Multiferroic materials, in which ferroelectricity and magnetic order coexist, are attracting conspicuous interest as candidates for novel applications in digital storage devices [11]. The requirement of having a strong magnetoelectric effect has focussed the research on compounds in which ferroelectricity appears as a consequence of magnetic ordering (so called ‘type-II multiferroics’), leading to the realisation that cycloidal multiferroics, such as TbMnO$_3$ [2] and Ni$_3$V$_2$O$_8$ [3], exhibit an exceptionally strong cross-coupling between the different types of order. In these compounds the atomic spins $S_i$ rotate within a plane that contains the propagation direction of the incommensurate modulation $\hat{r}_{i,i+1}$ which connects neighbouring atoms $S_i$ and $S_{i+1}$.

A phenomenological theory based on symmetry analysis of the magnetic and ferroelectric order parameters established that the magnetoelectric coupling has a trilinear form $\mathbf{P} \cdot (\mathbf{M} \cdot \nabla \mathbf{M}) - (\mathbf{M} \cdot \nabla \mathbf{M})$ in the free energy [3], leading to a polarisation given by $P \propto \hat{r}_{i,i+1} \times (S_i \times S_{i+1})$ [5]. A number of microscopic theories have been proposed that respect these symmetry constraints for the canonical multiferroic materials [6, 7].

An intense experimental effort and a refined understanding of the symmetry requirements for spin-driven ferroelectricity have expanded the range of candidate multiferroic materials. An interesting line of research has developed specifically on magnetochiral or proper-screw systems, in which the atomic spins rotate perpendicularly to the propagation direction of the screw [8]; the model in ref. 5 predicts no polarisation in this case. One mechanism that can lead to electrical polarisation in a proper-screw magnetic structure is the coupling to structural axiality (ferroaxial coupling) [9]. A crystal structure can be considered ‘axial’ if there exists a structural distortion that is unchanged by inversion and makes the two senses of rotation (clockwise or counterclockwise) about an axial vector $\mathbf{A}$ distinguishable. As pointed out in ref. 9 the magnetic helicity $\sigma$ can be coupled phenomenologically to the electric polarisation $\mathbf{P}$ and structural axiality $\mathbf{A}$ to create a trilinear form, $\sigma \mathbf{A} \cdot \mathbf{P}$, which is invariant under spacial inversion and time reversal. Very recently, “giant” magnetically-induced ferroelectricity has been reported in the ferroaxial system CaMn$_2$O$_{12}$ [10].

RbFe(MoO$_4$)$_2$ (RFMO, ferroaxial below 190 K) is an extremely interesting system to test the interplay between ferroaxiality, magnetism and ferroelectricity. Below $T_N \approx 4$ K, it orders magnetically in a complex structure that possesses both helicity and triangular chirality (see below), becoming ferroelectric at the same temperature [11]. Yet, its layered crystal structure and exchange pathways are sufficiently simple for it to be considered the “hydrogen atom” of ferroaxial multiferroics. In previous work, it has been suggested that the 120$^\circ$ magnetic structure in each layer is in itself sufficient to break inversion [11, 12]. Here, we demonstrate that the axiality and magnetic helicity also play a crucial role in the onset of ferroelectricity. We show that the helicity and triangular chirality are in fact coupled together in the free energy by the axial distortion, and we present data that show switching of both parameters simultaneously with an applied electric field.

RFMO undergoes a structural transition at $T_c = 190$ K in which the MoO$_4$ tetrahedra rotate (Fig. 1), lowering the symmetry from $P3m1$ to $P3$ (ferroaxial point group 3) [13, 14]. Below $T_N$ the Fe spins (one per unit cell) order magnetically in the $ab$ plane in a 120$^\circ$ structure, and rotate in a helix between one plane and the next with an incommensurate propagation along $c^*$ ($q_z \approx 0.44$, here always chosen to be positive). Fig. 1(a) shows a unit cell of RFMO with the location of the MoO$_4$ tetrahedra indicated (oxygen atoms mediate the relevant exchange paths — see below). One can see that there is a MoO$_4$ tetrahedron above (or below) each magnetic triangle. We define triangles as “positive” (“negative”) if...
the symmetric-exchange energy per Fe ion is

