent scattering at 175 K

The total energy-integrated scattering was also investigated at 175 K in order to determine the form of the Debye-Waller correction. Figure 4.16 shows the $\mathbf{q}$ -dependence of the total energy integrated scattering for positive energy transfers. While some anisotropy is still evident between the q_c and q_{110} directions at the highest q -values, this is less pronounced than at 150 K. Furthermore, there is a significant reduction in total intensity at high q on the order of 15-20% compared to the 150 K data, but less so at lower q , due to the loss of some of the broad quasielastic scattering mode that is outside the energy range of the experiment. Similarly, at 290 K, the anisotropy of total scattering had been reduced further, while a significant amount of quasielastic scattering is also outside the energy range of the experiment. To avoid over-correcting the $\mathbf{q}$ -dependence of the tetragonal phase data, for the analysis at 175 K and 290 K, anisotropic Debye-Waller factors were introduced as fitting parameters when fitting the absolute quasielastic

4.3. Rotational dynamics of CH₃NH₃ investigated by quasielastic neutron scattering

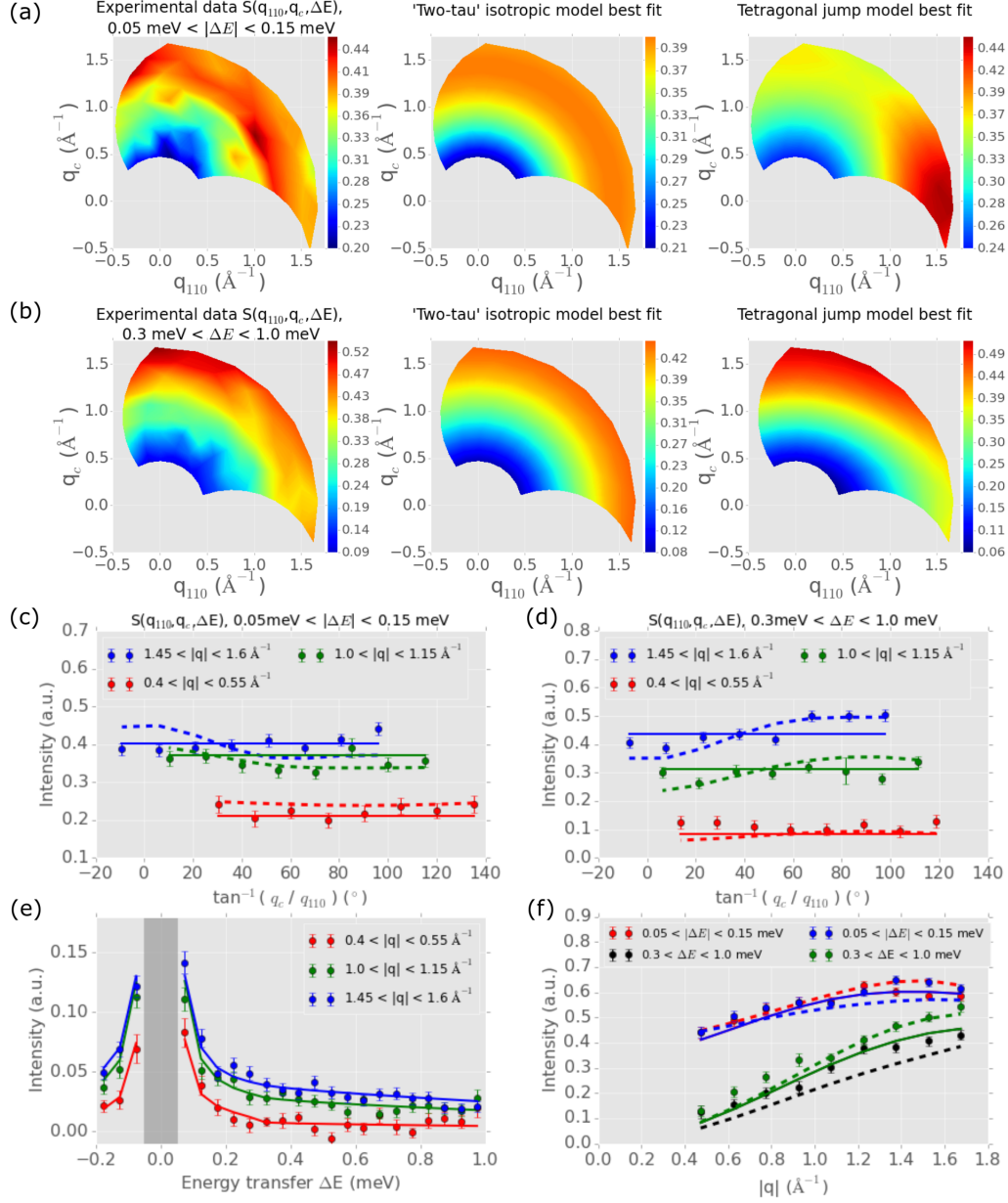


Figure 4.17: Experimental data for scattering in the q_{110} – q_c plane at 175 K, integrated over low energy transfers (a) and high energy transfers (b), alongside the best fit for the ‘two-tau’ isotropic model and tetragonal jump model. (c), (d) Angle dependence of scattering for low and high energy transfer, in addition to the energy transfer (e) and $|q|$ dependence (f). Solid lines show the best fit for the two-tau isotropic model ($\chi^2 = 1.22$), while the dashed lines (in (c), (d) & (f)) show the best fit for the tetragonal jump model ($\chi^2 = 1.38$). In (f), values are shown at two rotation angles corresponding to scattering predominantly along q_c (blue & green) and q_{110} (red & black), and the low energy transfer data is offset by 0.2 meV for clarity.

4.3. Rotational dynamics of CH₃NH₃ investigated by quasielastic neutron scattering

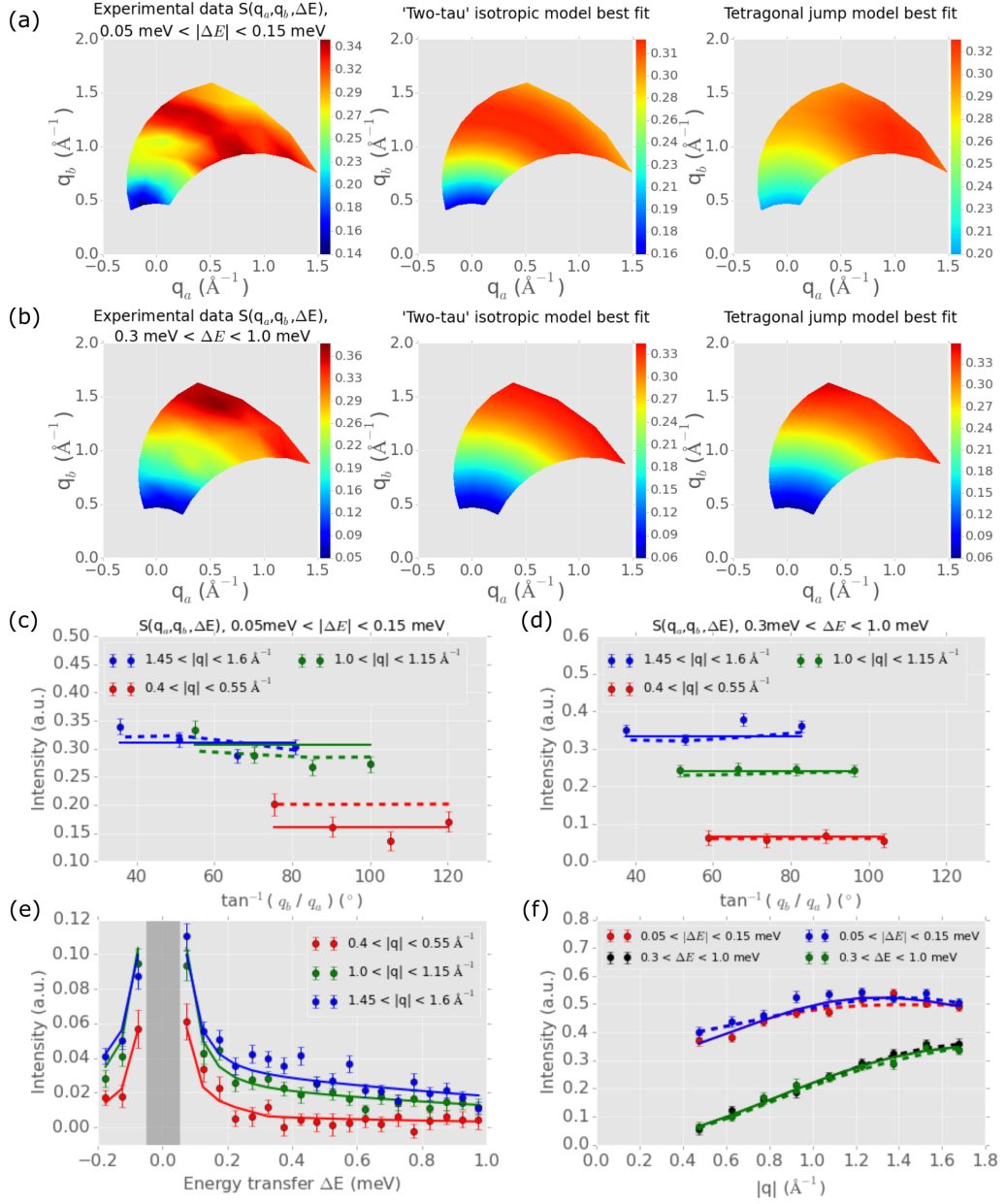


Figure 4.18: Experimental data for scattering in the $q_a - q_b$ plane at 175 K, integrated over low energy transfers (a) and high energy transfers (b), alongside the best fit for the ‘two-tau’ isotropic model and tetragonal jump model. (c), (d) Angle dependence of scattering for low and high energy transfer, in addition to the energy transfer (e) and $|q|$ dependence (f). Solid lines show the best fit for the two-tau isotropic model ($\chi^2 = 1.25$), while the dashed lines (in (c), (d) & (f)) show the best fit for the tetragonal jump model ($\chi^2 = 1.30$). In (f), values are shown at two rotation angles corresponding to scattering predominantly along q_b (blue & green) and q_{110} (red & black), and the low energy transfer data is offset by 0.2 meV for clarity.

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scattering intensity.

The experimental data, alongside the best fits for the tetragonal jump model and an isotropic model (discussed later), are shown in Figures 4.17 and 4.18. First, the tetragonal jump model was considered. Global fits were performed to the data, including anisotropic thermal parameters: the resultant fit parameters from the models considered are shown in Table 4.7. Fitting the $q_{110} - q_c$ data produced a best fit with a χ^2 of 1.38, while the fit to the $q_a - q_b$ data provided a slightly better fit with a χ^2 of 1.30. In both fits, no value could be determined for the τ_2 parameter; the τ_2 value was observed to diverge to values of $\tau_2 > 1000$ ps such that this motion gave no contribution to the fitted scattering intensity. Therefore the τ_2 motion either occurs on much longer timescales than the fourfold reorientational motion, or it does not occur at all. As such, the effect of the τ_2 parameter was excluded from the fits ($2/\tau_2$ was set to 0). Interestingly, if the correct description of molecular orientation was that of the $I4cm$ structure, then one would expect the τ_4 motion to diverge to large values with the τ_2 motion causing the observed low energy transfer scattering within the timescale of the measurement. Therefore the $I4cm$ structure is

plane	Model	χ^2	Fitted parameters	
$q_{110} - q_c$	$I4/mcm$ jump	1.38	$\tau_3 = 1.62(5)$ ps $\langle u_{ab}^2 \rangle = 0.13(1) \text{ \AA}^2$ $A = 0.134(3)$ a.u.	$\tau_4 = 1.69(5)$ ps $\langle u_c^2 \rangle = 0.16(1) \text{ \AA}^2$
	‘two-tau’	1.22	$\tau_{\text{uni}} = 0.44(2)$ ps $r_1 = 1.31(2) \text{ \AA}$ $\langle u^2 \rangle = 0.12(3) \text{ \AA}^2$	$\tau_{\text{iso}} = 50(17)$ ps $r_2 = 1.3(3) \text{ \AA}$ $A = 2.12(7)$ a.u.
$q_a - q_b$	$I4/mcm$ jump	1.30	$\tau_3 = 1.90(8)$ ps $\langle u_{ab}^2 \rangle = 0.19(1) \text{ \AA}^2$ $A = 0.110(3)$ a.u.	$\tau_4 = 182(9)$ ps $\langle u_c^2 \rangle = 0.10(12) \text{ \AA}^2$
	‘two-tau’	1.25	$\tau_{\text{uni}} = 0.53(3)$ ps $r_1 = 1.30(4) \text{ \AA}$ $\langle u^2 \rangle = 0.23(3) \text{ \AA}^2$	$\tau_{\text{iso}} = 97(21)$ ps $r_2 = 2.3(3) \text{ \AA}$ $A = 1.43(6)$ a.u.

Table 4.7: χ^2 goodness of fit values and fitted parameters for the models used to investigate the data at 175 K.

4.3. Rotational dynamics of CH₃NH₃ investigated by quasielastic neutron scattering

not consistent with the observed scattering.

Upon inspection of the fits (Figure 4.17), it is clear that there are significant discrepancies between the fit and the data, most notably for the low energy transfer scattering at higher q , where the model predicts substantial variation with angle in the $q_{110} - q_c$ plane that does not exist in the experimental data. Furthermore, while the fitted parameters show good agreement between fits, the τ_4 parameter is over twice as large as that obtained for the measurements on the large crystal. Additionally, large thermal parameters are needed to describe the data, suggesting significant thermal motion of the molecule.

As the scattering data at low energy transfer is more isotropic than the jump model suggests, a model of isotropic diffusion was investigated. The standard model of isotropic rotational diffusion described in [40] uses a single timescale of rotation, however this was not found to adequately describe the data due to the clear existence of two timescales of motion. As the motion of the molecule is expected to be a combination of a rotation about the C-N axis and reorientations of the C-N axis, the combined model of uniaxial rotation and isotropic rotational diffusion was considered, as described in Chapter 2. From the measurements on a large crystal, it is clear that the timescale of rotation about the C-N axis occurs on a timescale over an order of magnitude less than the slower reorientational motion. Therefore, under the assumption that the motions of axial rotation and axis reorientation are uncoupled, the simplification of Equation 2.25 to Equation 2.27 should be a good approximation, giving

$$S_{\text{inc}}(\mathbf{Q}, \omega) \approx \int \int \{J_0^2(Qr_1 \sin \theta) \left[j_0^2(Qr_2) \delta(\omega) + \sum_{l=1}^{\infty} (2l+1) j_l^2(Qr_2) L(\omega, \tau_l) \right] \right. \\ \left. + 2 \sum_{m=1}^{\infty} J_m^2(Qr_1 \sin \theta) L(\omega, \tau_m) \right\} d\theta d\phi. \quad (4.6)$$

The spherical averages of the bessel functions were calculated analytically, and

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Equation 4.6 was fitted to the data in the $q_a - q_b$ and $q_{110} - q_c$ planes, including a Debye-Waller factor with an isotropic thermal parameter. The expansion in l and m was limited to the first four terms and the model was refined with parameters τ_{uni} and r_1 (corresponding to the uniaxial rotation), τ_{iso} and r_2 (corresponding to isotropic rotational diffusion), $\langle u^2 \rangle$ and a global scale parameter A (I shall refer to this model as the ‘two-tau’ isotropic model). The fitted parameters are given in Table 4.7.

Fitting the two-tau isotropic model gave an improved fit to the $q_{110} - q_c$ data with a χ^2 of 1.22 and a slightly improved fit to the $q_a - q_b$ data with a χ^2 of 1.25. From visual inspection of the fits, the two-tau isotropic model provides a better description of the low energy transfer data but cannot account for the slightly increased scattering along the c direction at high energy transfers. However, based on the discussion of the total energy-integrated scattering, this feature is likely due to the effect of anisotropic high-frequency lattice vibrations. The r_1 parameter of 1.31(2) Å is slightly larger than expected based on the axial radius of the CH₃NH₃ molecule, which may be due to thermal motion of the molecular axis on short timescales. The r_2 parameter of 1.3(3) Å for the $q_{110} - q_c$ fit is in good agreement with the expected spherical radius of the CH₃NH₃ molecule (1.3 Å), however the value for the $q_a - q_b$ fit is fairly large but also has significant error. The $\langle u^2 \rangle$ parameters also indicate significant thermal motion due to the higher frequency vibrations.

