Spherical neutron polarimetry (SNP) study of magneto-electric coupling in the multiferroic MnWO$_4$

A Poole$^1$, P J Brown$^2$, A S Wills$^1$*

1Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, UK
2Institut Laue-Langevin, BP 156, 38042 Grenoble Cedex 9, France
E-mail: a.s.wills@ucl.ac.uk

Abstract.
The electric-field dependence of the magnetic structure of multiferroic MnWO$_4$ has been directly investigated using spherical neutron polarimetry as a function of temperature. The application of an electric field is shown to drive the magnetic structure to a single ‘chiral’ domain. The magnitude of the electric field required to do this is shown to increase upon cooling. The coupling between the magnetic order and electric polarization is further demonstrated.

1. Introduction
The magneto-electric effect, whereby the application of a magnetic field induces electric polarization and the application of an electric field induces magnetization, has generated enormous interest lately due to its many possible applications [1, 2]. The recent revival is partly due to the identification of materials that become ferroelectric and ferromagnetic simultaneously.

The frustrated, cycloidal, magnetic structure[3] of these strongly coupled magneto-electrics gives rise to inverse Dzyaloshinsky-Moriya (DM) interactions [4, 5, 6], which, in turn, gives rise to an incommensurate structural modulation with a propagation vector twice that of the magnetic propagation vector, $k_{1}=2k_{m}$ [7]. The ferroelectric polarization $P_{e}$ is proportional to the phase difference, $\phi$, between the chains of magnetically ordered ions $P_{e} \propto M_{1}M_{2} \sin \phi [k \times [e_{1} \times e_{2}]]$ where $M_{1}$ and $M_{2}$ are the magnitudes of the moments in the orthogonal directions $e_{1}$ and $e_{2}$ [8, 9]. The coupling shows great sensitivity to applied magnetic fields and, as we demonstrate in MnWO$_4$, to the application of an electric field [10, 11]. Furthermore, the size of the electric field required to change the magnetic order is shown to be highly sensitive to the temperature.

MnWO$_4$ belongs to the family of multiferroic materials with a frustrated, cycloidal magnetic order in the multiferroic phase [10, 12, 13]. MnWO$_4$ crystallizes in the wolframite structure with alternate layers of manganese and tungsten perpendicular to the a axis. The structure is best described by the monoclinic $P2/c$ space group, with $\beta = 91.1^\circ$ and lattice parameters $a = 4.82\text{Å}$, $b = 5.75\text{Å}$ and $c = 4.99\text{Å}$. The manganese is located at the 2f site and forms zig-zag chains of Mn$^{2+}(S=5/2)$ ions surrounded by edge-sharing oxygen octahedra. MnWO$_4$ has been shown to undergo three successive antiferromagnetic phase transitions that generate long wavelength magnetic structures [14, 15]. The first magnetically ordered state, AF3, occurs below $T_N = 13.5 \text{K}$ and is sinusoidally modulated with the easy direction in the ac plane forming an angle of $35^\circ$ to the a-axis. The second order transition to the AF2 phase at $T_2 = 12.5\text{K}$
introduces a component in the [010] direction that gives rise to the cycloidal magnetic order, with incommensurate (ICM) propagation vector $k_2 = (-0.214, 0.5, 0.457)$. The final, first order, transition into the commensurate (CM) AF1 phase occurs at $T_1 \approx 7K$ and the structure becomes sinusoidally modulated once more with propagation vector $k_1 = (\pm \frac{1}{4}, \frac{1}{2}, \frac{1}{2})$ shown to undergo three successive antiferromagnetic phase transitions that generate long wavelength magnetic structures [14, 15]. The AF2 phase has been demonstrated to be multiferroic, with the $P_e$ along with the $b$ axis, perpendicular to the easy plane [10, 12, 13].

The details of the magnetic structure was also determined using spherical neutron polarimetry (SNP), and these will be presented in a later paper [16].