\[ E = E_0 + (\sqrt{3}/2)\sigma_a\sigma_b(J_a - J_b)S^2\sin(2\pi q_z) \]  

where \( E_0 = -3J_1S^2/2 + (J_2 - J_a/2 - J_b/2)S^2\cos(2\pi q_z) \) doesn’t depend on the magnetic chiralities. Minimising with respect to \( q_z \) results in

\[ \tan(2\pi q_z) = \sqrt{3}\sigma_1\sigma_b(J_a - J_b)/(2J_2 - |J_a + J_b|). \]

We arrive here at our first important result: in the presence of a ferroaxial crystal structure, adjacent 120° triangular magnetic planes will rotate with respect to each other, forming a helix, without the need for antisymmetric or inter planar next-nearest neighbour interactions. In a real crystal, both ferroaxial domains will be present with roughly equal populations (one with \( J_a > J_b \), the other with \( J_b > J_a \)). Therefore, the lowest energy magnetic configurations will depend on the ‘axiality’ of the domain in question. Notating the chiralities of a particular magnetic structure as \( (\pm, \pm) \), \( (\pm, \mp) \) (as for \( J_a > J_b \), or vice versa for \( J_b > J_a \)). One important consequence is that each of the two structural axial domains will order with a distinct magnetic propagation vector, say \( q_1 \) for positive axiality and \( q_2 \) for negative axiality (the exact combination depends on the sign of the magneto-elastic interaction). Therefore, each set of distinct magnetic peaks \( (q_1 \) or \( q_2 \) peaks) probes a single axial domain.

Spherical neutron polarimetry is an ideal technique to study these magnetic structures and their relationship with the electrical polarisation, since it has the ability to distinguish domains with different chiralities. In the present case the magnetic peaks do not overlap with the nuclear peaks in reciprocal space, so it is possible to calculate the polarisation of the scattered beam purely from the magnetic structure factor \( M \). For this we work in the Blume reference frame, in which the \( X \)-axis is along the scattering vector \( Q \), the \( Z \)-axis is vertical, and the \( Y \)-axis completes the right-handed set (see inset to Fig. 2). Magnetic neutron diffraction is only sensitive to the component of \( M \) perpendicular to \( Q \), which we write \( M_{\perp} \) \((0,M_{\perp X},M_{\perp Z})\). For a structure with one magnetic ion per unit cell, the 1th moment (in the unit cell of the lattice vector \( R_i \)) is given by \( \mu_i = \mu_0(\hat{u} \mp i\hat{v})\exp(\mathbf{q}_i \cdot \mathbf{R}_i) + \text{c.c.} \). For \( (+,+) \) or \((-,+)\) structures; and is given by \( \mu_i = \mu_0(\hat{u} \pm i\hat{v})\exp(\mathbf{q}_i \cdot \mathbf{R}_i) + \text{c.c.} \) for \((+,+)\) or \((-,+)\), where \( \mathbf{u} \) and \( \mathbf{v} \) are orthogonal unit vectors in the plane of the spins. Thus the magnetic structure factor \( M(Q) = P^\text{mag}(Q)(\hat{u} \pm i\hat{v}) \) where \( p \) is a constant, \( f^\text{mag} \) is the magnetic form factor, and the \( \pm \) is determined by the magnetic chiralities (see table I). Given a fully polarised incident beam directed along \( i \), the polarisation measured along \( j \) is written \( P_{ij} \) \((i,j = X,Y,Z)\). For our geometry, the equations reduce

\[ P_{ij} = P_{ji} = \begin{cases} 0 & \text{if} \quad i = j \text{ or } i = j \pm 2 \text{ (mod 3)}, \\ \frac{1}{2}(\hat{u} \mp i\hat{v}) & \text{if} \quad i = j \pm 1 \text{ (mod 3)} \end{cases} \]
FIG. 2: (Color online) c-axis polarisation (obtained by integrating the pyroelectric current) and intensity of the (1/3, 1/3, q_z) magnetic reflection (measured without polarisation analysis) as a function of temperature. Inset: the experimental geometry showing the crystal orientation, direction of applied E-field, and scattering vector Q = k’ – k.