Given that the orthorhombic scattering suggests the presence of translational motion, a combination of translational and rotational motion was considered for the tetragonal phase, to see if this could account for the isotropic scattering at low energy transfer. One way that the hydrogen positions could be uncorrelated on a long timescale but still undergo the fourfold jump rotations of the $I4/mcm$ structure is if the molecule is able to undergo bound translational motion along the c direction over long timescales. To consider this possibility, a combined model of

4.3. Rotational dynamics of CH₃NH₃ investigated by quasielastic neutron scattering

the tetragonal jump model plus bound translational diffusion along c was investigated. In this model, Equation 2.18 was convoluted with the form of scattering from the tetragonal jump model, with the sum over n being restricted to the first four terms. Including translational diffusion reduced the χ^2 of the $q_{110} - q_c$ plane fit from 1.38 to 1.29, however this was for a translational diffusive motion with $L_z = 5.26(7)$ Å and $\tau_{\text{trans}} = 149(10)$ ps. The $q_a - q_b$ data was not sensitive to the translational c component to enable a reliable fit. Such a large bounding-box for diffusive motion is physically unrealistic for the CH₃NH₃PbI₃ structure, and the fit is still worse than the two-tau isotropic model. Additionally, this diffusive model also underestimates the scattering along c at high energy transfers.

Overall, the two-tau isotropic model is found to provide the best description of the data. The $I4/mcm$ jump model requires a large scattering anisotropy at low energy transfers, which is not observed experimentally, while the fourfold rotational timescale obtained from the best fit is over twice that obtained from the measurements on the large crystal. The fact that the molecule does not settle into four symmetry equivalent orientations due to the crystal symmetry implies that there are many orientations of the CH₃NH₃ with similar energies.

4.3.4.4 q -dependent scattering at 290 K

At 290 K, a clear difference in the χ^2 values between a model of rotational diffusion and a fourfold jump rotational motion was found. As expected based on the isotropy of scattering, a model of uniaxial rotation about the C-N axis, in addition to isotropic diffusion of the C-N axis, provided an excellent description of the experimental data.

From the measurements on a large crystal, at 290 K there is still an order of magnitude difference between the rotational timescales, and the simplification of Equation 2.25 to Equation 2.27 should still be valid. The two-tau model was used to fit the 290 K data; this resulted in excellent fits, with χ^2 values of 1.03 and 1.21

4.3. Rotational dynamics of CH₃NH₃ investigated by quasielastic neutron scattering

for the $q_a - q_b$ and $q_{110} - q_c$ planes respectively. The $\langle u^2 \rangle$ parameters were found to refine to small negative values ($-0.01(3) \text{ \AA}^2, -0.04(2) \text{ \AA}^2$) and therefore were set to zero in the fits. The experimental data, alongside the fits for the two-tau isotropic model and the tetragonal jump model is shown in Figures 4.19 and 4.20 for the $q_{110} - q_c$ and $q_a - q_b$ planes. The fitted parameters for the two-tau model and the tetragonal jump model are summarised in Table 4.8.

The parameters show good general agreement between fits, with the uniaxial motion an order of magnitude faster than the isotropic diffusion of the C-N axis, consistent with the assumptions made for the model. The r_1 parameter is significantly larger than the rotational radius of the CH₃NH₃ molecule ($\sim 1.1 \text{ \AA}$), which may be due to the diffuse motion of the C-N axis, causing uniaxial rotation on a larger radius, while the average radius of isotropic diffusion is consistent with the expected radius of the CH₃NH₃ molecule ($\sim 1.3 \text{ \AA}$). As a reliability check regarding the $\langle u^2 \rangle$ values, a fit was performed to the $q_c - q_{110}$ data with a more physically realistic $\langle u^2 \rangle = 0.12 \text{ \AA}^2$ (the same value as refined at 175 K). This

plane	Model	χ^2	Fitted parameters	
$q_{110} - q_c$	$I4/mcm$ jump	1.65	$\tau_3 = 2.6(1) \text{ ps}$ $\langle u_{ab}^2 \rangle = 0.31(1) \text{ \AA}^2$ $A = 0.110(2) \text{ a.u.}$	$\tau_4 = 8.6(2) \text{ ps}$ $\langle u_c^2 \rangle = 0.0 \text{ \AA}^{2*}$
	two-tau	1.21	$\tau_{\text{uni}} = 0.72(4) \text{ ps}$ $r_1 = 1.49(2) \text{ \AA}$ $\langle u^2 \rangle = 0.0 \text{ \AA}^{2*}$	$\tau_{\text{iso}} = 7.6(3) \text{ ps}$ $r_2 = 1.23(2) \text{ \AA}$ $A = 1.84(4) \text{ a.u.}$
$q_a - q_b$	$I4/mcm$ jump	1.60	$\tau_3 = 2.2(6) \text{ ps}$ $\langle u_{ab}^2 \rangle = 0.31(3) \text{ \AA}^2$ $A = 0.081(2) \text{ a.u.}$	$\tau_4 = 8.1(4) \text{ ps}$ $\langle u_c^2 \rangle = 0.01(6) \text{ \AA}^2$
	two-tau	1.03	$\tau_{\text{uni}} = 0.52(4) \text{ ps}$ $r_1 = 1.49(2) \text{ \AA}$ $\langle u^2 \rangle = 0.0 \text{ \AA}^{2*}$	$\tau_{\text{iso}} = 7.4(4) \text{ ps}$ $r_2 = 1.42(4) \text{ \AA}$ $A = 1.40(5) \text{ a.u.}$

Table 4.8: χ^2 goodness of fit values and fitted parameters for the models used to investigate the data at 290 K. * Value fixed to zero to avoid an unphysical negative parameter.

4.3. Rotational dynamics of CH_3NH_3 investigated by quasielastic neutron scattering

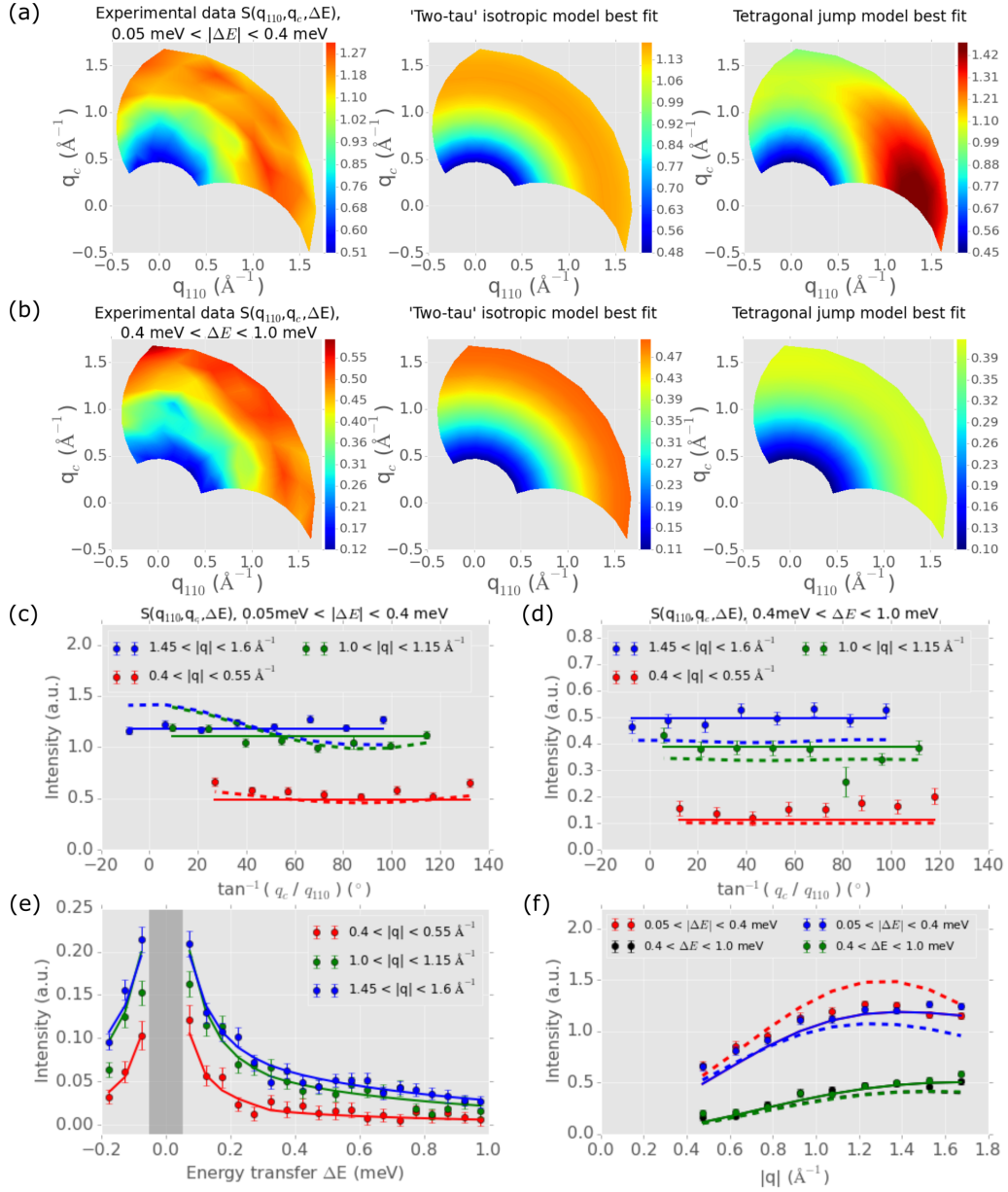


Figure 4.19: Experimental data for scattering in the q_{110} - q_c plane at 290 K, integrated over low energy transfers (a) and high energy transfers (b), alongside the best fit for the ‘two-tau’ isotropic model and tetragonal jump model with an isotropic $\langle u^2 \rangle$, showing good agreement only with the two-tau model. (c), (d) Angle dependence of scattering for low and high energy transfer, in addition to the energy transfer (e) and $|q|$ dependence (f). Solid lines show the best fit for the two-tau isotropic model ($\chi^2 = 1.21$), while the dashed lines (in (c), (d) & (f)) show the best fit for the tetragonal jump model ($\chi^2 = 2.10$). In (f), values are shown at two rotation angles corresponding to scattering predominantly along q_c (blue & green) and q_{110} (red & black).

4.3. Rotational dynamics of CH₃NH₃ investigated by quasielastic neutron scattering

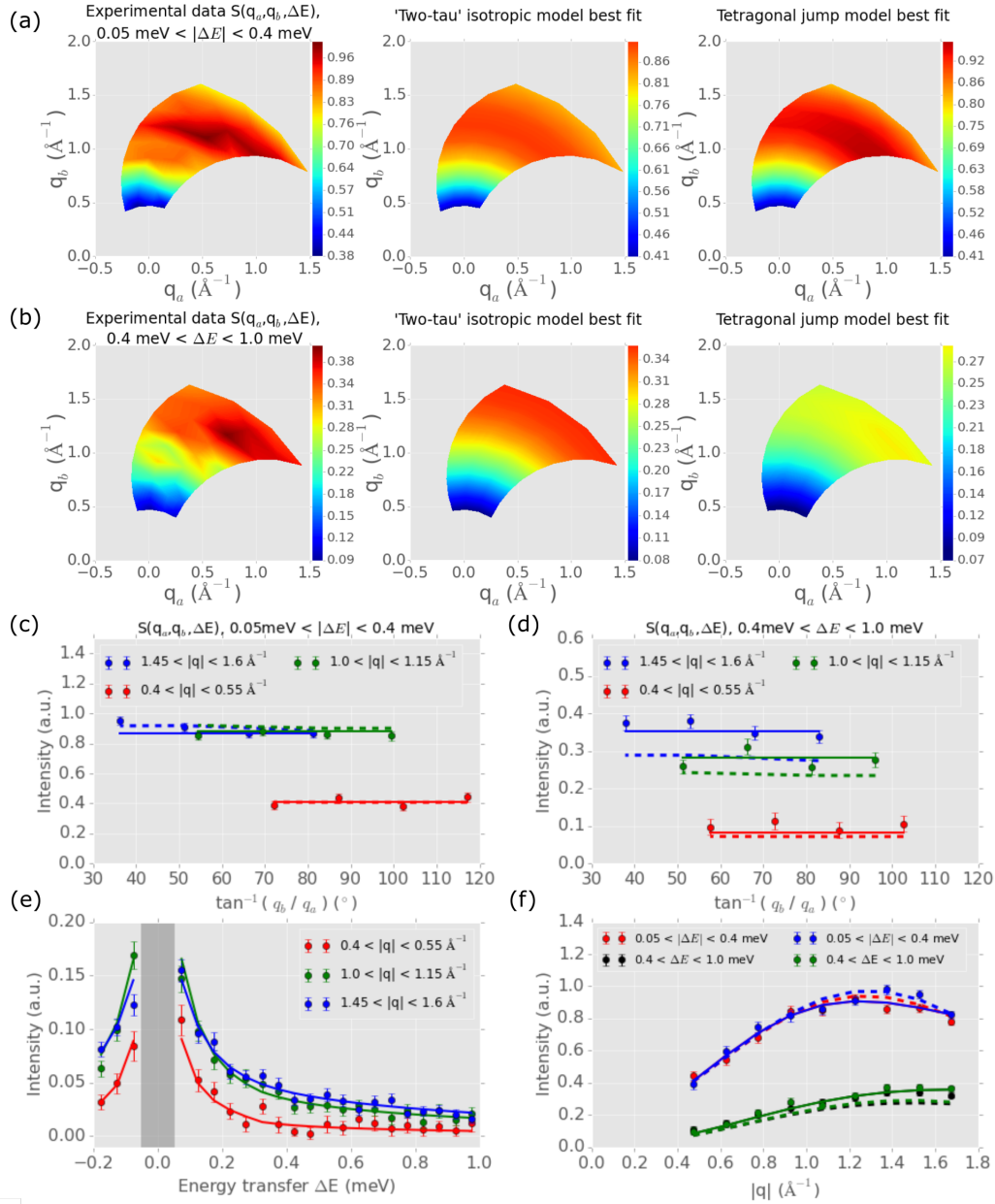


Figure 4.20: Experimental data for scattering in the $q_a - q_b$ plane at 290 K, integrated over low energy transfers (a) and high energy transfers (b), alongside the best fit for the ‘two-tau’ isotropic model and tetragonal jump model with an isotropic $\langle u^2 \rangle$, showing better agreement with the two-tau model. (c), (d) Angle dependence of scattering for low and high energy transfer, in addition to the energy transfer (e) and $|q|$ dependence (f). Solid lines show the best fit for the two-tau isotropic model ($\chi^2 = 1.03$), while the dashed lines (in (c), (d) & (f)) show the best fit for the tetragonal jump model ($\chi^2 = 1.62$). In (f), values are shown at two rotation angles corresponding to scattering predominantly along q_b (blue & green) and q_{110} (red & black).

4.3. Rotational dynamics of CH₃NH₃ investigated by quasielastic neutron scattering

resulted in only a slightly increased χ^2 value of 1.25, with timescale parameters unchanged within error and r values of $r_1 = 1.30(2)$ Å and $r_2 = 1.16(2)$ Å. While the r parameters are somewhat reduced, these values are still physically reasonable, particularly as the increased $\langle u^2 \rangle$ value adds to the effective radius of rotation of the molecule. Overall, this model reproduces the main features of the observed scattering; the angular isotropy in both planes, the energy transfer dependence and the $|q|$ dependence, with the only discrepancy being a slight underestimation of the intensities at low q and at low energy transfer. This could occur if the molecule is able to explore a larger volume of its ionic cage on long timescales.

As a comparison, the fourfold jump model was also investigated. Higher χ^2 values of 1.65 and 1.60 were obtained for fits to the $q_{110} - q_c$ and $q_a - q_b$ planes: the fitted parameters are given in Table 4.8. Furthermore, there was a large divergence between the anisotropic parameters in each fit, suggesting unphysical overfitting of the model. Restricting to an isotropic thermal parameter increased the χ^2 values to 2.10 and 1.62 respectively, clearly indicating a poor fit for the $q_{110} - q_c$ plane. This can clearly be seen in the difference between the best fit and experimental data plotted in Figure 4.19. As is the case for the low temperature tetragonal data, the fourfold jump model produces a large variation with angle in the $q_{110} - q_c$ plane at lower energy transfers, in clear disagreement with the experimental data. Furthermore, the model underestimated the scattering intensity at higher energy transfer. As the fourfold jump model predicts less variation in the $q_a - q_b$ plane, the fit to the data was better than for the $q_{110} - q_c$ plane, but the scattering intensity was also underestimated by the model at high energy transfers. The model of combined jump rotations plus translational diffusion along c was also tested (with an isotropic $\langle u^2 \rangle$), however this still gave a high χ^2 of 1.80. A simpler model of isotropic diffusion was also considered, consisting of solely isotropic rotational diffusion of the C-N axis (a model considered for the cubic and room temperature phase in Ref. [104]). It was found that this model could not

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adequately describe the data, giving a χ^2 value of 1.75 for the $q_{110} - q_c$ plane and 1.84 for the $q_a - q_b$ plane, with unphysically low r values of 0.70(1) Å/0.67(1) Å. The main reason for the poor fit was that a single τ parameter cannot adequately describe the energy transfer dependence of the scattering intensity, which requires the two distinct rotation timescales of the two-tau isotropic model.

