Control of chiral magnetism in multiferroic MnWO₄ through an electric field

T. Finger,¹ D. Senff,¹ K. Schmalzl,² W. Schmidt,² L.P. Reginault,³ P. Becker,⁴ and M. Braden¹

¹II. Physikalisches Institut, Universität zu Köln, Zülpicher Str. 77, D-50937 Köln, Germany
²Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, JCSN at ILL, 38042 Grenoble Cedex 9, France
³Institut Nanosciences et Cryogénie, SPSMS-MDN, DRFMC-SPSMS-MDN, F-38054 Grenoble Cedex 9, France
⁴Institut für Kristallographie, Universität zu Köln, Zülpicher Str. 49b, D-50674 Köln, Germany
(Dated: July 30, 2009)

The chiral components in the magnetic order in multiferroic MnWO₄ have been studied by neutron diffraction using spherical polarization analysis as a function of temperature and of external electric field. We show that sufficiently close to the ferroelectric transition it is possible to switch the chiral component by applying moderate electric fields at constant temperature. Full hysteresis cycles can be observed which indicate strong pinning of the magnetic order. MnWO₄, furthermore, exhibits a magnetoelectric memory effect across heating into the paramagnetic and paraelectric phase.

PACS numbers:

Magnetoelectric materials allow one to tune the electric polarization by an external magnetic field and to tune magnetic polarization by an electric field. In particular, the control of magnetic order by an electric field has a strong application potential in the context of data storage, but in spite of strong efforts no suitable materials have been discovered so far.

Concerning the recently discovered multiferroic transition-metal oxides, it has been well established that the ferroelectric polarization can be modified by an external magnetic field. Using polarized neutron scattering in TbMnO₃, LiCu₂O₂ and in MnWO₄ it has been shown that the chiral component of the magnetic order can be polied by an electric field when cooling through the ferroelectric transition. However, in general there have been only very few reports on a change of a magnetic order induced by applying an electric field at constant temperature. Furthermore, it was shown that by varying the electric field in MnWO₄ one may induce a hysteresis in the ferroelectric polarization and in the second harmonic generation associated with magnetic domains. However, the direct observation of the electric-field induced switching of the chiral magnetism at constant temperature has not been reported so far in the spiral multiferroics, although this effect is most important in view of applications.

In most of the recently discovered multiferroics, the ferroelectric polarization can be explained by the inverse Dzyaloshinski-Moriya effect, where the induced electric polarization of a single pair of spins S_i,S_j separated by a distance vector r_{ij} is given by

$$\mathbf{P}_{FE} \propto \mathbf{r}_{ij} \times (\mathbf{S}_i \times \mathbf{S}_j).$$

(1)

The required non-collinear magnetic structure may arise from strong frustration. Since in addition the interaction (1) is only a second-order effect, the ferroelectric polarization is rather small in these materials. In the REMnO₃ series and in MnWO₄ the electric polarization is about two to three orders of magnitude smaller than that in a standard ferroelectric perovskite such as BaTiO₃, hindering the observation of electric-field induced effects in the magnetic structure. Nevertheless, we show in this work that it is possible in these chiral multiferroics to switch the magnetic order by the application of a moderate electric field at constant temperature.

The magnetic order in MnWO₄ (space group P2₁/c, a=4.835Å, b=5.762Å, c=4.992Å and β=91.08°) has been determined by neutron diffraction. Upon cooling, MnWO₄ first undergoes a transition into an incommensurate magnetic phase labelled AF3 with propagation vector q_{AF3}=(0.214,0.5,0.457) and collinear moments aligned

![FIG. 1: (color online) (a) Crystal and (b and c) magnetic structure in MnWO₄; b) and c) show the two opposite chiral arrangements; d) and e) temperature dependence of magnetic scattering at q_{AF3} and q_{FE} studied with polarized neutron diffraction. The experiment was performed in the (0,1,0),(-0.214,0.0,0.457) scattering plane; part d) shows the magnetic scattering polarized parallel to the easy axis and that parallel to b and part e) the product of the magnetic components along these two directions, \sqrt{\sigma_{yy}} \sqrt{\sigma_{zz}}, which scales well with the ferroelectric polarization.](image)
in the $a,c$-plane, $T_{AF3}=13.2$ K. At the second transition, $T_{AF2}=12.3$ K, the $b$-component develops giving rise to a still incommensurate but non-collinear phase, AF2. At the transition AF3$\rightarrow$AF2 the ferroelectric polarization develops, as independently discovered by three groups \cite{17,18,19}. At further cooling, the magnetic order transforms into a commensurate collinear AF1 state with $q_c=\langle-0.25,0.5,0.5\rangle$, $T_{AF1}=7.0$ K.