To P_xx = -1; P_xy = P_yx = P_yz = P_zx = 0; and

P_yy = 2M_{2\parallel}/M_{1\parallel} - 1; \quad (3)
P_zz = 2M_{2\perp}/M_{1\perp} - 1; \quad (4)
P_xz = P_{zx} = 2(M_{y\parallel}M_{z\perp})/M_{1\parallel}^2, \quad (5)

where M_{1\parallel} = M_{1\parallel} \cdot M_{1\parallel}^* and M_{2\perp} = M_{2\perp} \cdot M_{2\perp}^*. Thus, the sign of the P_{yx} and P_{zx} elements, together with the position of the satellites (±q_1, ±q_2) uniquely determines the domain population for each of the (σ_i, σ_j).

RFMO single crystals were grown by a flux technique using high purity (> 99.9%) Rb_2CO_3, Fe_2O_3, and MoO_3 in a molar ratio of 2:1:6 according to the recipe described in 11. They were heated together in air using a platinum crucible to 825°C and kept at this temperature for 48 h. The homogenized melt was slowly cooled to 600°C at a rate of 3°C/h, followed by a faster rate of cooling to room temperature. Single crystal thin platelets (up to 1 cm in diameter) were separated from the flux, their quality and orientation were checked using an Agilent Technologies SuperNova diffractometer, and pyroelectric currents were measured and integrated to give the ferroelectric polarisation (along c) as a function of temperature (see Fig. 2). Gold contacts were evaporated onto the (0, 0, ±1) surfaces and the OrientExpress neutron back-reflection Laue diffractometer 16 at the Institut Laue-Langevin (ILL), Grenoble, France was used to mount the sample with a^* + b^* parallel to the Y-axis (see inset to Fig. 2). This allowed us to access peaks of the form (hhl). The contacts were connected to gold wires with silver epoxy to allow high voltage to be applied. An ILL ‘orange’ cryostat provided cooling during the neutron scattering experiment (using a fixed neutron wavelength of 0.825 Å), which was carried out using the CryoPad 17 set-up on beamline D3 at the ILL.

Initially the sample was cooled below T_c, fixing the population of axial structural domains for the rest of the experiment. Fig. 2 shows the temperature dependence of the intensity of the (1/3, 1/3, 0.44) magnetic peak (corresponding to the propagation vector q_1), which fits the pyroelectric data well and confirms the simultaneous onset of magnetic ordering and ferroelectricity at T_N ≈ 4K. The same sample was cooled in an applied electric field of both ± 7.5 kV/cm and zero field, and the polarimetry components measured. The results for the (−1/3, −1/3, 0.56) peak are shown in Fig. 3(a), together with the calculations (which contain no free parameters) from equations (3) to (5). It is clear that the components P_{yx} and P_{zx} couple to the electric field (slight differences in these components, which should be equal in magnitude, are due to experimental uncertainty).

Table 1 lists the magnetic peaks and associated magnetic structure factors originating from different chiral structures. Peaks with propagation vectors q_1 and q_2 are present with similar intensities, yielding four satellites around each reciprocal lattice node; this shows that the crystal contains a roughly equal population of both axial domains. We examined the behaviour of several magnetic peaks, including at least one from each combi-

FIG. 3: (Color online) (a) Polarimetry components following negative, positive, and zero field cooling (with field strength 7.5 kV/cm). Solid bars indicate observed values and rectangles show the calculations. (b) Hysteresis loops in P_{xx} as a function of applied electric field for two magnetic reflections. The chiralities, (σ_i, σ_j) = (±, ±) are indicated.
TABLE I: The eight possible contributions of the magnetic structure to the scattered intensity. \( \sigma_\text{t} \): the triangular chirality; \( \sigma_\text{h} \): the helical chirality; \( \mathbf{Q} \): the position of the peak in reciprocal space; \( \mathbf{G} \): a reciprocal lattice vector; \( \mathbf{q}_\text{f} = (1,3/1,3,q_z) \); \( \mathbf{q}_\text{z} = (-1,3,1/3,q_z) \). The magnetic structure factor \( \mathbf{M} \) is given in terms of the orthonormal vectors \( \mathbf{u} \) and \( \mathbf{v} \).