From this investigation we can conclude that an isotropic model of rotation, including uniaxial rotation of each end of the molecule about the C-N axis, combined with isotropic rotational diffusion of the C-N axis, provides a much better description of the experimental data than a fourfold jump model based on the tetragonal symmetry of the crystal. At 290 K, the molecular reorientation can be considered to be isotropic in space, while the molecule also rotates about its own axis on picosecond timescales.

4.3.5 Discussion

From the investigation of various fitting models, we can draw the following conclusions about the temperature dependence of the molecular motion. In the orthorhombic phase, a slight increase in absolute scattering is seen along the q_c direction, however a consideration of the total energy-integrated scattering shows that this is due to anisotropy of the high frequency motions of the lattice. After correcting for this factor, the anisotropy between the q_c and q_{110} directions is removed within error. The best fit to the data implies that there is significant translational motion associated with the threefold jump rotations, which both occur on a timescale of ~ 50 ps. This model gives a fairly isotropic scattering distribution, with some weak angular features in the $q_c - q_{110}$ plane similar to that seen in the data. This gives a better fit to the data than purely threefold rotations as given by the $Pnma$ structure, which predict significant anisotropy in the $q_c - q_{110}$ plane, although the contrast is reduced by orthorhombic and tetragonal twinning.

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In the tetragonal phase at 175 K, two timescales of motion are observed; a threefold rotation on a short timescale on the order of 1 ps, and a slower reorientational motion on the order of 80 ps. The scattering at low energy transfers, corresponding to the long timescales of molecular reorientation, is observed to be isotropic, while a slight increase in scattering is seen along the c direction at high energy transfers. However this is likely to be due to the effect of anisotropic thermal motions due to higher frequency lattice vibrations, as is the case for the orthorhombic phase. Overall, the observed scattering cannot be well described by a jump model based on the hydrogen positions from structural neutron scattering studies which predicts significant anisotropy at low energy transfers, inconsistent with the experimental data. Instead, the data shows that the molecule is free to explore many orientations which can be better described with a two-tau isotropic model. This model describes a CH₃NH₃ molecule that is freely rotating inside the crystal cage, such that the molecular axis can be pointing in any direction in space, causing the threefold rotations about the molecular axis to give scattering in all directions on a time-average. In the tetragonal phase at 290 K, the scattering is isotropic in both the low and high energy modes, and a clear divergence between a fourfold jump model and an isotropic model is observed, with the two-tau isotropic model giving an excellent description of the observed scattering. The two-tau model can be considered an approximation to a molecule reorienting between many pseudocubic orientations that are equivalent in the cubic phase.

This is somewhat in contrast to previous experimental studies on powder samples. In a study by Chen *et al.* [104], the isotropic model was found to give a good description of the motion in the cubic phase, but it was found that a $C_4 \times C_3$ rotational model was significantly better than an isotropic model for the tetragonal phase, particularly as the temperature was reduced. However, the isotropic model used in the study was the model of diffuse isotropic motion of the C-N axis, with

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only a single timescale τ characterising the motion. Given that there are two clear timescales of rotation, which are similar in value in the cubic phase but which diverge as the temperature is reduced, one would expect a model with a single τ to give a progressively worse fit as the temperature is reduced, compared to a rotational jump model with two τ parameters. Furthermore, the powder averaging of scattering in this study means that it would not be possible to determine if the timescales correspond to jumps between well defined sites or isotropic rotations of the molecule.

In contrast, the data provided here provide unambiguous evidence that the rotational motion is well described by the model of uniaxial diffusion about the C-N axis, combined with isotropic diffusion of the C-N axis. This model provides a good description of the rotational motion at room temperature and at the lowest temperatures in the tetragonal phase, with no indication that the motion settles into jumps between four symmetry equivalent orientations within the crystal at 175 K. At 150 K only one timescale of motion is seen in the energy-transfer dependence of scattering, in agreement with previous studies, however by measuring the $\mathbf{q}$ -dependence a large thermal motion associated with these reorientations can be seen for the first time.

While these results are somewhat in contrast to crystal structures determined from neutron diffraction, these studies were not able to definitively determine the H positions and required large thermal parameters, suggesting significant uncertainty in the given CH_3NH_3 positions [63, 108]. A recent study used a DFT approach to calculate the energy landscape of the CH_3NH_3 molecular orientation in the cubic phase, also allowing for translations of the CH_3NH_3 away from the A site of the perovskite structure [113]. This study found that the minimum energy orientation is along the cubic $[1\ 0\ 0]$ direction, with a translation off the A site of 0.6 Å due to the NHI interactions (however as the molecule reorients the average position of the

4.3. Rotational dynamics of CH_3NH_3 investigated by quasielastic neutron scattering

CH_3NH_3 molecule will still be the A site). Interestingly, the energy for a $[1\ 1\ 1]$ orientation was calculated to be only $\sim 20\text{ meV}$ greater and separated by an energy barrier of $\sim 90\text{ meV}$ relative to the $[1\ 0\ 0]$ orientation. This calculated energy barrier is in excellent agreement with the activation energy of $79(4)\text{ meV}$ of the reorientational motion determined from the measurements on the large crystal. While the energy landscape will change slightly in the tetragonal phase, the cubic-tetragonal phase transition is characterised by a continuous rotation of the PbI_6 octahedra, and at 290 K one would expect a similar energy landscape but with a loss of equivalence of some orientations. Given that the thermal energy ($\sim k_B T$) is $\sim 25\text{ meV}$ at 290 K , the pseudocubic $[1\ 0\ 0]$ and $[1\ 1\ 1]$ orientation states should have similar thermal populations on a time-average. Clearly, reorientations between these 14 pseudocubic orientations, in addition to the threefold rotations, would give a very similar quasielastic scattering pattern to the two-tau model which was found to best describe the data in the tetragonal phase. At 175 K , the thermal energy is still $\sim 15\text{ meV}$ and it is certainly plausible that the pseudocubic $[1\ 0\ 0]$ and $[1\ 1\ 1]$ orientation states still have similar thermal populations at this temperature.

In order to compare the timescales between the two-tau isotropic model and the jump model, one must consider the expectation value of the mean displacement as a function of time. For n -dimensional diffusive motion the mean square angular deviation in time t is given by

$$\langle \theta^2 \rangle = 2nD_r t. \quad (4.7)$$

For a simple comparison, I shall use the approximation $\langle |\theta| \rangle^2 \approx \langle \theta^2 \rangle$. For uniaxial motion, $\tau_{\text{uni}} = 1/D_r$, so for a step change of 120° (~ 2.1 radians), one obtains $2.2 \approx t/\tau_{\text{uni}}$. For isotropic diffusion, $1/\tau_{\text{iso}} = 2D_r$, hence the time taken to undergo a diffusion over 90° (1.57 radians) is given by $1.23 \approx t/\tau_{\text{iso}}$. The transformed rotational timescales are plotted alongside the derived timescales from the measurements on the large cubic crystal in Figure 4.21, showing good agreement between the two sets of

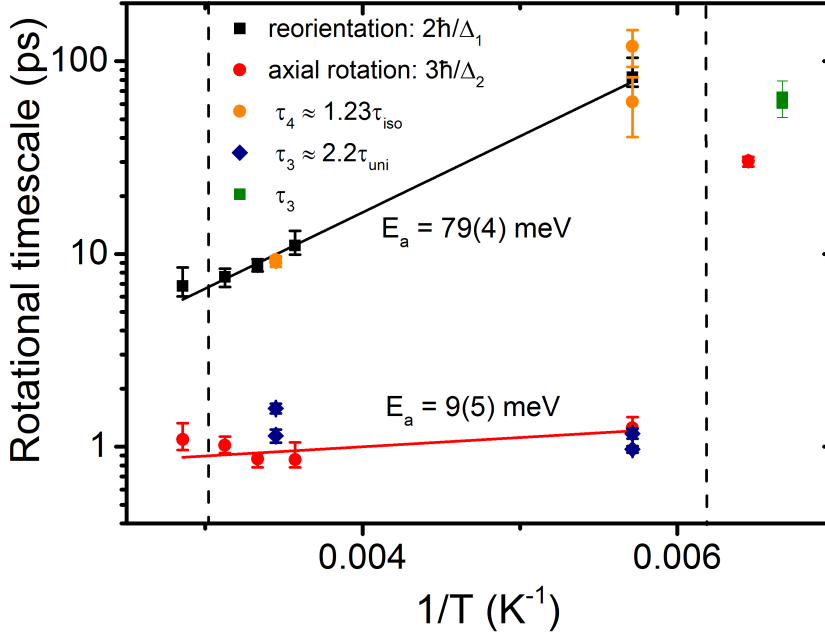


Figure 4.21: Logarithmic plot of the rotational timescales as a function of inverse temperature, including the data for the array of tetragonal crystals. For the tetragonal crystal array, an approximation is used to convert the uniaxial/rotational diffusion timescales to comparable values of the tetragonal jump model in the tetragonal phase. In the orthorhombic phase, the green datapoints are the values obtained from fitting the combined jump-diffusion model: this gives a larger timescale compared to the measurement on the large crystal as the diffusive motion also contributes to the Lorentzian width.

measurements.

4.4 Conclusion

I have investigated the structural details of $\text{CH}_3\text{NH}_3\text{PbI}_3$, using X-ray and neutron scattering techniques. The X-ray diffraction measurements give no indication that the Pb-I lattice is polar at room temperature, and the observed diffraction is consistent with an $I4/mcm$ space group, when tetragonal symmetry twinning is accounted for. It is also observed that the extent of twinning in small crystals ($< 100 \mu\text{m}$) is reduced in

crystals grown below the cubic-tetragonal phase transition, although a small fraction of twin domains still persist.

In order to investigate the orientation and dynamics of the CH_3NH_3 molecule within the crystal structure, I undertook quasielastic incoherent neutron scattering measurements, a technique with high sensitivity to the motion of hydrogen atoms due to hydrogen's large incoherent scattering cross section. Quasielastic measurements on an array of coaligned tetragonal crystals allowed the $\mathbf{q}$ -dependence of scattering to be investigated in detail, which revealed that the orientation of the CH_3NH_3 dipole is highly disordered at room temperature, and can be considered to be undergoing isotropic rotational diffusion on a timescale of < 10 ps. The reorientation of the CH_3NH_3 dipole between four discrete symmetry-equivalent orientations can be conclusively ruled out at room temperature. Clearly, such a rapidly-diffusing isotropic orientational disorder is incompatible with a molecular ferroelectric ordering in this material. As the temperature is reduced in the tetragonal phase, the reorientational motion slows significantly, before freezing at the tetragonal-orthorhombic phase transition. Before the phase transition, there is still a high degree of reorientational isotropy, best described by a model of isotropic rotational diffusion rather than a fourfold jump model. In the orthorhombic phase at 150 K the effect of thermal motion is still evident, with the best description given by a model where some translational diffusion accompanies the threefold axial rotations.

Chapter 5

Ferroelectric polarisation and memory effects in multiferroic CuFeO_2

5.1 Introduction

The discovery of type-II multiferroics has generated significant interest over the past decade, with an increasing number of compounds known to manifest strong coupling between their magnetic and ferroelectric ordering. One particularly interesting material is CuFeO_2 , which exhibits frustrated antiferromagnetic interactions between Fe^{3+} spins located on a hexagonal lattice. This results in a variety of magnetic spin structures at low temperature ($<14\text{ K}$) in applied magnetic fields, including a ferroelectric phase where ferroelectricity is induced by an incommensurate proper-screw magnetic order [25, 114–116]. The proper-screw magnetic structure results in a ferroelectric polarisation that is dependent on the handedness of the magnetic screw order and was the first known example of such behaviour. The coupling between a proper-screw magnetic order and ferroelectric ordering could not

be explained by the known mechanisms of multiferroicity at the time (spin-current and exchange-striction). A new mechanism, known as spin-dependent orbital hybridisation, was later proposed by Arima [26] to explain how a ferroelectric polarisation could arise in a proper-screw magnetic structure in CuFeO_2 . More recently, Xiang *et al.* [117] have described how a generalised spin current mechanism may also contribute to the polarisation in CuFeO_2 .

While the magnetic phase diagram of CuFeO_2 has now been well characterised, the dielectric and ferroelectric properties of CuFeO_2 are still the subject of significant debate. A history dependence of the ferroelectric polarisation has been observed in pulsed-field measurements by Mitamura *et al.* [118], while a residual polarisation was also observed in the adjacent magnetic phases to the proper-screw phase [118,119]. Additionally, a ferroelectric memory effect has been reported for the analogous proper-screw phase in $\text{CuFe}_{1-x}\text{Ga}_x\text{O}_2$ [120,121]. These effects have so far been attributed to the presence of magnetoelastic q -domains and trapped residual charges, however the origins of these effects is far from clear.

Understanding the nature of these memory effects and their relation to the multiferroic phase transitions has implications for the wider field of multiferroics. Similar polarisation memory/hysteresis effects have also been reported in CuO [122] and MnWO_4 [123], where it was found that a memory of the polarity of an incommensurate multiferroic phase was retained in a collinear antiferromagnetic phase. In these studies, the existence of multiferroic nanoregions was suggested as the cause of the observed memory effects. Understanding the origin of such memory effects, and whether they are a general feature of certain types of multiferroic phase transition, is important for understanding the physics of multiferroic phase transitions and the role of domains in both ferroelectric and non-ferroelectric phases. From a device perspective, understanding the role of domain structure and memory effects is important as such hysteresis effects could impede switching

between ferroelectric states in a memory device.

5.1.1 The magnetic and structural phase diagram of CuFeO_2

A number of studies have investigated the magnetic and accompanying structural transitions of CuFeO_2 and the magnetic phase diagram is now well established. The room-temperature crystal structure of CuFeO_2 is a layered structure with space group $R\bar{3}m$, consisting of planes of Cu^+ and Fe^{3+} ions separated by O^{2-} ions [124]. A schematic of the crystal structure, in the hexagonal setting of the unit cell, is shown in Figure 5.1(a).

In the absence of magnetic field, CuFeO_2 undergoes two magnetic transitions upon cooling from its room temperature paramagnetic phase, which are accompanied by structural distortions due to magnetoelastic coupling [125–127]. At $T_{\text{N1}} = 14 \text{ K}$, the Fe^{3+} spins magnetically order into a collinear-incommensurate state (spin-density wave (SDW)), with spins aligned along the hexagonal c axis [128]. This state has a wavevector $Q = (q_{\text{IC}}, q_{\text{IC}}, 3/2)$, with a temperature-dependent $q_{\text{IC}}(T)$ that varies from 0.19 to 0.22. At $T_{\text{N2}} = 11 \text{ K}$, the spins lock-in to a collinear constant-moment $\uparrow\uparrow\downarrow\downarrow$ four-sublattice (4SL) ground state with $Q = (1/4, 1/4, 3/2)$. Magnetoelastic distortions lower the crystal symmetry to $C2/m$ at T_{N1} and result in a scalene-triangle distortion at T_{N2} , which lifts the degeneracy of the in-plane exchange interactions to stabilise the 4SL structure [125, 127]. The second transition is associated with the loss of C -centering, as confirmed by the appearance of additional Bragg reflections [127, 129], further lowering the symmetry to either $P2/c$ or $P2$, depending on whether or not inversion symmetry is maintained.