2. Spherical Neutron Polarimetry

The SNP technique allows the polarized moments of the neutron beam to be arbitrarily oriented using a combination of two rotations corresponding to the spherical coordinate system [17, 18]. All components of the polarization matrix, with polarization axes defined with $x$ parallel to the scattering vector $Q$, $z$ with the zone axis of the crystal and $y$ completing the right handed cartesian set, are recorded, Figure 1. The polarization matrix is the experimental quantity that is most closely related to the polarization tensor form of the Blume Maleev equations, fully described in [19, 20]. The perpendicular sine and cosine components of the cycloidal magnetic structure, when they lie perpendicular to the $Q$, give rise to a non-zero ‘chiral term’ as polarization is generated in the $x$ direction, described by the cross product term in the Blume Maleev equations,$\nonumber P_{f,\text{chiral}} = -i(M_\perp \times M_\perp)$. An idealized experimental arrangement, which would have both components perpendicular to $Q$, is shown in Figure 2. In this instance the polarization tensor will have the simplified form:

$$P = \begin{pmatrix} -1 & 0 & 0 \\ B & A & 0 \\ B & 0 & -A \end{pmatrix} \quad \text{or} \quad P = \begin{pmatrix} -1 & 0 & 0 \\ -B & A & 0 \\ -B & 0 & -A \end{pmatrix},$$

(1)

with the terms,

$$A = \frac{M_1(k^2) - M_2(k^2)}{M_1(k^2) + M_2(k^2)} \quad \text{and} \quad B = \frac{2M_1(k^2)M_2(k^2)}{M_1(k^2) + M_2(k^2)}$$

(2)

The $A$ component of the matrix defines the ellipticity of the cycloid, it is unity when the structure is spherical and the sine and cosine components have equivalent magnitudes. The $B$ component is the chiral term of the matrix, the magnitude is dependent on the population of each of the ‘chiral’ domains, $\pm k$; when $\pm k$ are equally populated $B=0$; when the magnetism...
idealized orientation, with the propagation vector $k_1$ lying fully in the scattering plane with the sine component and electric polarization $P_e$ parallel to $z$ and the cosine component with $y$. The applied electric field is along $E$ parallel to $P_e$. The scattering vector is denoted $Q$. The polarization axes are marked $x$, $y$ and $z$ and the direction of polarization of the incoming beam is with $P_i$ and the final polarization, due to the ‘chiral’ scattering is with $P_f$.

is ordered as a single $k$ domain $B$ will have a magnitude of unity, with the sign of $B$ dependent on the handedness of $k$, shown in Figure 2.

As stated previously this is an idealised experimental arrangement, however, the matrix element $B$ is always non-zero when there is a real and imaginary part of the magnetic interaction vector perpendicular to $Q$.

3. Results and Discussion
The polarization matrix was measured using CRYOPAD on D3 at the ILL. The crystal was oriented with the [111] direction as the zone axis, along the $z$ direction. The polarization of the reflection (1 $\bar{1}$ $\bar{1}$) - $k_2$ was measured to follow the changes in the $B$ component. The electric field was applied along the $b$ axis of the single crystal via sputtered gold contacts. The field was ramped from 0Vmm$^{-1}$ to 180Vmm$^{-1}$ to 0Vmm$^{-1}$ with constant temperature and then the polarity of the field was reversed and the process repeated. The crystals were cooled to the constant temperatures, 12K, 11, and 10K with a poling electric field applied.

The coercive field at 12K is $\approx 50$Vmm$^{-1}$ a reduction in temperature by 1K to 11K increased the coercive field to $\approx 100$Vmm$^{-1}$. At 10K the coercive field could not be achieved with 180Vmm$^{-1}$, but a reduction in the spin polarization was observed, an indication that at $\approx 200$Vmm$^{-1}$ the sign of $B$ would be reversed. The complete hysteresis loops recorded can be seen in Figure 3.

The experiment was repeated at 13K in the higher temperature, incommensurate AF3 phase and at 6K in the lower temperature commensurate AF1 phase. There was no significant contribution to the ‘chiral’ terms of the polarization matrix at either of these temperatures and no hysteresis was recorded.