| Contribution | Magnetic Structure Factor | Chirality Combination |
|--------------|---------------------------|-----------------------|
| \( \sigma_\text{t} = 1 \) \( \sigma_\text{h} = 1 \) | \( \mathbf{Q} = \mathbf{G} \pm \mathbf{q}_\text{f} \), \( \mathbf{M} \propto (\mathbf{u} + i\mathbf{v}) \) | (+, +) |
| \( \sigma_\text{t} = -1 \) \( \sigma_\text{h} = 1 \) | \( \mathbf{Q} = \mathbf{G} \pm \mathbf{q}_\text{z} \), \( \mathbf{M} \propto (\mathbf{u} + i\mathbf{v}) \) | (-, +) |
| \( \sigma_\text{t} = 1 \) \( \sigma_\text{h} = -1 \) | \( \mathbf{Q} = \mathbf{G} \pm \mathbf{q}_\text{f} \), \( \mathbf{M} \propto (\mathbf{u} + i\mathbf{v}) \) | (+, -) |
| \( \sigma_\text{t} = -1 \) \( \sigma_\text{h} = -1 \) | \( \mathbf{Q} = \mathbf{G} \pm \mathbf{q}_\text{z} \), \( \mathbf{M} \propto (\mathbf{u} + i\mathbf{v}) \) | (-, -) |

The relative effect of the magnetic structure on the scattered intensity is shown by the \( \pm \) signs.

| Contribution | Magnetic Structure Factor | Chirality Combination |
|--------------|---------------------------|-----------------------|
| \( \sigma_\text{t} = 1 \) \( \sigma_\text{h} = 1 \) | \( \mathbf{Q} = \mathbf{G} \pm \mathbf{q}_\text{f} \), \( \mathbf{M} \propto (\mathbf{u} + i\mathbf{v}) \) | (+, +) |
| \( \sigma_\text{t} = -1 \) \( \sigma_\text{h} = 1 \) | \( \mathbf{Q} = \mathbf{G} \pm \mathbf{q}_\text{z} \), \( \mathbf{M} \propto (\mathbf{u} + i\mathbf{v}) \) | (-, +) |
| \( \sigma_\text{t} = 1 \) \( \sigma_\text{h} = -1 \) | \( \mathbf{Q} = \mathbf{G} \pm \mathbf{q}_\text{f} \), \( \mathbf{M} \propto (\mathbf{u} + i\mathbf{v}) \) | (+, -) |
| \( \sigma_\text{t} = -1 \) \( \sigma_\text{h} = -1 \) | \( \mathbf{Q} = \mathbf{G} \pm \mathbf{q}_\text{z} \), \( \mathbf{M} \propto (\mathbf{u} + i\mathbf{v}) \) | (-, -) |

The relative effect of the magnetic structure on the scattered intensity is shown by the \( \pm \) signs.

**FIG. 4:** (Color online) Magnetic structures present in (a) positive, and (b) negative field cooling, each of which has two contributions (from each axial domain). The direction of the ferroelectric polarization (\( \mathbf{P} \)) is shown, and the axial distortion is indicated by the direction of the circular arrows. The direction of the MoO\(_4\) tetrahedron associated with each triangle is shown by the \( \pm \) signs.

We have demonstrated that the axial distortion of the crystal structure plays a crucial role in stabilising the helical magnetic structure of RbFe(MoO\(_4\))\(_2\), linking triangular chirality with helicity. By means of neutron spherical polarimetry, we determined uniquely the populations of domains with each of the combinations of helical and
triangular chiralities in the two axial domains. By applying an external electric field, the domain population switches between the pairs of magnetic structures that are energetically preferred in each axial domain. The coupling between magnetic structure and electrical polarization is of relativistic origin, and involves both triangular chirality and helicity, the latter term being proportional to the axial distortion (ferroaxial coupling).

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