Upon application of a magnetic field B along the trigonal c axis, the ground state of CuFeO_2 undergoes a further series of magnetic transitions [130]. Between 7.5 T and 13 T the Fe^{3+} spins form an incommensurate proper-screw magnetic structure, which shall be referred to as the ferroelectric incommensurate (FEIC) phase, with

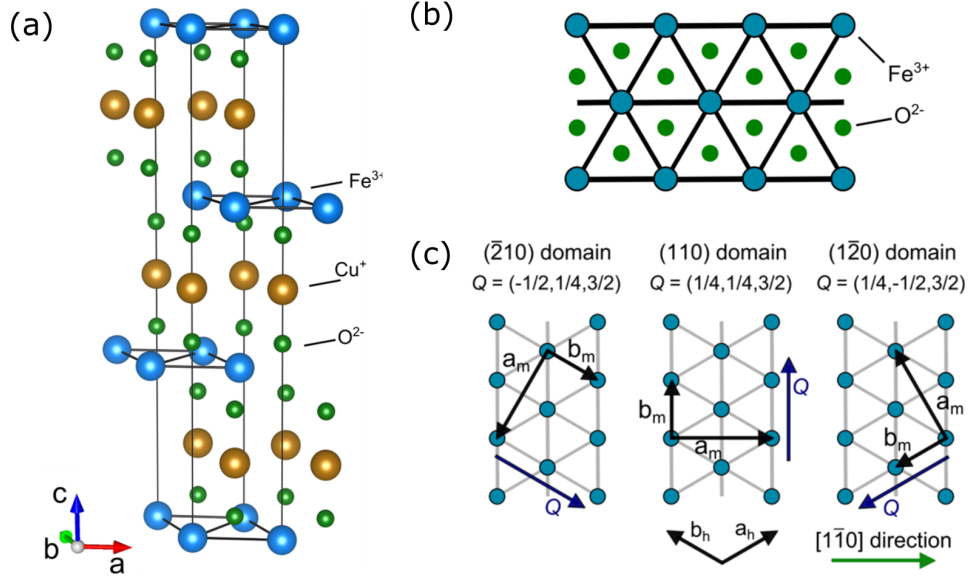


Figure 5.1: (a) Crystal structure of CuFeO_2 , which consists of planes of Cu^+ and Fe^{3+} ions separated by O^{2-} ions, shown in the hexagonal setting of the unit cell. (b) The Fe^{3+} ions, with $S = 5/2$, are the only magnetic ions. The magnetism of CuFeO_2 can be described as a triangular lattice antiferromagnet, where the strongest interactions are frustrated antiferromagnetic interactions in the ab plane. (c) Relationship between the axes of the three monoclinic domains and the parent hexagonal structure. The monoclinic domains are distorted relative to the hexagonal structure, with an increase in b_m and a decrease in a_m , which form upon cooling at $T_{N1} = 14$ K [125–127].

$Q = (q_{1C}, q_{1C}, 3/2)$, where $q_{1C} \sim 0.21$. This produces a ferroelectric polarisation along the $[1\ 1\ 0]$ direction, with the sign of $P_{[110]}$ being determined by the handedness of the magnetic structure. At 13 T there is a transition to a $\uparrow\uparrow\uparrow\downarrow$ five-sublattice (5SL) phase with $Q = (1/5, 1/5, 3/2)$. The transition to the 5SL phase is accompanied by spin-driven bond ordering which removes the scalene-triangle distortion and restores the crystal symmetry to $C2/m$ [131]. There are further magnetic transitions at 20 T and 33 T to a $\uparrow\uparrow\downarrow$ three-sublattice (3SL) and canted-3SL phase respectively [130].

Upon symmetry lowering at T_{N1} from $R\bar{3}m$ to $C2/m$, three magnetic domains will form due to the loss of the trigonal threefold symmetry. Due to the magnetoelastic distortion, these magnetic domains will have a one-to-one correspondence with three structural monoclinic domains, hence the domains shall

5.1. Introduction

be referred to as magnetoelastic domains. In the magnetic ground state the magnetic unit cell is double the crystal cell, leading to two antiferromagnetic phase domains within each magnetoelastic domain. The loss of C -centering at T_{N2} will further result in two magnetic translation domains, giving four antiferromagnetic domains within each magnetoelastic domain in the 4SL ground state. The magnetoelastic domains of the 4SL phase are shown in Figure 5.1(c). These magnetoelastic domains shall be referred to as the $(\bar{2}10)$, (110) and $(1\bar{2}0)$ domains, where the labels refer to the ordering wavevector with respect to the hexagonal parent structure. In the ferroelectric phase two helical domain types are possible within each magnetoelastic domain, corresponding to left and right handed magnetic structures, giving six helical ferroelectric domains in total. In the 5SL phase the $C2/m$ symmetry is restored, however the magnetic unit cell is five primitive cells, giving five phase domains within each magnetoelastic domain [131].

5.1.2 Ferroelectric properties of CuFeO_2

5.1.2.1 Previous studies in the literature

The ferroelectric polarisation in the FEIC phase has been investigated in a number of studies. Kimura *et al.* [25] measured a polarisation of up to $400 \mu\text{C m}^{-2}$ in the ab plane in the FEIC phase. Mitamura *et al.* [118] showed that the polarisation is aligned along the $[1\ 1\ 0]$ direction, however a lower magnitude of polarisation of $80 \mu\text{C m}^{-2}$ was determined. It has also been found that the FEIC phase can be stabilised as the ground state in zero applied field by a small amount of non-magnetic impurity doping, where the Fe^{3+} is replaced by Ga^{3+} [132] or Al^{3+} [133, 134].

In several studies of the ferroelectricity of CuFeO_2 and related compounds, a number of unusual effects have been observed. A history dependence of the ferroelectric polarisation of CuFeO_2 was reported for pulsed B -field measurements by Mitamura *et al.* [118], whereby several B -field pulses were needed to saturate the

value of P . This was suggested to result from successive domain alignment and repopulation of the three magnetoelastic q -domains, however its origin is not clear. Recently, another study showed that the net ferroelectric polarisation in CuFeO_2 could be increased by repeatedly sweeping a magnetic field within the ferroelectric phase [135]. This was interpreted as arising due to a change in the helicity domain volume fractions within each magnetoelastic domain, a consequence of the movement of helicity domain walls. Another issue that remains to be clarified is the observation in pulsed-field measurements of a residual polarisation in the 4SL and 5SL phases (i.e. the measured polarisation does not return to zero upon leaving the FEIC phase) [118, 119]. A ferroelectric polarisation memory effect has also been reported for the analogous phase of $\text{CuFe}_{1-x}\text{Ga}_x\text{O}_2$ [120, 121]. In these studies, a net ferroelectric polarisation was recovered after warming out of the ferroelectric phase and then cooling without electrical bias, which was attributed to residual charges trapped at magnetoelastic q -domain boundaries. In this chapter, I shall use the term ‘polarisation memory effect’ to mean when the direction and strength of the electrical polarisation is retained through a history involving a non-ferroelectric phase, achieved either through temperature or magnetic field cycling.

5.1.2.2 Discussion of preliminary pulsed-field measurements

As part of this research project to investigate the ferroelectric properties of CuFeO_2 , initial polarisation measurements of CuFeO_2 were performed in pulsed magnetic fields by S. Magorrian and F. Foronda, where a residual polarisation and strong memory effect was identified, as described in [136]. This pulsed-field data (described below), alongside the measurements, simulations and interpretation presented in this chapter were published in the following article [137].

In the work of S. Magorrian [136], the ferroelectric polarisation of CuFeO_2 was measured in pulsed magnetic fields. Figure 5.2(a) shows $P_{[110]}$ for $B \parallel c$, measured

with an applied biasing electric field E of 200 V mm^{-1} . Upon increasing B , a polarisation of $180 \mu\text{C m}^{-2}$ was measured in the FEIC phase between 7.5 T and 13 T, however P was not observed to return to zero above 13 T in the 5SL phase, with a residual value of $\sim 40 \mu\text{C m}^{-2}$. Furthermore, upon reducing B from the FEIC phase into the 4SL phase, a residual polarisation of $75 \mu\text{C m}^{-2}$ was measured at 0 T. These observations of residual polarisation are consistent with previous reports of a residual polarisation in both the 4SL and 5SL phase [118, 119].

Figure 5.2(b) shows a set of sequential polarisation measurements, which revealed the existence of a strong polarisation memory effect. In the set of sequential measurements, the zero of P is redefined at the start of each measurement for clarity. During the first measurement, P was measured for a 10 T pulse with $E = -400 \text{ V mm}^{-1}$, giving a P of $-310 \mu\text{C m}^{-2}$. In all subsequent measurements, a bias of $+400 \text{ V mm}^{-1}$ was applied, in an attempt to switch the direction of P . Upon switching the external bias in the non-polar phase, one would expect to measure a reversed polarisation of equal magnitude upon re-entering the ferroelectric phase, as the $\pm \mathbf{P}$ states should have equal energy relative to a non-polar parent phase when coupled to a field of $\pm \mathbf{E}$. However, upon reversing E to $+400 \text{ V mm}^{-1}$ a polarisation of $-160 \mu\text{C m}^{-2}$ was measured, and in each subsequent measurement with $+400 \text{ V mm}^{-1}$, the polarisation gradually increased in the direction of E , until the magnitude of $\mathbf{P}$ started to saturate at $100 \mu\text{C m}^{-2}$. A large, but not fully reversed, P of $270 \mu\text{C m}^{-2}$ was only recovered on the down-sweep of an 18 T pulse, once the system had been driven into the 5SL phase. In another set of measurements with $|E| = 200 \text{ V mm}^{-1}$ and 18 T B -field pulses, it was found that two 18 T B -field pulses were needed before the direction of P was reversed.

These measurements revealed that a memory of the polarisation state is retained in both the 4SL and 5SL phases, however the memory appears to be strongest in the 4SL ground state. The implication of this data is that between subsequent

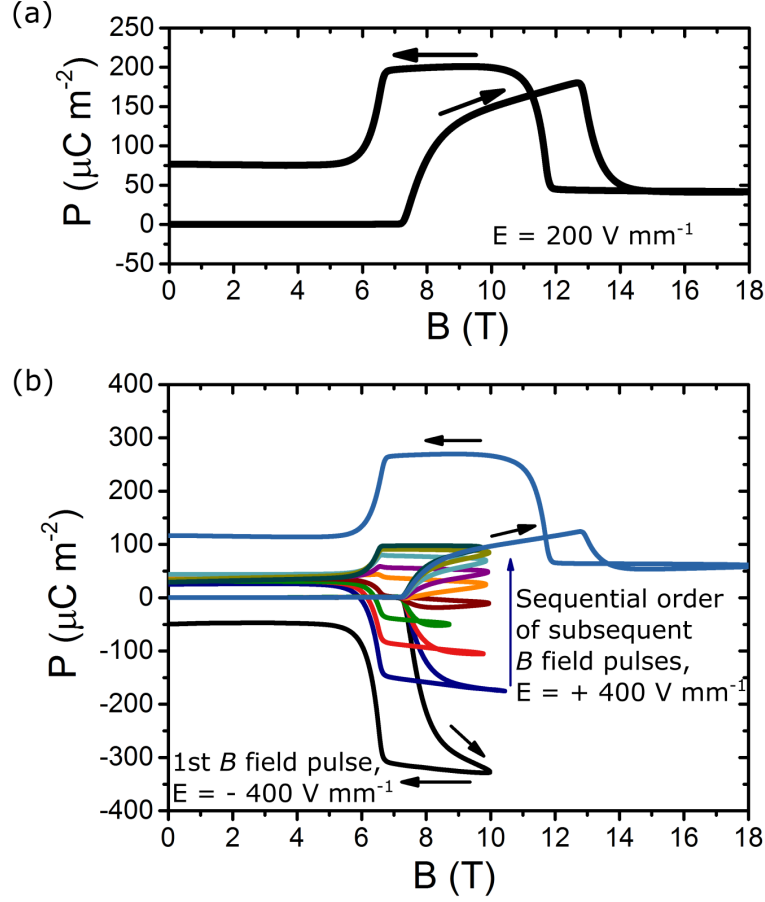


Figure 5.2: Results of previous pulsed-field polarisation measurements [136]. (a) B -field dependence of polarisation along $[1\ 1\ 0]$ measured during an 18 T-field pulse. The measured polarisation in the 4SL and 5SL phase does not return to zero, giving the appearance of a residual polarisation. (b) Measured polarisation for a set of sequential measurements, which exhibits a strong history dependence or polarisation memory. After an initial 10 T B -field pulse with a negative electrical bias (-400 V mm^{-1}), several pulses with reversed bias ($+400\text{ V mm}^{-1}$) were required to switch the direction of P . A significant polarisation reversal was only obtained on the 11th pulse after driving the system into the 5SL phase.

measurements, the ferroelectric domain volume fractions (i.e. helical spin-domain fractions) are gradually changed by each B -field pulse, as opposed to the complete switching from one configuration to the polarisation-reversed configuration that would be expected. The observation that the polarisation in the FEIC phase can be opposite the external bias is unique, and is evidence of a stronger memory effect than suggested by previous reports of memory effects in CuFeO_2 and related

compounds [118, 120, 121].

The measurements in pulsed magnetic fields enable one to draw the following conclusions. Firstly, the sign of the residual polarisation at $B = 0$ T follows the sign of the external bias, rather than the sign of the polarisation in the FEIC phase. Additionally, the residual polarisation is similar for all 10 T pulses with $E = 400 \text{ V mm}^{-1}$, despite the fact that the magnitude and sign of the ferroelectric polarisation varies significantly between pulses. This strongly suggests that the residual polarisation is an artefact due to a spurious current due to the applied bias, which gives a non-zero net charge flow over the whole field pulse, and is not a physical ferroelectric polarisation. This current may be greatest during the phase transitions, however this is difficult to determine because of the hysteresis. I shall investigate this further through measurements in persistent magnetic fields. Secondly, the observation of a polarisation in the FEIC phase in the opposite direction to the external bias, as well as the indication of leakage currents under bias, should rule out the possibility that any memory effects are due to trapped charges within the material, such as at magnetoelastic domain boundaries as suggested in previous studies [120, 121]. Any trapped charges should be removed by the reversed bias, and I shall show later that a strong memory effect still exists in predominantly single- q -domain samples.

In this chapter I will present a series of pyrocurrent/magnetocurrent measurements on single crystals of CuFeO_2 , including measurements on mechanically detwinned single crystals, in order to characterise the polarisation memory effect and investigate the role of magnetoelastic domains. I will also present Monte Carlo simulations of the ground state magnetic domain wall structures, which predict the existence of helical domain walls between antiferromagnetic phase domains; I propose that these helical domain walls can explain the observed memory effects in CuFeO_2 .

5.2 Experimental details

5.2.1 Crystal characterisation

Single crystals of CuFeO_2 were grown using a floating-zone method ^a. Samples were structurally characterised by single-crystal X-ray diffraction using a SuperNova diffractometer (Oxford Diffraction) and SmartLab diffractometer (Rigaku). The crystals were found to be essentially a single obverse/reverse domain, with less than 3% fraction of the other twin present. Cuboid samples for polarisation measurements were cut to give a large (110) face (area $\sim 15 \text{ mm}^2$), with a thickness of 0.5 mm for unstrained samples and 1.0 mm for strained samples (see below). X-ray micro-diffraction revealed a small degree of mosaicity, corresponding to the existence of large crystallites with dimensions on the order of several millimeters aligned along a common c axis but with a slight misalignment of up to 5° in the ab plane. As such, the applied electric fields, strain and measured polarisation will have components $> 99\%$ along the desired crystal directions of all crystallites, giving negligible effect due to the mosaicity. Gold electrodes were evaporated onto the (110) faces and wires were contacted using conductive silver paint.

Crystals of CuFeO_2 were characterised by DC magnetometry using a Magnetic Property Measurement System (Quantum Design). The DC magnetisation was measured as a function of temperature in an applied field of $B = 1.0 \text{ T}$; features were observed at 11 K and 14 K, in agreement with previous reports [25]. Furthermore, pulsed-field magnetisation measurements were carried out up to 40 T at the Oxford high field magnet facility, using a pulse time-width of 14 ms. A series of magnetic transitions and plateaus in magnetisation were observed, in good agreement with previous reports [130].

^aI am grateful to Dr D. Prabhakaran for growing large crystals of CuFeO_2 that were used for the measurements presented in this chapter.

5.2.2 Pyrocurrent technique

Polarisation measurements in persistent magnetic fields were performed in a 13.5 T superconducting magnet (Oxford Instruments). First, a poling voltage was applied upon cooling from 15 K at 10 T using a high voltage supply (Trek 610E). This was to ensure the formation of a net ferroelectric polarisation by favouring ferroelectric domains aligned with the poling field. At 5 K, the poling field was removed and the sample electrodes were short circuited for at least 10 minutes. The ferroelectric polarisation of CuFeO_2 was measured using the pyrocurrent/magnetocurrent technique. In this technique, the change in ferroelectric polarisation upon going through a phase transition is determined by integrating the current that flows to compensate the ferroelectric polarisation density at the surface of the sample. The current is measured as a function of temperature (pyrocurrent) or magnetic field (magnetocurrent) and integrated analytically to determine the total charge as a function of temperature/magnetic field. The current was amplified using a transimpedance amplifier (Femto), and a background current was subtracted: the background current was determined from the current before and after the temperature/field sweep. Some measurements were also made under a biasing voltage, which is maintained throughout the polarisation measurement. The circuit diagram for the pyrocurrent measurements under bias is shown in Figure 5.3(a). For measurements without bias, the left hand side contact of the sample is connected to ground.