The polarized neutron-diffraction experiments were performed on the IN12 cold triple-axis spectrometer at the Institut Laue-Langevin using either Helmholtz coils or the zero-field Cryopad for polarization analysis. An untwinned single crystal \cite{17} was set in a $(0,1,0),(-0.214,0,0.457)$ scattering plane. On a structural Bragg reflection we have determined the flipping ratio of our polarization setup to 40 and 35 in the two experimental runs.

The unpolarized neutron-scattering intensity is given by the square of the magnetic structure factor, $M_{ij}(Q) = n_0 N^{1/2} \sum_j (M_j - (Q \cdot M_j)) \cdot Q_j e^{iQ_j R_j}$, where $r_0 = 5.4 f/m$, $Q$ denotes the wave vector, and the sum runs over the atoms in the cell with complex moment $M_j$ at position $R_j$. We use the common cartesian coordinate system with $x$ along $Q$, $y$ in the scattering plane but perpendicular to $Q$ and $z$ vertical. The polarization analysis \cite{21} adds additional selection rules: In the spin-flip (SF) scattering the contributing magnetization must be perpendicular to the neutron polarization. By measuring the three SF channels for $P||x, y$ and $P||z$, we may thus follow the components as a function of temperature, see Fig 1. In the AF3 phase the magnetic moment aligns along an easy axis, $e_{easy}$, in the $a,c$-plane nearly perpendicular to the propagation vector $q_{ic}$ (the angle amounts to 83°). Therefore, almost all elastic magnetic scattering is found in the $P||y$ channel, and no magnetic signal is found for $P||z$. The latter channel directly senses the $b$-component and becomes finite upon the phase transition into the AF2 phase. The ferroelectric polarization \cite{17,18,19} only crudely scales with the $b$-component, see Fig 1d). At the transition into the AF1 phase the $b$-component measured in the $P||z$ channel disappears as does the ferroelectric polarization \cite{17,18,19}.

The three-dimensional polarization analysis using Cryopad allows one to determine the full polarization tensor by analyzing the outgoing and incoming polarization independently \cite{21}. $\sigma_{ij}^{\text{inj}}$ denotes the intensity in the channel with the outgoing polarization along $j$ when the incoming polarization is set along $i$ with the arrows indicating the directions of polarizations. The magnetic scattering can be decomposed into the $M_y(Q) \cdot M_y^*(Q)$ and $M_z(Q) \cdot M_z^*(Q)$ contributions and the chiral term, $M_{ch}(Q) = i[M_L(Q) \times M_1^*(Q)]$, which rotates the neutron polarization towards the scattering vector, and which possesses only a finite $x$ component $M_{ch}(Q)$.

The chiral term is determined in three spherical polarization channels. In comparison to the total magnetic scattering it is measured in the $xx$ channel as

\begin{equation}
\sigma_{xx}^{\text{ch}} = M_y(Q) \cdot M_y^*(Q) + M_z(Q) \cdot M_z^*(Q) + M_{ch}(Q)
\end{equation}

and

\begin{equation}
\sigma_{xy}^{\text{ch}} = M_y(Q) \cdot M_x^*(Q) + M_z(Q) \cdot M^*_y(Q) + M_{ch}(Q)
\end{equation}

and similarly in the $yx$ channels. In equations (2) and (3) we may neglect any nuclear contribution as the Bragg-peaks studied are purely magnetic. Polarized neutron scattering directly probes the chiral term.