Overall, the application of a poling electric field whilst cooling MnWO$_4$ was shown to generate a magnetic monodomain. The population of this domain was controlled by varying both the magnitude and the polarity of the electric field. The coercive field, when the $B$ term of the neutron polarisation matrix appears to be zero, is the point at which the two opposing domains are equally populated. The coercive field was seen to be surprisingly sensitive to the temperature, with the magnitude of the field approximately doubling with an 1K reduction in temperature. The ferroelectric dipole moments are driven by the electric field to change direction, which will lead to an inversion of the atomic displacement that gives rise to the dipole moment. Hence, the handedness of the magnetisation is also inverted in response to this change in the local structure.
The distortions may then nucleate as the field increases until the point at which the field is strong enough to drive the entire system to the inverse polarity. The interconversion can occur readily in a crystal with a cycloidal distortion and magnetic structure as the cycloid is not truly chiral as the handedness can be changed by a rotation-translation.

4. Conclusion
SNP shows that the magnetic domain population of MnWO$_4$ in the multiferroic phase can be controlled by the application of an electric field, evidencing a direct link between magnetism and ferroelectricity. The electric field had no influence on the magnetic structures in the AF3 or the AF1 phases showing that they possess no magneto-electric coupling.

5. Acknowledgments
We would like to thank the EPSRC (grant number EP/D053560/1) for financial support; A. T. Boothroyd and D. Prabhakaran for supplying the sample; and Z. Davies for useful discussions.

References
[1] Hill N A 2000 J. Phys. Chem. B 104 6694
[2] Eerenstein W, Mathur N D and Scott J F 2006 Nature 442 759
[3] Wills A S 2007 Z. Kristallogr. 26 53
[4] Moriya T 1960 Phys. Rev. 120 91
[5] Dzyaloshinsky I 1957 J. Phys. Chem. Solids 4 241
[6] Sergienko I A and Dagotto E 2006 Phys. Rev. B 73 094434
[7] Taniguchi K, Abe N, Sagayama H et al 2008 Phys. Rev. B 77 64408
[8] Davies Z, Poole A and Wills A S J. Phys.: Condens. Matter Awaiting publication
[9] Mostovoy M 2006 Phys. Rev. Lett. 96 067601
[10] Taniguchi K, Abe N, Ohtani S et al 2006 Phys. Rev. Lett. 97 097203
[11] Yamasaki Y, Sagayama H, Goto T et al 2008 Phys. Rev. Lett. 98 219902
[12] Heyer O, Hollmann N, Klassen I et al 2006 J. Phys.: Condens. Matter 18 L471
[13] Arkenbout A H, Palstra T T M, Siegrist T and Kimura T 2006 Phys. Rev. B 74 184431
[14] Lautenschläger G, Weitzel H, Vogt T et al 1993 Phys. Rev. B 48 6087
[15] Ehrenberg H, Weitzel H, Heid C et al 1997 J. Phys.: Condens. Matter 9 3189
[16] Poole A, Wills A S, Boothroyd A et al unpublished work
[17] Lelièvre-Berna E, Bourgeat-Lami E, Fouilloux P, et al 2005 Physica B 356 131
[18] Poole A, Wills A S and Lelièvre-Berna E 2007 J. Phys.: Condens. Matter 19 452201
[19] Blume M 1963 Phys. Rev. 130 1670
[20] Brown P J, Forsyth J B and Tasset F 1993 Proc. R. Soc. Lond. A 442 147

Figure 3. Hysteresis of magnetic domain population determined by measurement of the chiral term of the polarization matrices recorded at 11K (top) and 12K (bottom). The coercive field can be seen to be $\approx 100\text{V mm}^{-1}$ and $\approx 50\text{V mm}^{-1}$ respectively. The polarization does not achieve the arbitrary value of -1 due to the magnetic reflection not being completely aligned in the plane. Thus, some of the information that would be transmitted in the x channel of the polarization matrix is transmitted in the z. The lines are a guide for the eyes.