5.2.3 Application of uniaxial stress

As the crystal structure of CuFeO_2 undergoes a structural distortion at the first magnetic phase transition, manipulation of the magnetic domain structure becomes possible by favouring the structural distortion of one domain over the others. Upon cooling through T_{N1} the unit cell length is increased along the monoclinic b axis

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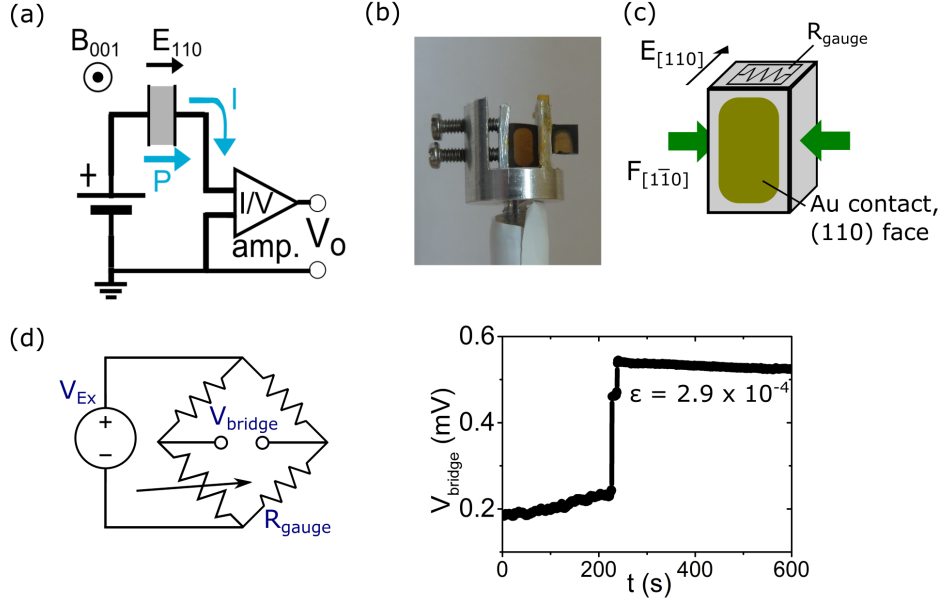


Figure 5.3: (a) Circuit diagram for pyrocurrent/magnetocurrent measurements using a transimpedance amplifier. In pulsed-field measurements, a biasing field is applied during the whole measurements. In typical persistent B -field measurements, the poling E -field is only applied upon cooling and then removed (during the measurement of P , the left hand side electrode is connected to ground). (b) Photograph of the custom-built strain device with a sample held between two aluminium plates. (c) A schematic of the straining method used for cuboid shaped samples. For one set of measurements, uniaxial force was applied to the crystal along the $[1\bar{1}0]$ direction at room temperature in order to favour the $\mathbf{q} = (q, q, 3/2)$ domain upon cooling through T_{N1} . The strain of the sample was measured using a strain gauge (R_{gauge}) adhered to the top of the sample and a balanced bridge circuit. (d) The relative strain was measured upon destraining (occurring from $t = 220$ s-240 s) to be 2.9×10^{-4} , using a balanced bridge circuit.

($\Delta b/b = 1.9 \times 10^{-3}$) and reduced along the monoclinic a axis ($\Delta a/a = -1.3 \times 10^{-3}$) [127]. By considering the distortion of each of the magnetoelastic domains relative to the hexagonal parent structure along the $[1\bar{1}0]$ direction $\Delta x_{[1\bar{1}0]}$, one finds that $\Delta x_{[1\bar{1}0]}/x_{[1\bar{1}0]} = \Delta a/a < 0$ for the (110) domain, whereas $\Delta x_{[1\bar{1}0]}/x_{[1\bar{1}0]} = \frac{1}{2}(\Delta a/a + \Delta b/b) > 0$ for the $(\bar{1}20)$ and $(\bar{2}10)$ domains. Therefore, in the presence of uniaxial force along the $[1\bar{1}0]$ direction, it is energetically favourable for the (110) magnetoelastic domain to form upon cooling through T_{N1} .

To investigate domain effects, I designed and configured a strain device to apply uniaxial stress to 1.0 mm-thick samples. A photograph of the device is shown in Figure 5.3(b). This consisted of an aluminium holder with two screws which could be tightened to apply uniaxial pressure to the side of the cuboid-shaped samples via an aluminium plate. The induced strain was measured using a strain gauge (Vishay), adhered to the top of the crystal with an epoxy resin, and a balanced bridge circuit. Compressive stress was applied to samples along the $[1 \bar{1} 0]$ direction at room temperature. For the strain measurements presented in this chapter, the relative strain was measured upon de-straining to be 2.9×10^{-4} . Based on the high pressure lattice parameters reported in Ref. [138], this corresponds to a pressure of approximately 110 MPa. To check that the device maintained the pressure at low temperatures, the voltage of a balanced bridge circuit with a dummy unstrained sample in one arm and the strained sample in the other arm was measured upon cooling through T_{N1} . This was used to infer the relative change in lattice parameters of the strained and unstrained samples, and gave good agreement with the strain measured at room temperature upon destaining in a separate measurement.

5.3 Experimental results

5.3.1 Persistent-field measurements

First, a basic characterisation of the ferroelectric polarisation was performed, in the absence of applied stress. The ferroelectric polarisation was measured upon warming at 10 T using the pyrocurrent technique after the sample had been cooled from 15 K in a poling E -field. Measurements were made for a set of poling E -fields; Figure 5.4(a) shows the temperature dependence of the measured polarisation and the poling E -field dependence of the polarisation at 5 K is shown in Figure 5.4(b). This revealed a strong poling-field dependence of P ; for a poling field of 100 V mm^{-1}

5.3. Experimental results

a net polarisation of $100 \mu\text{C m}^{-2}$ was obtained, whereas for a poling field of 600 V mm^{-1} a net polarisation of $320 \mu\text{C m}^{-2}$ was obtained. Furthermore, the rate of change of P was greatest at low poling fields, and some saturation of P is observed for poling fields above 400 V mm^{-1} . This shows that one cannot easily obtain a ferroelectric monodomain within each magnetoelastic domain, and implies a significant energy barrier for ferroelectric domain wall motion [139].

The intrinsic reversibility of the ferroelectric polarisation was tested by poling with E -fields of $\pm 200 \text{ V mm}^{-1}$ from the paramagnetic phase at 10 T, and measuring the polarisation upon warming. The measured polarisation is shown in Figure 5.4(c) and reveals that the polarisation does not intrinsically lie along a particular direction.

One way to explicitly determine the value of any residual polarisation is by comparing the results of magnetocurrent and pyrocurrent measurements. One can use the fact that the pyrocurrent measurement at 10 T gives an absolute value of P relative to the paramagnetic phase. By comparing this absolute value of P to the change in polarisation across the FEIC-4SL phase transition, the absolute value of P for the 4SL phase can be determined. Figure 5.4(d) shows the result of two magnetocurrent measurements at 5 K, for poling voltages $E = 200 \text{ V mm}^{-1}$ and 400 V mm^{-1} . The value of P was found to reduce to zero in the 4SL phase within measurement error, giving no evidence for a residual ferroelectric polarisation. Furthermore, the pyrocurrent was measured upon warming at 0 T and no depolarisation of the 4SL phase was observed. These measurements confirm that the residual polarisation in pulsed-field measurements can be attributed to a spurious current due to the applied bias, which must be maintained throughout the measurement due to the short time-width of the pulse. Additionally, these results indicate that the crystal structure of the 4SL phase should be described by a non-polar space group such as $P2/c$, as opposed to $P2$. Furthermore, if residual

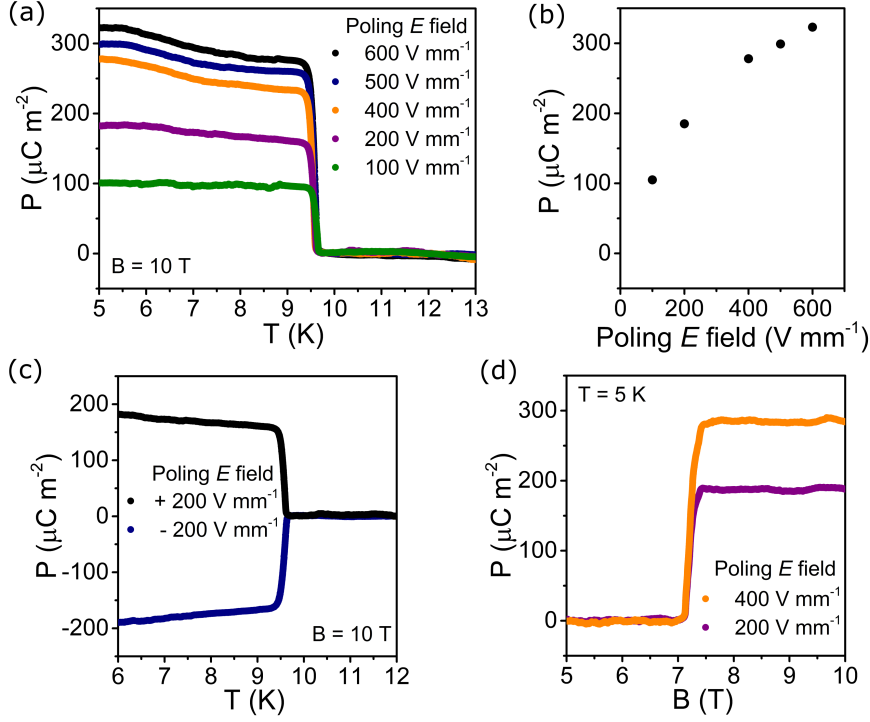


Figure 5.4: (a) Temperature dependence of the ferroelectric polarisation, after poling with a given E -field upon cooling. (b) The poling E -field dependence of the polarisation at 5 K, showing that saturation of $P \sim 325 \mu\text{C m}^{-2}$ only occurs at high poling E -fields above $\sim 500 \text{ V mm}^{-1}$. (c) Measured polarisation upon warming for a poling E -field of $\pm 200 \text{ V mm}^{-1}$. The direction of P is fully reversible, as expected for a good ferroelectric. (d) Magnetocurrent measurements of the polarisation for reducing B . By comparing the absolute values of P determined in (a) and (d), the polarisation of the 4SL phase is determined to be zero, giving no indication of a physical residual ferroelectric polarisation.

regions of the FEIC phase are responsible for the memory effect, then they must have a small volume fraction, or a pyrocurrent would be detected upon warming at 0 T.

Next, the history dependence of the polarisation was investigated. Figures 5.5(a) and (b) show the measured polarisation as a function of B and T for three sample histories illustrated in Figures 5.5(c)-(e). At the start of each measurement, the sample was cooled from the paramagnetic phase at 10 T under a poling field of 200 V mm^{-1} to give an initial polarisation of $180 \mu\text{C m}^{-2}$. The poling field was

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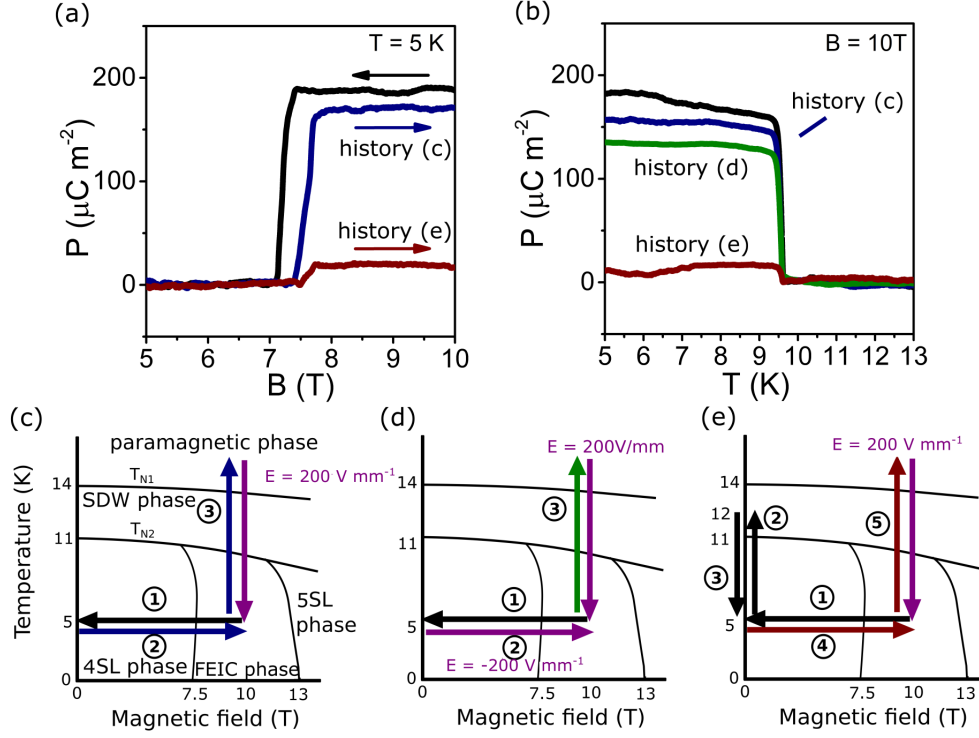


Figure 5.5: History dependence of the ferroelectric polarisation in CuFeO_2 . Magnetocurrent (a) and pyrocurrent (b) measurements, all taken in the absence of any bias E -field, showing the measured polarisation for three different sample histories, as shown in (c), (d), (e). The schematic of the phase diagram is based on that reported by Kimura *et al.* [25]. For each measurement, the sample is poled with $E = 200 \text{ V mm}^{-1}$ upon cooling at 10 T, giving a polarisation shown by the black curve. In (c), B is reduced to 0 T and the FEIC phase is reentered with zero bias, recovering 88% of P (blue curves). In (d), a reverse bias of -200 V mm^{-1} is applied upon reentering the FEIC phase, which reduces P to 73% of its initial value, in the direction of the *initial* poling field (green curve). In (e), a thermal cycle from 5 K to 12 K to 5 K is performed at 0 T, which reduces the recovered P to only 11% of its initial value (red curves).

removed at 5 K before the contacts were short circuited for at least 10 minutes. In the first sample history (Figure 5.5(c)), the magnitude of the polarisation memory under zero applied bias was tested. The polarisation was measured during a field sweep from 10 T to 0 T to 10 T. Upon reentering the ferroelectric phase with zero bias, a net polarisation was recovered, with 88% of its initial value (blue curves in Figures 5.5(a),(b)). In the second sample history (Figure 5.5(d)), the effect of

applying a reverse bias was investigated. An E -field of -200 V mm^{-1} was applied upon reentering the ferroelectric phase from 0 T to 10 T, and the pyrocurrent was measured upon warming at 10 T under zero bias. In this case, it was found that 73% of the initial polarisation was recovered in the direction of the initial poling E -field (green curve in Figure 5.5(b)). The strength of the polarisation memory against a reversed bias in persistent-field measurements is similar to that observed in the pulsed field measurements. In the third sample history (Figure 5.5(e)), the effect of warming into the SDW phase was investigated. After leaving the ferroelectric phase at 5 K, the system is warmed to 12 K at 0 T before cooling back to 5 K and increasing B to 10 T, all in the absence of external bias. In this case, upon reentering the ferroelectric phase, only a small net polarisation is recovered, at 11% of its initial value, indicating that the majority of the polarisation memory had been lost by warming out of the 4SL phase.

5.3.2 Persistent-field measurements under applied stress

To test the possibility that the memory affect is associated with the presence of magnetoelastic domain boundaries, measurements of the history dependence of the polarisation were repeated under applied uniaxial stress. Stress was applied to the sample at room temperature, resulting in a strain of $\epsilon = 2.9 \times 10^{-4}$, which corresponds to a pressure of approximately 110 MPa. In a study by Nakajima *et al.* [140], it was found that applying uniaxial pressure of 10 MPa along the $[1 \bar{1} 0]$ direction resulted in a volume fraction of 0.973 of the (110) domain. Furthermore, it is known that the magnetic ground state is stable up to pressures above 2 GPa [141]. Therefore it is expected that the uniaxial pressure of 110 MPa forms almost a complete magnetoelastic monodomain upon cooling through T_{N1} , without significantly affecting the magnetic phase diagram.

Firstly, the poling-field dependence of P under applied stress was characterised.