If the magnetic order in the sample crystal is a perfect transverse spiral with the spiral plane perpendicular to the propagation vector $q_{ic}$ parallel to $Q$, the spin flip scattering $\sigma_{xx}^{\text{ch}}$ or $\sigma_{yy}^{\text{ch}}$ is finite for only one incident polarization, since $M_{ch}(Q)$ and $M_y(Q) \cdot M_y^*(Q) + M_z(Q) \cdot M_z^*(Q)$ are of the same absolute size yielding $r_{chir}=\pm1$. If the geometrical condition that $Q$ is perpendicular to the chiral plane, is no longer fulfilled the chiral contribution to the scattering $r_{chir}$ is reduced even for the ideal monodomain transverse spiral. In order to detect a strong chiral term one needs to chose an appropriate scattering vector. Furthermore, with a real crystal it is necessary to align the chiral domains, which in the multiferroics can be obtained by applying an electric field \cite{1,2,3}. After cooling the sample to $T=7.7$ K applying an electric field of 3500V/4mm we have measured the full three-dimensional polarization

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{(color online) Temperature dependence of the magnetic scattering in the $\sigma_{xx}^{\text{ch}}$ and $\sigma_{yy}^{\text{ch}}$ channels measured upon cooling the MnWO$_4$ crystal with and without electric field. Note that the intensity in the two $xx$ spin-flip channels are proportional to the volumes of the two chiral arrangements A) and B) shown in Fig. 1b) and 1c). After a first cooling in negative field the thermal cycles a)-d) were successively recorded by cooling in -3500, 0, +3500 and 0 V. Before starting the second run of thermal cycles, e)-h), we heated the sample up to room temperature and then measured the cooling cycles in +3500, 0, -3500, and 0V.}
\end{figure}
matrix at \( Q = (-0.214, 0.5, 0.457) \) and \((-0.214, 1.5, 0.457)\) as well as at the \((0, 2, 0)\) structural Bragg reflections. At the first magnetic reflection the chiral contribution is dominant: the obtained chiral ratio amounts to 80.8%. We also find strong contributions in the \( yz \) and \( zx \) channels, which, according to equation (3) indicate \( r_{\text{chir}} = 80.3\% \) and 80.6\%, respectively, in perfect agreement with the value found by the diagonal term. The chiral contributions are much weaker at the second reflection since the large \( b \)-component of the scattering vector suppresses the scattering strength of this magnetic component compared to that along \( e_{\text{easy}} \). For \( Q = (-0.214, 1.5, 0.457)\), we only find chiral contributions of 31.0, 32.9 and 32.3% in the \( xx \), \( yz \) and \( zx \) channels, respectively. In the refinements of the magnetic structure \( ^{2} \) it was not possible to determine the phase between the \( e_{\text{easy}} \) and \( b \) components of the ordered magnetic moment, which however determines the collinear or chiral nature of the magnetic structure and thereby the strength of the multiferroic coupling, see equation (1). Analyzing the full spherical polarization tensor we may confirm that the phase between the two components is close to 90° corresponding to a chiral arrangement. Therefore, we may confirm that equation (1) fully explains the occurrence and the direction of the ferroelectric polarization in MnWO\(_4\) \( ^{23} \). Indeed, the product of the magnetic components along the easy direction and along \( b \) measured by \( \sqrt{\sigma_{yy}^2} \), \( \sqrt{\sigma_{zz}^2} \) scales very well with the temperature dependence of the ferroelectric polarization, see Fig. 1c). From the depolarization of the beam polarized initially along \( y \) or \( z \) we further estimate that with the applied field one obtains a nearly perfect alignment of the chiral component; only \( \sim 5\% \) of the sample remain in the opposed chiral state.