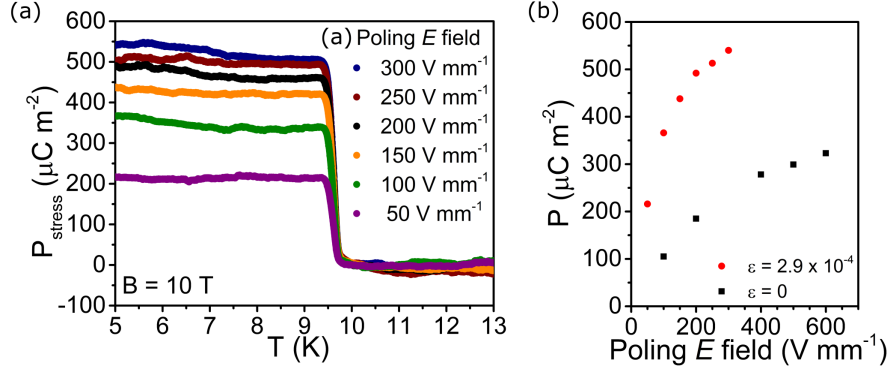


Figure 5.6: (a) Poling E -field dependence of the ferroelectric polarisation under applied uniaxial stress ($\sim 110 \text{ MPa}$ at room temperature). (b) Comparison of the measured polarisation under stress and in the absence of stress, for different poling E -fields. The increase in P under stress is consistent with the removal of the $(1\bar{2}0)$ and $(\bar{2}10)$ magnetoelastic domains, which increases the average component of P along the measurement direction as well as the E -field experienced along the distortion direction. Some strain enhancement of P may also be present, as seen in $\text{CuFe}_{1-x}\text{Ga}_x\text{O}_2$ [142].

Figure 5.6 shows the measured polarisation for a set of poling E -fields between 50 V mm^{-1} and 300 V mm^{-1} , alongside a comparison to the poling field dependence in the absence of strain. The poling field dependence shows similar behaviour to the case of no applied stress, with a large change in P at low poling E -fields and some saturation at higher E . A large increase is seen in the polarisation under applied stress compared to the unstrained sample, as expected for removal of the $(1\bar{2}0)$ and $(\bar{2}10)$ q -domains. Under stress, the whole crystal will distort along the $[1\ 1\ 0]$ direction, and therefore there will be a greater component of P along the measured $[1\ 1\ 0]$ direction. Furthermore, given the fact that the polarisation has a poling-field dependence, there will be a further increase in P at a given E as the whole crystal experiences E along the direction of P , whereas in the unstrained sample the component of E along the direction of P is reduced in the $(1\bar{2}0)$ and $(\bar{2}10)$ domains. In the case where the helical domain fraction is fully saturated, one would expect an increase in P of 50% due to the fact that the full component of P is along the

5.3. Experimental results

measurement direction. Taking $P_{\epsilon=0} = 325 \text{ V mm}^{-1}$ for the limiting polarisation of the unstrained sample, one would expect $P = 488 \text{ } \mu\text{C m}^{-2}$ for the strained sample. In fact, $P_{\epsilon} = 540 \text{ } \mu\text{C m}^{-2}$ is greater than this at 300 V mm^{-1} and still increasing with E . This increase by greater than 50% is likely due to the fact that the polarisation is not fully saturated in the unstrained sample, while it is also possible that the strain itself has enhanced the polarisation. In a study of $\text{CuFe}_{1-x}\text{Ga}_x\text{O}_2$ under strain [142], it was found that the application of $\sim 80 \text{ MPa}$ of pressure caused a further increase in P of $\sim 10\%$ that was not related to the volume fractions of ferroelectric domains. From the comparison of the bias dependence, we can conclude that almost a complete magnetoelastic monodomain has been formed by the application of stress. Additionally, for a poling E -field of 300 V mm^{-1} , the fact that P is starting to saturate implies that almost a complete ferroelectric monodomain has been formed.

Having established the existence of a predominantly magnetic monodomain, the history dependence was investigated, to see if the removal of magnetoelastic domain boundaries would reduce the memory effect. Figures 5.7(a) and (b) show the polarisation measured upon warming and as a fraction relative to the initial P state, for different magnetothermal histories as shown in Figure 5.7(c). In all measurements, the initial polarisation state is set at $540 \text{ } \mu\text{C m}^{-2}$ by cooling with a poling field of 300 V mm^{-1} at 10 T . After the poling field was removed and the contacts were short circuited for at least 10 minutes, the B field was reduced to 0 T . At 0 T , a thermal cycle was performed from 5 K to T_W to 5 K , where T_W is the maximum temperature reached during the thermal cycle. After the thermal cycle, the field was increased to 10 T and the pyrocurrent was measured upon warming out of the ferroelectric phase. A set of values of T_W of 10 K , 12 K and 15 K was chosen to compare the effect of remaining in the 4SL phase, and warming into the SDW phase and paramagnetic phase. This was also compared to the case when no

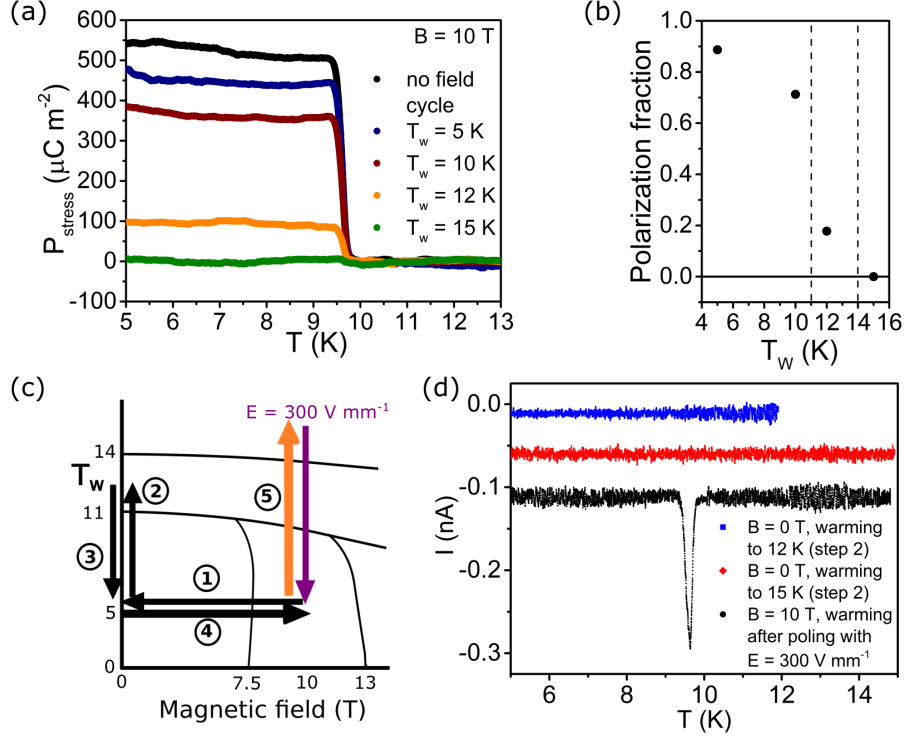


Figure 5.7: Characterisation of the polarisation memory effect under applied stress. (a), (b) The measured polarisation memory of the ferroelectric phase, for the magnetothermal history shown in (c). During each measurement, after the initial polarisation state had been set by poling upon cooling at 10 T, the system was warmed to one of a set of temperatures T_w at 0 T, before the polarisation was measured upon warming at 10 T. The polarisation fraction in (b) is the net polarisation recovered relative to the initial polarisation (black curve in (a)). Dashed lines indicate the magnetic transition temperatures. A large reduction in the polarisation memory is seen after warming into the SDW phase, and the memory is completely removed for warming into the paramagnetic phase. (d) The measured pyrocurrents upon warming during the thermal cycle at 0 T (each offset by -0.05 nA) showed no evidence of depolarisation at the magnetic phase boundaries or thermally stimulated currents. The pyrocurrent from the ferroelectric phase at 10 T is shown for comparison.

thermal cycle is performed ($T_w = 5 \text{ K}$). These measurements revealed that the strong polarisation memory effect is still present in the magnetoelastic monodomain sample. In the case where no thermal cycle is performed (blue curve), the net polarisation recovered 89% of its initial value. Performing a thermal cycle to $T_w = 10 \text{ K}$ reduced the polarisation memory somewhat, but the polarisation still recovered 71% of its initial value. However, a large reduction in the polarisation memory was

5.3. Experimental results

seen after warming out of the 4SL phase. For $T_W = 12$ K, the polarisation memory was reduced to 18% of its initial value and after warming to $T_W = 15$ K, the polarisation memory effect had been completely removed. The pyrocurrent from the sample was also measured during the warming cycle for $T_W = 12$ K, 15 K, as shown in Figure 5.7(d). No charge flow or depolarisation was observed upon warming, confirming that the memory is not due to any intrinsic polar nature of the 4SL phase or due to charge stored within the material. This set of measurements show that the polarisation memory effect is not related to the magnetoelastic domain composition, which is formed at $T_{N1} = 14$ K, but is strongly related to the magnetic state of the material. Furthermore, the only other in-plane domain walls that could become charged are obverse/reverse domain walls, however our samples contains only a small amount of these domains, as discussed in Section 5.2. Therefore this study rules out charging at structural domain walls as the cause of the polarisation memory effect.

5.3.3 Discussion

The characterisation of the polarisation memory effect presented here enables us to draw several conclusions about its origin. Primarily, the polarisation memory is not dependent on the magnetoelastic domain structure, as a strong polarisation memory is observed in both the strained and unstrained sample. In the strained sample, the enhanced polarisation under stress is strong evidence of the formation of almost a complete magnetoelastic monodomain, while for $E = 300 \text{ V mm}^{-1}$ the ferroelectric domain population is expected to be close to saturation in the direction of E . This is in contrast to the unstrained sample, where there are three magnetoelastic q -domains; under a poling field of $E = 200 \text{ V mm}^{-1}$ the polarisation is unsaturated, indicating a mixture of helical domains within each magnetoelastic domain. However in both cases the net polarisation recovered after a transition to the 4SL phase and returning

5.3. Experimental results

into the ferroelectric phase is $\sim 88\%$ of its initial value, even though the initial polarisation state is very different ($540 \mu\text{C m}^{-2}$ and $185 \mu\text{C m}^{-2}$). This fact suggests that the 4SL ground state is preserving the helical domain fractions of the FEIC phase. Additionally, the fact that the polarisation memory is greatly reduced after warming out of the 4SL phase to 12 K suggests that the polarisation memory is strongly correlated to the magnetic structure in the 4SL phase. The measurements on unstrained samples, in pulsed and persistent fields, also indicate that the polarisation state is fairly insensitive to further biasing, once the initial polarisation state has been set. Furthermore, the residual polarisation of the 4SL phase observed in pulsed field measurements has been shown to be an artefact of the pulsed field technique, and is not present in persistent field measurements.

As mentioned in the introduction to this chapter, the lower symmetry of the 4SL and 5SL phases relative to the paramagnetic phase is expected to cause antiferromagnetic domains to form. A possible explanation of the observed memory effect is that the 4SL and 5SL phases may be able to retain the helicity configuration of the ferroelectric phase through their magnetic domain configuration, in particular through Bloch-type magnetic domain walls. If the 4SL phase were able to retain regions of helical-spin structures, in the ratio of the helical domains of the FEIC phase, then these could act as nucleation centres upon reentering the FEIC phase to produce a ferroelectric phase with a memory of its previous helicity domain configuration. This scenario of helical domain walls will be considered in the following section through simulation of the magnetic domain wall structures of the 4SL and 5SL phases.

5.4 Simulation of magnetic domain wall spin structures in CuFeO₂

To investigate the magnetic spin structures of CuFeO₂, the minimum energy classical spin configurations were determined using a Monte Carlo method. Monte Carlo methods are a powerful technique for minimising an energy function that does not have a simple analytic form, or which depends on many variables such as the spin configuration of a lattice of spins. In the Monte Carlo algorithm used to calculate spin structures, a random change is made to the spin configuration at each iteration, and the difference in energy $\Delta E = E_{i+1} - E_i$ between the new and old configurations is calculated. The change in configuration is either accepted or rejected by comparing an exponential cost function $f = \exp(-\Delta E/T_{MC})$ to a randomly generated number p in the interval 0 to 1, where T_{MC} is the Monte Carlo ‘temperature’. The change is accepted if $f \geq p$, which always accepts a lower energy structure, and will sometimes accept a higher energy structure depending on the energy cost relative to p . This prevents trapping in local minima, provided a suitable T_{MC} is chosen. The process is iterated until convergence is reached. To enable convergence onto the global minimum, the method of simulated annealing was used. In this method, the Monte Carlo algorithm is repeated for a series of reducing T_{MC} , where the starting configuration for each instance of the algorithm is the final configuration of the previous calculation. This enables the algorithm to explore a large configurational space at high T_{MC} and gradually fall into the global energy minimum as T_{MC} is reduced.

To calculate the total energy due to the magnetic spin configuration, the three dimensional Hamiltonian and exchange constants determined by Nakajima *et al.* [143]

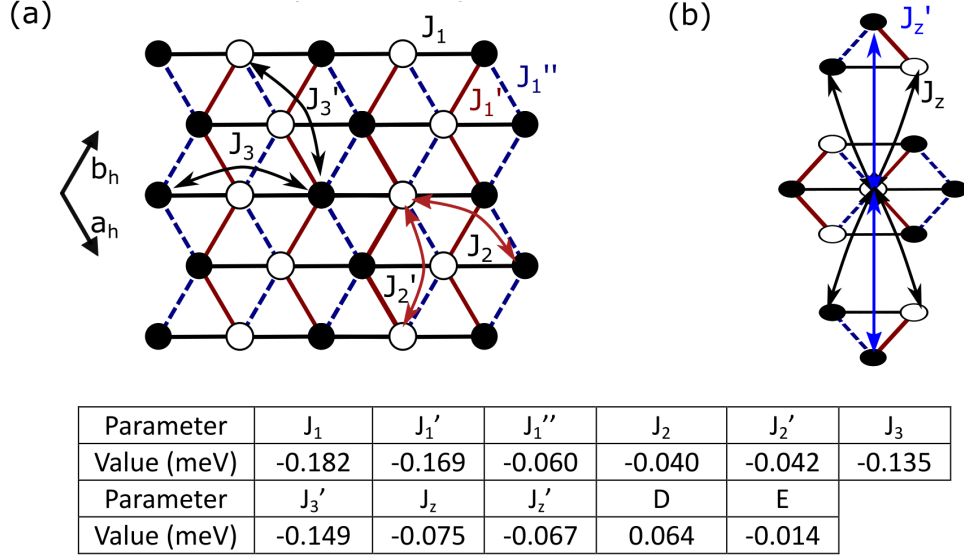


Figure 5.8: Exchange constants in the 4SL phase, as described by Nakajima *et al.* [143], within the hexagonal ab plane (a), and between planes (b). The exchange constants are split into two values, indicated by the primed and unprimed constants, due to the monoclinic distortion at T_{N1} . Furthermore, the effect of a distortion at T_{N2} further splits J_1' into J_1' and J_1'' . The values given in the table are the exchange constants and anisotropy terms determined by Nakajima *et al.* [143].

were used. The form of the Hamiltonian is:

$$\begin{aligned}
 \mathcal{H} = & -\frac{1}{2} \sum_{i,j} J_1 S_i \cdot S_j - \frac{1}{2} \sum_{i,j} J_2 S_i \cdot S_j - \frac{1}{2} \sum_{i,j} J_3 S_i \cdot S_j \\
 & - \frac{1}{2} \sum_{i,j} J_z S_i \cdot S_j - \sum_i D(S_i^z)^2 - \sum_i E\{(S_i^x)^2 - (S_i^y)^2\}
 \end{aligned} \tag{5.1}$$

A diagram of the exchange couplings between the Fe^{3+} atoms is shown in Figure 5.8, alongside a table of the exchange constants determined in Ref. [143]. The J_1 term in the Hamiltonian is the in-plane exchange coupling between nearest neighbours, while the J_2 and J_3 terms are the next nearest neighbour interactions. J_z is the exchange interaction between neighbouring planes of atoms, while the D and E terms are the z axis and in-plane anisotropy terms.

In their study of spin-wave spectra in the 4SL phase, Nakajima *et al.* [143]

determined that it was necessary to include the effects of the monoclinic distortion at T_{N1} and a ‘scalene triangle’ distortion at T_{N2} in order to fully describe the spin wave spectrum. The effect of the monoclinic distortion is to split each exchange interaction into two values, which are indicated by primed and unprimed exchange constants (I shall refer to this as the isosceles triangle (IT) distortion). Furthermore a splitting of the J'_1 constant into two values, J'_1 and J''_1 , was necessary to account for the effect of the scalene triangle distortion at T_{N2} [143].