In various heating-cooling cycles we found that MnWO\(_4\) remembers its chiral state even after heating into the paramagnetic and paraelectric phase. The memory and hysteresis behavior of MnWO\(_4\) appears to be very complex and is very difficult to be fully reproduced as it seems to depend on the cooling velocity across the magnetic transitions. To illustrate the complex memory effect in MnWO\(_4\) we show in Fig. 2 two sets of thermal cycles, Fig. 2 a)-d) and e)-h), which were separated by heating to high temperature (\( \sim 295 \) K). First we cooled the crystal in \(-3500\) V obtaining the almost perfectly aligned chiral component which we label arrangement A), see Fig. 1b) and c). After heating to 15 K, i.e. into the paramagnetic and paraelectric state, and re-cooling in zero field we find the identical chiral component, see Fig. 2b). Heating once more and re-cooling in the opposed field allows one to fully switch the chiral alignment to arrangement B). Finally another heating to 15 K with successive zero-field cooling results in the same arrangement A) although the preceding \(+3500\) V experiment yielded arrangement B). This clearly documents that the crystal remembers the alignment of the chiral contribution even in the paraelectric and paramagnetic phase. Apparently the first cooling in electric field results in a preference of the crystal for arrangement A) which is not erased by forcing the sample with the opposed field into arrangement B). After heating the sample to room-temperature we performed a similar series of thermal cycling starting with the positive field. Again one may pole the sample into both arrangements, although the alignment is less perfect. But now the state B) is the one observed in the zero-field cooling cycles independently of the preceding direction of the electric field. One can force the sample crystal into a preferred chiral arrangement depending on a first cooling from high temperature (most likely cooling velocity). This finding resembles the previously reported memory effect across the paraelectric collinear magnetic phase AF1 \( ^{24} \) and the magnetic-field driven reversibility \( ^{14} \). The fact that the preference is robust against heating deeply into the paramagnetic state, however, seems to exclude the given interpretation \( ^{24} \) in terms of ferroelectric embryos. It appears more likely that the hysteresis and preference arise from domain-wall pinning by defects, see below.

In two sets of experiments we studied the possibility to control the chiral arrangement by varying the electric field at constant temperature. After cooling the sample in negative voltage we have measured a hysteresis cycle of the chiral ratio versus electric field at \( T = 8.3 \) K. When fully reducing the voltage to zero the chiral ratio is unchanged; the voltage may even be inverted and increased to \(+1000\) V without any significant change in the chiral component documenting the effective pinning of the magnetism in MnWO\(_4\). But further increase of the voltage significantly reduces the chiral ratio. Upon cycling the voltage back to the initial negative value the chiral ratio rapidly approaches the starting value. A quite different hysteresis curve is observed when the cycle is
recorded after cooling with a positive voltage from about 15 K, following cooling from room temperature in negative voltage, see Fig. 3a). The initial chiral term is of opposite sign but of the same size as that obtained with the negative voltage, but when lowering the voltage the chiral term immediately diminishes and even fully changes sign when the voltage is increased in the negative direction. When driving the voltage from -2000V back to zero the weaker positive chiral ratio remains unchanged and only partially recovers the initial value for increasing the voltage to +2000V. Other hysteresis cycles at higher temperatures were obtained after field-cooling at -2000V from 15 K. When approaching the AF2 to AF3 transition larger effects are induced in these cycles and the width of the hysteresis becomes smaller, but all hysteresis curves remain asymmetric indicating the preferred chiral arrangement. At T=12.0 K we can induce a complete inversion of the chiral arrangement through the inversion of the electric field. Such processes form the basis of the desired application of multiferroics in data storage techniques.

In a following run we recorded several hysteresis cycles after cooling from high temperature in negative voltage attaining U=-3500V at low temperatures, see Figure 3e)-3l). The same asymmetric hysteresis curves are obtained and again it is possible to fully control the chiral component by the electric field. At T=10.5 K nearly identical hysteresis cycles were obtained at the four Q-positions (±0.214,0.5,±0.457) and (±0.214,-0.5,±0.457). With increasing temperature the height of the hysteresis passes a maximum as the control is facilitated closer to the magnetic transition whereas the size of the chiral component diminishes, see Fig. 3m). The width of the asymmetric hysteresis continuously decreases upon approaching the paraelectric phase as one may expect due to a weaker pinning, see Fig. 3n).

The hysteresis cycles shown in Fig. 3a-3l) offer a view on the processes pinning the magnetism in the multiferroic material. Well below T_{AF2}, the chiral domains seem to be efficiently pinned, and an inversion cannot be obtained in our large crystal with the moderate electric fields. Close to the transition the full magnetic inversion is possible but the hysteresis cycle remains very asymmetric. Even after passing into the paramagnetic phase the sample crystal exhibits a pronounced memory for the chiral domains forced in preceding field-cooling cycles. It must be left to future experiments to study the exact temperature (apparently well above 30 K) which is needed in the heating cycle in order to erase this memory. The strong pinning and asymmetry of the chiral domains must be based on strong magnetoelastic coupling. If the ferroelectric polarization is purely electronic in origin the associated pinning force should be negligible, whereas a ferroelectric polarization due to ionic displacements should posses an intrinsic pinning capability. The pinning of the chiral may also arise from higher harmonic components which we indeed observe in MnWO₄. The second-order harmonics of the magnetic modulation studied at Q=(-0.428,1.0,0.914) shows magnetic and sizeable nuclear components. The magnetism in MnWO₄ is thus not only associated with an anharmonic magnetic contribution, but also with a structural modulation. One may speculate that the latter is important to understand the pinning of the chiral domains.

In conclusion we have studied the impact of an external electric field on the magnetic structure in MnWO₄. The electric poling of the chiral terms exhibits a memory effect even when heating into the paramagnetic and paralectric phase, which most likely appears due to pinning of domain walls by defects. Most importantly, we show that one may control the chiral magnetism by varying the electric field at constant temperature in the multiferroic phase. It is possible to observe full multiferroic hysteresis curves.

This work was supported by the Deutsche Forschungsgemeinschaft in the Sonderforschungsbereich 608.

[1] W. Eerenstein et al., nature 442, 759 (2006).
[2] G.A. Smolenskii and I.E. Chapuis, Sov. Phys. Usp. 25, 475 (1983).
[3] S.-W. Cheong and M. Mostovoy, Nature Materials 6, 13 (2007).
[4] T. Kimura et al., Nature 426, 55 (2003).
[5] T. Goto et al., Phys. Rev. Lett. 92, 257201 (2004).
[6] Y. Yamasaki et al., Phys. Rev. Lett. 98, 147204 (2007).
[7] S. Seki et al., Phys. Rev. Lett. 100, 127201 (2008).
[8] H. Sagayama et al., Phys. Rev. B 77, 220407 (2008).
[9] E. Asher et al., J. of Appl. Physics 37, 1404 (1966).
[10] T. Lottermoser et al., nature 430, 541 (2004).
[11] Y. Bodenthin et al., Phys. Rev. Lett. 100, 027201 (2008).
[12] T. Zhao et al., nature materials 5, 823 (2006).
[13] B. Kundys et al., Phys. Rev. B 77, 172402 (2008).
[14] D. Meier et al., Phys. Rev. Lett. 102, 107209 (2009).
[15] H. Katsura et al., Phys. Rev. Lett. 95, 057205 (2005); M. Mostovoy, Phys. Rev. Lett. 96, 067601 (2006); I. Sergienko and E. Dagotto, Phys. Rev. B 73, 094434 (2006).
[16] T. Kimura et al., Phys. Rev. B 71, 224425 (2005).
[17] O. Heyer et al., J. Phys. Condens. Matter 18, L471 (2006).
[18] K. Taniguchi et al., Phys. Rev. Lett. 97, 097203 (2006).
[19] A.H. Arkenbout et al., Phys. Rev. B 74, 184431 (2006).
[20] G. Lautenschläger et al., Phys. Rev. B 48, 6087 (1993).
[21] T. Chatterji, Neutron Scattering from Magnetic Materials, Elsevier, Amsterdam, 2006.
[22] It is not possible to assign a chirality (or handedness) to a cycloid since the propagation vector and the spiral-plane are parallel. Therefore, we refer to the chiral component M_A in order to access the chiral domains.
[23] In the case of MnWO₄ it is not sufficient to analyse the nearest-neighbour spins in order to explain the ferroelectric polarization along b, since the spin-wave dispersion shows that this interaction is not dominating. However summing equation (1) over all spin pairs the spiral arrangement with e_easy and b components also generates a ferroelectric polarization along b.
[24] K. Taniguchi et al., Phys. Rev. Lett. 102, 147201 (2009).