5.4.1 Domain wall structures in the 4SL phase

Given that the magnetic unit cell in the ab plane is four times the primitive unit cell, the 4SL magnetic structure can nucleate on one of four sites, creating the possibility for four magnetic phase domains relative to the parent hexagonal structure. This will create magnetic domain walls at the interface of the phase domains, with relative phases of either $\pi/2$, π or $3\pi/2$ between adjacent domains. Due to the bond ordering that is associated with the magnetic order, phase differences of $\pi/2$ or $3\pi/2$ imply a break in the bond ordering, whereas for domains separated by a phase difference of π , the bond order will be maintained across the domain boundary. As such, to calculate the magnetic domain wall structures for a π phase domain boundary, the ordering on the bond lattice shown in Figure 5.9(a) is considered, whereas for $\pi/2$ or $3\pi/2$, a structural domain boundary is introduced, as shown in Figure 5.9(b). The two structural domains on either side of the boundary are the domains that are formed due to the loss of C centering upon cooling through T_{N2} ($C2/m \rightarrow P2/c$), while the π phase boundary is the boundary between translation domains within each $P2/c$ domain due to the magnetic ordering having double the periodicity of the primitive $P2/c$ cell.

To simulate the domain boundary, the outermost spins on the bond lattices were fixed to give the desired phase differences between domains. The central N spins were

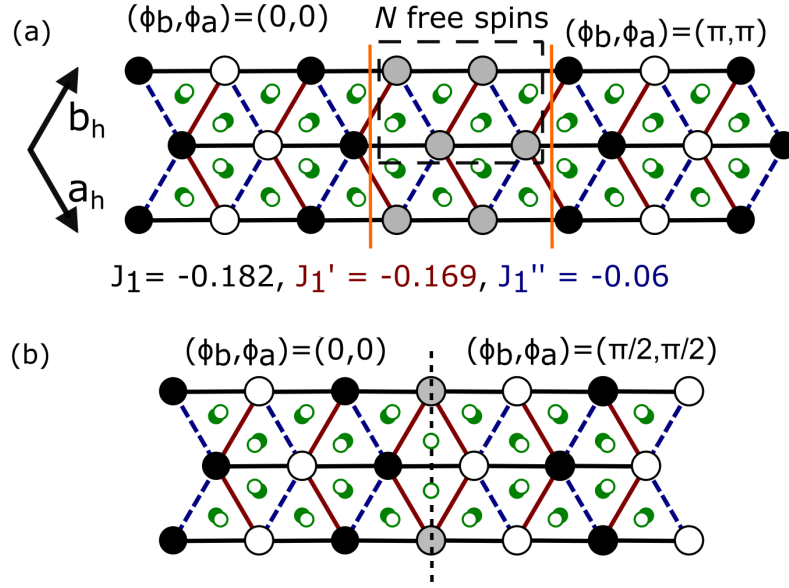


Figure 5.9: (a) Model bond lattice used to describe antiferromagnetic phase domains with phase shift of π . Black and white circles represent the Fe^{3+} spins (black = $\downarrow$, white = $\uparrow$). Open green circles indicate the oxygen positions which are displaced from their high temperature positions (filled circles). The outermost spins were fixed to impose the phase difference, and the central N spins (grey) were relaxed from random initial orientations. Periodicity was imposed along the $[1 \bar{1} 0]$ direction. (b) Phase boundaries of $\pi/2$ and $3\pi/2$ imply a break in the bond order. To model this, a structural boundary is introduced (dashed line), where the bond order is reversed.

relaxed from a random initial configuration, and periodicity was imposed in the $[1 \bar{1} 0]$ direction, to match the periodicity of the 4SL phase. The classical minimum energy configurations for the three different domain types were determined using a simulated-annealing Monte Carlo method. The algorithm was iterated until energy convergence was reached and was repeated to check for consistent results. The minimum energy spin configurations for the three domain wall types are shown in Figure 5.10. N was varied from 2 to 24, to determine the point at which allowing further spins to relax does not lower the total energy. For the π phase domain walls, the energy cost was found to be lowest for $N \geq 12$, with a total domain wall cost of 1.49 meV relative to the energy of the 4SL structure of an equivalent number of spins. As can be seen in Figure 5.10, the spins were found to form a helix, with the spins rotating about the

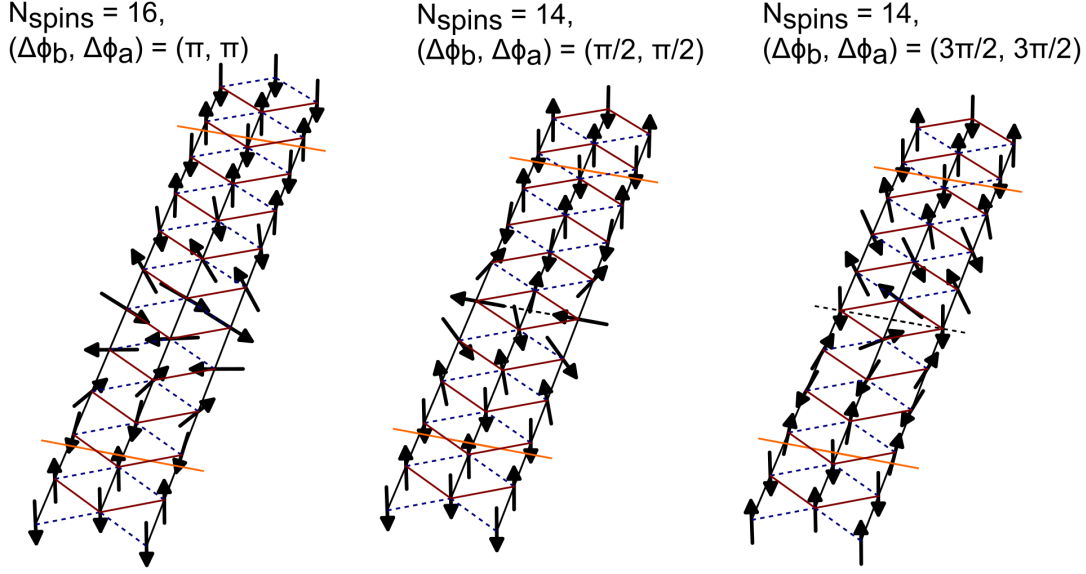


Figure 5.10: Minimum energy spin configurations for the three types of domain walls of the 4SL phase, calculated by a Monte Carlo method. One layer of spins is shown, alternate layers stacked along c are related by a 180° spin rotation. The domain wall with a phase difference of π was found to contain a full helical rotation of the spins, with $q \sim 0.21$, which closely resembles the spin structure of the FEIC phase. Domain walls for phase differences of $\pi/2$ and $3\pi/2$ were found to contain a helix on one row of spins along the $[1\ 1\ 0]$ direction and antiferromagnetic order on the other. Therefore, the handedness of the ferroelectric phase can be retained within all the 4SL domain walls.

monoclinic b axis with $q \sim 0.21\ b_m^*$. This structure closely resembles the spin structure of the ferroelectric phase. For the $\pi/2$ and $3\pi/2$ domain walls, the lowest energy spin configurations also had a helical nature with one row of spins forming a helix, and the other row ordering predominantly antiferromagnetically, but with some canting away from the c axis. The total energy costs for the domain walls were 1.55 meV and 2.65 meV for the $\pi/2$ and $3\pi/2$ domain walls, for $N \geq 12$ and $N \geq 14$ in each case. Importantly, each type of domain wall has a definite helicity and there is an equal energy cost for structures with opposite helicities for a given phase boundary.

These simulations reveal that helical spin structures can form as the natural domain wall structures between antiferromagnetic domains in the 4SL phase. The

energy cost of these domain walls, at ~ 0.13 meV per spin, is low compared to the thermal energy $\sim k_B T = 0.43$ meV at 5 K. As such, there is not a large energy penalty that would hinder the formation of antiferromagnetic domains. These calculations therefore give the following model to describe the memory effect. During the phase transition from the FEIC to 4SL phase, as the 4SL domains nucleate and grow, the domain wall spin structures will retain the helicity of the ferroelectric phase from which they grew. The volume ratio of left to right handed domain walls is expected to be similar to the ratio of left to right handed helicity domains of the ferroelectric phase. Upon reentering the ferroelectric phase, the domain walls will act as nucleation centres for the ferroelectric phase, creating a ferroelectric helicity domain configuration similar to the initial configuration, giving a net polarisation in the absence of any external biasing.

5.4.2 Domain wall structures in the 5SL phase

The domain wall spin structures of the 5SL phase were also investigated. In a study of spin-wave spectra of the 5SL phase, Nakajima *et al.* [131] determined a spin-driven bond ordering, which causes the J_1 parameter to split into four values, creating a bond lattice comprised of five monoclinic unit cells. The unit cell of this bond ordering is indicated in Figure 5.11(a). As the magnetic unit cell is five times the primitive monoclinic cell, five different antiferromagnetic phase domains can form, creating domain walls between domains with relative phase shifts of $2\pi/5$, $4\pi/5$, $6\pi/5$ and $8\pi/5$. In each case, this will cause a discontinuity in the bond ordering at the phase boundary. This creates a challenge for modelling the spin structure of the domain wall, as the J coupling constants and the spin ordering are directly related, giving uncertainty over which J parameters should be used in the domain wall. This is less of an issue for the 4SL walls, as the helical ordering should only give a slight modification to the J values of the 4SL bond lattice: a study on the FEIC phase of

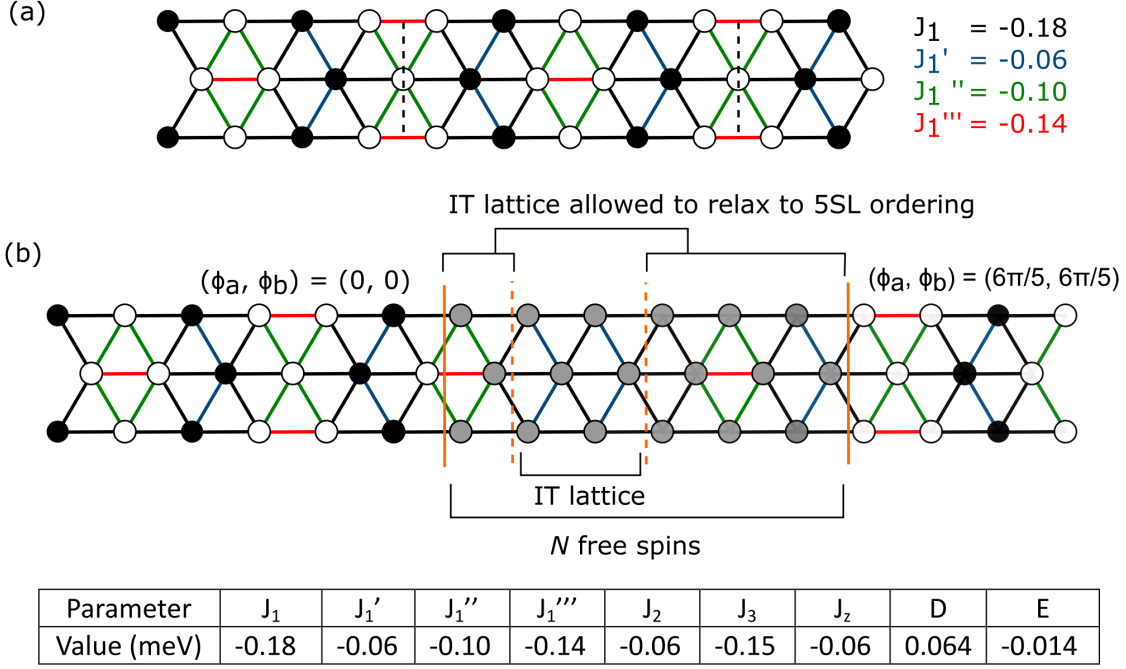


Figure 5.11: (a) Bond ordering of the 5SL phase, as determined in Ref. [131]. Magnetoelastic coupling causes J_1 to split into four values, giving a unit cell of five primitive monoclinic cells (indicated as the region between the dashed lines, black = $\downarrow$, white = $\uparrow$). (b) Bond model used to simulate domain walls of the 5SL phase. To account for the bond mismatch across the domain wall, a central region of the isosceles triangle (IT) lattice was considered between extended regions of the 5SL lattices. The minimum energy spin configuration was calculated for all possible lengths of the IT lattice (up to 10 primitive monoclinic unit cells), and the bond arrangement giving the lowest energy magnetic structure was determined as the domain wall structure. The table shows the exchange parameters used in the simulations, which were determined in Ref. [131].

$\text{CuFe}_{1-x}\text{Ga}_x\text{O}_2$ determined similar J parameters to the 4SL phase, particularly for the J_1 and J_1' parameters [144].

As a simple approximation I shall assume the isosceles triangle J model for the region of the domain wall where the spins deviate from the 5SL structures. The isosceles triangle model consists of only J_1 and J_1' , which describes the exchange parameters a monoclinic unit cell in the absence of further spin-lattice distortions. Given that the domain wall width is initially unknown, all possible lengths of isosceles triangle bond ordering between extended regions of the 5SL bond ordering

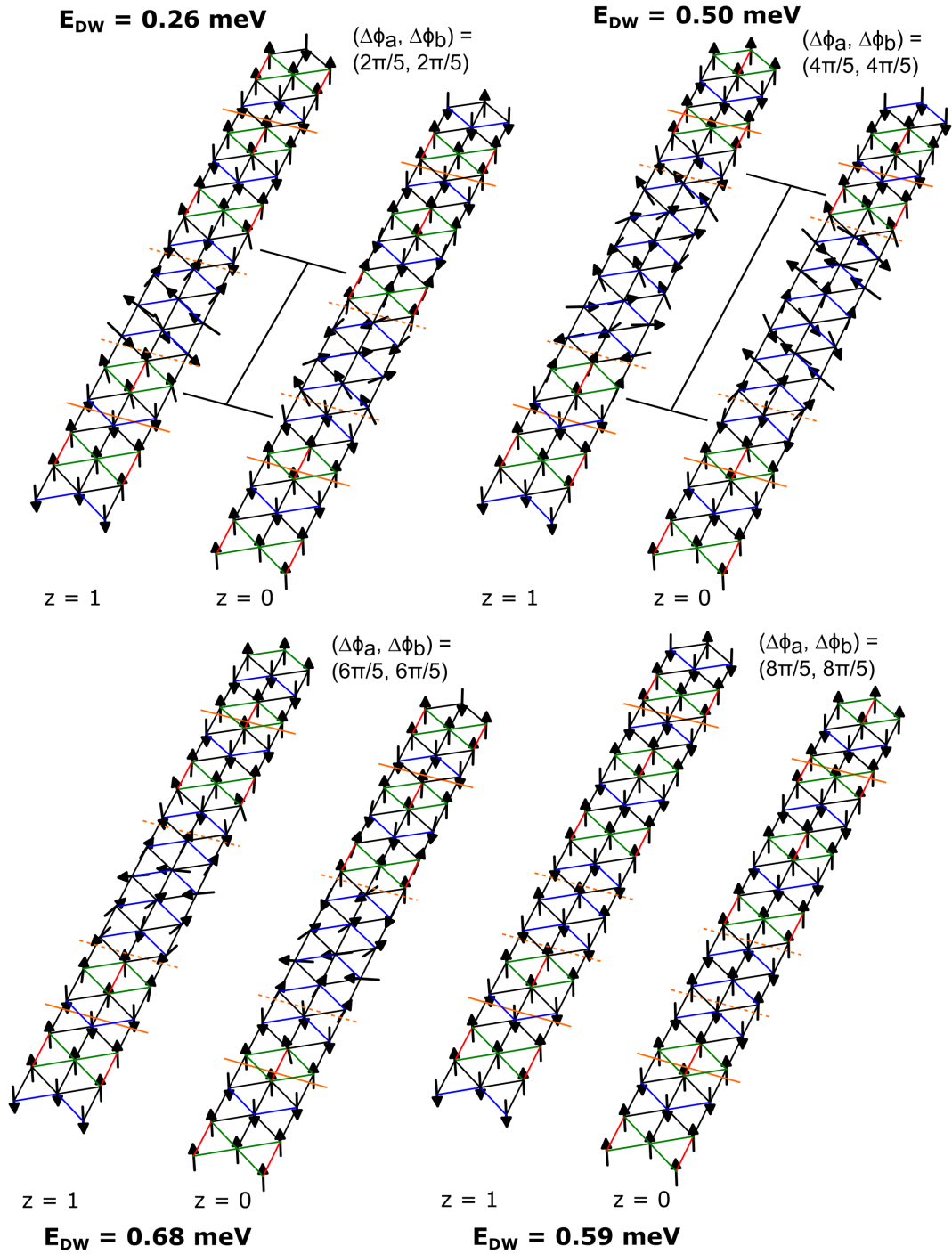


Figure 5.12: Domain wall structures for phase domain walls of the 5SL phase calculated with $B_z = 15$ T, shown for alternate layers stacked along c ($z = 0, 1$). For phase differences of $2\pi/5$ and $4\pi/5$, a helical spin arrangement is seen (indicated on the plot), albeit with canting along the $+c$ direction due to the effect of B . For phase differences of $6\pi/5$ and $8\pi/5$, antiferromagnetic arrangements are obtained. Therefore not all domain wall structures can retain the helicity of the FEIC phase.

were considered, as shown in Figure 5.11(b). The minimum energy magnetic spin configurations were calculated for these bond configurations, and the lowest energy spin configuration out of all possible bond orderings was taken as the domain wall that would form to minimise the total energy of the system. For each calculation, 20 spins in each ab layer were allowed to relax from random initial orientations. Again, periodicity was imposed in the $[1 \bar{1} 0]$ direction and a Zeeman term with $B_z = 15.0 \text{ T}$ was also included in the Hamiltonian. The exchange parameters determined in the literature were used [131], which did not include splitting of the next nearest neighbour or inter-layer coupling terms.

The calculated minimum energy spin configurations are shown for the four types of phase boundaries in Figure 5.12. Due to the existence of the Zeeman term, alternate layers stacked along the c axis are no longer related by a 180° spin rotation, and the spins are canted towards the $+c$ direction in both layers. The calculated domain walls are distinct from those of the 4SL phase. For the $2\pi/5$ and $4\pi/5$ domain walls, the spin structure can be considered to have some degree of helicity, with canting towards $+c$ due to the applied B field. However, for the $6\pi/5$ and $8\pi/5$ domain walls, the spin ordering is similar to the 4SL antiferromagnetic ordering, rather than helical, with canting towards the $+c$ direction. The energies of the lowest energy domain walls for each phase boundary were 0.260 meV , 0.496 meV , 0.678 meV and 0.588 meV , consisting of 6, 12, 8 and 4 spins in each plane respectively. The results of the simulation can be understood physically in light of the energies of the different magnetic structures discussed in the following section.

Therefore in the 5SL phase, only some of the domain walls have the potential to retain the helicity configuration of the FEIC phase. Furthermore, the canting induced by the applied B field may further distort the spin structure at higher B fields, causing a loss of information on the helicity. It is also unclear how, or if, the $6\pi/5$ and $8\pi/5$ domain walls would act as nucleation centres for the FEIC phase. These

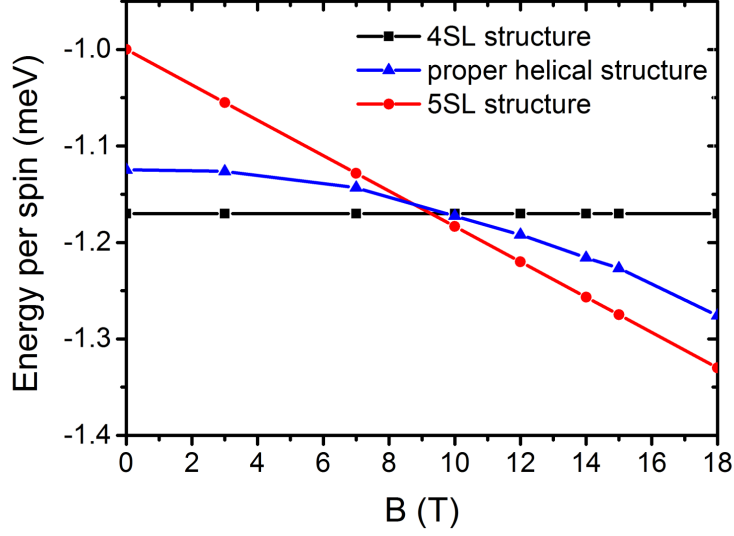


Figure 5.13: Calculation of energy of spin structures as a function of magnetic field. The energy of the proper helix structure was calculated on the 4SL bond lattice by initialising the Monte Carlo algorithm with a helical spin structure and using a low T_{MC} to avoid relaxation into the 4SL structure.

simulations therefore account for the fact that the polarisation memory is reduced, but still present, for histories involving the 5SL phase in pulsed-field measurements.

5.4.3 B-field dependence of spin structures

To check the validity of the bond models used to describe the 4SL and 5SL phases, the minimum energy structures of a single bond-lattice domain were calculated. As expected, the $\uparrow\uparrow\downarrow\downarrow$ magnetic structure was found to be the lowest energy structure at 0 T for the 4SL lattice model used. For the 5SL lattice model, the $\uparrow\uparrow\uparrow\downarrow\downarrow$ was found to be the lowest energy structure at 0 T. Figure 5.13 shows the calculated B -field dependence of the energy of these fixed structures. The Zeeman term reduces the energy of the 5SL phase for increasing field, while the energy of the 4SL phase is constant in B , giving a crossover at 9.3 T. The energy of a proper helix structure on the 4SL bond lattice was also calculated, by starting the Monte Carlo algorithm with an initial helical structure and using a low value of T_{MC} , to stop the algorithm

converging to the global minimum energy 4SL structure. The 4SL bond lattice should give a good approximation to the J parameters as a study on the FEIC phase of $\text{CuFe}_{1-x}\text{Ga}_x\text{O}_2$ determined similar J parameters to the 4SL phase, particularly for the J_1 and J'_1 parameters [144]. At 0 T the helical structure has an energy between the 4SL and 5SL structures and the helical structure is able to cant along the c direction to reduce the Zeeman energy for increasing B . This leads to a crossover at between the 4SL structure and helical structure at 9.7 T, slightly higher than the actual transition. Furthermore, this meant that the helical structure was not the lowest energy structure out of the three structures at any B -field.

In reality, there is likely to be some spin-lattice distortion that accompanies the helical structure to reduce the overall exchange energy relative to the 4SL phase. Additionally, the elastic energy of the lattices are not considered, which will also change the relative total energies of each magnetic phase. For example, reducing the energy of the helical structure by $\sim 0.03 \text{ meV}$ per spin would give a 4SL to FEIC transition at $\sim 7 \text{ T}$ and a transition from the FEIC to 5SL phase at $\sim 12 \text{ T}$ in close agreement to the actual transitions in CuFeO_2 . Overall, the bond models used correctly describe the helical structure as having a higher energy than the 4SL phase at 0 T, and as having an energy between the 5SL and 4SL phases at 15 T. As such, in the domain wall simulations, there is no inherent unphysical instability towards a helical structure. Additionally the B -field dependencies display the correct physical trends and so the models should give a good description of the physical system.

This calculation of the relative energies in applied field can help give a physical understanding of the domain wall structures of the 5SL phase. Within the domain wall, the Zeeman term in the Hamiltonian favours large extensions of the 5SL bond lattice, with helical ordering between 5SL phase domains. This is indeed found for the $2\pi/5$ domain wall, which was the lowest energy domain wall structure. However, depending on the phase difference, it may not be possible for a short helix to form

inbetween large extensions of the 5SL phase. In this case there will be competition between two types of structures. The first type will have long extensions of the 5SL lattices plus a short 4SL-type ordering inbetween, as found for the $6\pi/5$ and $8\pi/5$ domain walls. The second type will have a larger 4SL lattice that can accommodate a longer helix, and shorter extensions of the 5SL lattices, as found for the $4\pi/5$ domain wall.

5.4.4 Discussion

The simulations of the domain wall structures lead to the following scenario to explain the memory effect. During the FEIC to 4SL phase transition, the helical domains of the FEIC phase shrink between expanding 4SL domains and define the helicity of the 4SL domain walls, all of which have a definite helicity. When reentering the ferroelectric phase, these act as nucleation centers, causing the growth of the FEIC phase with a similar volume fraction of helical domains to previously. During the FEIC to 5SL transition, some domain walls are forced into antiferromagnetic spin arrangements as the FEIC phase shrinks between 5SL domains. This causes the domain walls to lose information on the spin helicity of the FEIC phase, while other domain walls maintain a helical ordering, at least at low fields. Upon reentering the FEIC phase, particularly under bias, only some FEIC domains will nucleate from the helical domain walls, reducing the polarisation memory fraction.

The domain wall model can also explain the history dependences seen in the literature [118]. If there is an initial cooling into the 4SL phase in zero B and E field, then an equal proportion of left and right handed domain walls would form, hindering the formation of a ferroelectric helical monodomain upon application of B -field. The presence of helical domain walls would also explain why the polarisation memory is not particularly sensitive to a reverse bias, as these walls would have a high energy barrier to flip the handedness of rotation, and do not give rise to a bulk polarisation

that could couple to the applied E -field. Upon warming out of the 4SL phase into the SDW phase, the domain structure will undergo a large rearrangement, explaining the large drop in polarisation memory for histories involving warming into the SDW phase at 0 T. In measurements of the polarisation memory, no memory was observed after warming into the SDW phase at 10 T, and therefore the small memory observed for $T_W = 12$ K may be due to some phase coexistence of the 4SL and SDW phase.

The model proposed here is similar to the concept of nanoregions proposed to explain similar memory effects in CuO [122] and MnWO₄ [123]. However, in the model proposed here, the helical domain walls are the lowest energy state of the system in the presence of antiferromagnetic domains of a single magnetic phase, as opposed to being small metastable regions of a ferroelectric phase embedded within collinear order.

5.5 Conclusion

The results presented in this chapter have characterised a strong polarisation memory effect in the multiferroic phase of CuFeO₂. The polarisation memory is insensitive to the magnetoelastic domain composition, is resistant to reverse electrical bias and is strongly correlated to the 4SL magnetic ground state. Through simulations of the domain wall spins structures, I have shown that the lowest energy domain wall structures in the magnetic ground state are helical, which can be considered as the antiferromagnetic analogy of a Bloch domain wall. I propose that these domain walls can retain information on the helicity configuration of the ferroelectric phase and act to nucleate a ferroelectric phase with similar helicity configuration upon increasing B -field. Only some of the domain walls structures of the higher-field 5SL phase are helical, explaining the reduction in polarisation memory for histories involving the 5SL phase. More generally, given that similar memory effects are also reported for

CuO [122] and MnWO_4 [123], these polarisation memory effects caused by helical or cycloidal domain walls may be a universal feature of ferroelectric-incommensurate to collinear-antiferromagnetic transitions. Further calculations of domain wall spin structures in these antiferromagnets would be interesting to test these ideas. In theory, the fact that information about the ferroelectric state can be contained in domain walls of another magnetic phase could be used to extend the range of magnetoelectric coupling in multiferroic materials, offering additional routes for functional behaviour.

Chapter 6

Conclusions

In this thesis, I have set out to answer a number of questions regarding the structural and electrical details of the lead halide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ and to further investigate polarisation memory effects in the multiferroic material CuFeO_2 .

Regarding the origin of the current-voltage hysteresis observed in perovskite solar cells, I have clearly shown that ferroelectricity does not occur in the tetragonal phase of $\text{CH}_3\text{NH}_3\text{PbI}_3$ at room temperature, and therefore cannot be considered as a potential origin of current-voltage hysteresis. By separating out the hysteretic and non-hysteretic response using the double wave method, it was shown that the magnitude of the hysteretic charge density is linear in $1/f$ for $4\text{ Hz} < f < 150\text{ Hz}$, indicating a conductive origin. Furthermore, giant values were obtained for $f < 1\text{ Hz}$, while no evidence was seen for a ferroelectric response above the conductive contribution. This is in agreement with the structural characterisation by X-ray diffraction and neutron scattering. X-ray diffraction measurements gave no indication of a polar distortion of the Pb-I lattice, with the $I4/mcm$ structure giving the best agreement with the data. Furthermore, quasielastic neutron scattering on partially detwinned crystals revealed isotropic scattering at both low and high neutron energy transfers and molecular reorientation on a timescale

between 8 ps and 80 ps, clearly ruling out any kind of ordering of the CH_3NH_3 molecule down to 175 K in the tetragonal phase.

Instead, frequency- and temperature-dependent measurements on $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$ crystals revealed dispersive conduction at frequencies between 10 Hz and 100 kHz and thermally activated hopping conduction indicative of ionic conduction. Low activation energies of 0.305(3) eV and 0.260(6) eV were determined for $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$, which are very similar to the activated halide vacancy conduction known to occur in other lead-halides compounds. The low activation energies mean that ionic conduction will affect the charge transport properties of perovskite solar cells on a timescale on the order of 0.1 s to 1 s under working conditions. This correlates well to the linear $1/f$ dependence and subsequent saturation observed in the hysteresis loop measurements and therefore these results present strong evidence for ionic migration as the underlying cause of the current-voltage hysteresis in perovskite solar cells. By considering the magnitude of hysteretic charge observed, it is clear that the effect of ionic vacancy migration must also cause a modification of the electrical properties of perovskite films, which is the main contribution to current-voltage hysteresis. This can be understood in terms of electronic band bending, where the existence of an ionic space charge density affects the electron band energies, modifying the electronic extraction efficiencies at the electrodes.

These measurements reveal the fascinating physics of the organic-inorganic semiconductor $\text{CH}_3\text{NH}_3\text{PbI}_3$. The CH_3NH_3 molecular dipole undergoes rapid reorientations between many orientations which are within the range of the thermal energy of the molecule throughout the cubic and tetragonal phase. Temperature-dependent dielectric measurements reveal that this reorientational motion freezes in the orthorhombic phase below 162 K, however quasielastic neutron scattering still suggests dynamic behaviour of the threefold axial rotations that may

be coupled to translational motion on a length scale of 1 Å. Given the large motions of the CH₃NH₃ molecules and their bonding to the I atoms, it is likely that the I atoms also undergo significant distortions from their equilibrium positions; this is supported by the large anisotropic thermal parameters determined by X-ray diffraction. With significant thermal motion of the ionic constituents, it is perhaps not surprising that vacancy conduction occurs with a low activation energy, which may be assisted by the rapidly changing energy landscape as the CH₃NH₃ molecules reorient.

Understanding the structural and electrical details of CH₃NH₃PbI₃ has clear implications for the development of functional photovoltaic devices. If it is necessary to reduce halide vacancy conduction for long-term device stability, then careful management of the growth process may be necessary to reduce defect concentrations, as the low activation energies mean that vacancy migration will always occur if possible under working conditions. Furthermore, the freely rotating nature of the CH₃NH₃ molecule must be taken into account and a non-ferroelectric structure used when performing *ab initio* simulations in order to obtain physically meaningful results and guide future materials design.

Regarding the nature of polarisation memory effects in CuFeO₂, I have characterised the nature of a strong polarisation memory of the multiferroic phase by performing a detailed investigation of the magnetic history-dependence of polarisation. Through measurements under applied stress, I have shown that the memory is not related to the presence of magnetoelastic *q*-domains, but is greatly reduced when warming out of the magnetic ground state. To further consider its origin, I simulated the magnetic structures of magnetic domain walls in the ground state using Monte Carlo methods and known exchange parameters. This revealed Bloch-type antiferromagnetic domain walls with a helical nature closely resembling the multiferroic phase. This gives an explanation for the observed memory effect,

whereby the helical domain configuration of the multiferroic phase is retained within the domain wall spin structures, which act as nucleation sites upon re-entering the multiferroic phase enabling almost a full recovery of the previous helical domain configuration. Similar calculations for the higher-field $q = (1/5, 1/5, 3/2)$ phase reveal that helical domain walls only occur for some phase domain walls, consistent with a weaker memory effect in the higher field phase previously observed in pulsed-field measurements.

The proposed mechanism for polarisation memory effects may be applicable in general to other multiferroic materials, particularly those with antiferromagnetic to incommensurate-multiferroic phase transitions that are known to display similar memory effects such as CuO and MnWO₄. It would certainly be interesting to simulate spin structures for magnetic domain boundaries in these materials, to see if similar domain structures to the multiferroic phases are predicted. Of course, in the vicinity of a phase transition both phases are very similar in energy, therefore the presence of the magnetic structure of one phase as the domain walls of the other is one possibility for a low energy domain wall configuration. The fact that information about the ferroelectric state can be retained within a non-ferroelectric phase reveals the importance of domain walls in the physics of multiferroics, while the extended range of magnetoelectric coupling could offer additional routes for functional behaviour in multiferroic devices.

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