Kinetics of the Multiferroic Switching in MnWO$_4$

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The time dependence of switching multiferroic domains in MnWO$_4$ has been studied by time-resolved polarized neutron diffraction. Inverting an external electric field inverts the chiral magnetic component within rise times ranging between a few and some tens of milliseconds in perfect agreement with macroscopic techniques. There is no evidence for any faster process in the inversion of the chiral magnetic structure. The time dependence is well described by a temperature-dependent rise time suggesting a well-defined process of domain reversion. As expected, the rise times decrease when heating towards the upper boundary of the ferroelectric phase. However, switching also becomes faster upon cooling towards the lower boundary, which is associated with a first-order phase transition.

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I. INTRODUCTION

Magnetoelectric materials allow one to tune both the electric polarization by an external magnetic field as well as the magnetic polarization by an electric field\cite{12}. In particular, the control of magnetic order by an electric field has large application potential in the context of data storage, but in spite of strong efforts no suitable materials have been discovered for a long time\cite{13}. In the recently discovered multiferroic transition-metal oxides ferroelectric polarization arises from a complex – in most cases chiral – magnetic structure. The ferroelectric order can be modified by an external magnetic field\cite{11} in these multiferroic materials. The opposite direction is more difficult to study, as the complex antiferromagnetic order requires a microscopic technique directly probing the spin arrangement\cite{12}. Using polarized neutron scattering it has been shown in TbMnO$_3$\cite{13}, LiCu$_2$O$_2$\cite{13} and in MnWO$_4$\cite{19} that the chiral component (i.e. sense of rotation) of the magnetic order can be poled by an electric field when cooling through the ferroelectric transition. However, the direct observation of the electric-field induced switching of the chiral magnetism in these multiferroics has only been recently observed in measurements on multiferroic MnWO$_4$\cite{19} and Ni$_3$V$_2$O$_7$\cite{15} where full hysteresis cycles were recorded.

The space group of MnWO$_4$ is P2$_1$/c (a = 4.823 Å, b = 5.753 Å, c = 4.992 Å, β = 91.08° at 300 K). MnWO$_4$ undergoes a sequence of magnetic phase transitions\cite{19}. Below 13.5 K an incommensurate spin density wave with collinear moments in the ac-plane and propagation vector $k = (-0.241, \frac{1}{2}, 0.457)$ sets in (AF3). Below 12.3 K an additional $b$-component evolves and the moments order in an elliptical spiral (AF2). Below 7.5 K\cite{20} the system orders again collinearly with moments in the ac-plane but with a commensurate propagation vector $k = (-\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (AF1)\cite{19}. At the transition to the non-collinear state (AF3 $\rightarrow$ AF2) spontaneous electric polarization parallel $b$ develops continuously. At the transition back into the collinear but anharmonic state (AF2 $\rightarrow$ AF1) the electric polarization disappears discontinuously\cite{21,22}.

Multiferroicity in MnWO$_4$ can be explained by the inverse Dzyaloshinskii-Moriya interaction\cite{23}. The direction of the electric polarization $P$ is given by $P \propto e_{ij} \times (S_i \times S_j)$ where $S_i$ and $S_j$ are the magnetic moments of manganese ions and $e_{ij}$ points along the connection line of the corresponding ion.\cite{23} Summing up these contributions over all pairs of magnetic ions yields the total ferroelectric polarization, which in case of MnWO$_4$ points along the $b$ direction.

While the microscopic coupling leading to multiferroic order seems well understood in MnWO$_4$ as well as in the other chiral multiferroics, very little is known about the dynamics of the domain inversion. In this work we
present investigations on the kinetics of electric-field induced switching of chiral magnetic structures in multiferroic MnWO$_4$. We applied a stroboscopic technique combined with polarized neutron diffraction in order to investigate how fast the magnetic chirality adapts to an instantaneously switched electric field.

II. EXPERIMENTAL

A. General aspects of neutron scattering on chiral multiferroics

Scattering experiments with polarized neutrons are ideally suited for studying magnetic structures with a non-vanishing term $S_i \times S_j$, as they give access to the so-called chiral term: $-i\langle M_L \times M_{L}^\dagger \rangle_x$. We use the common right-handed coordinate system with orthogonal axes: $-x \parallel Q = k - k_i$, $z$ vertical, $y = z \times x$. $M_L(Q)$ is the part of the three-dimensional magnetic structure factor (i.e. the Fourier coefficient of the magnetization density) $M^\dagger(Q)$ perpendicular to the scattering vector $Q$. We define the chiral ratio as the quotient of chiral and total magnetic scattering at a given $Q$:

$$ r_{\text{chir}} = \frac{-i\langle M_L \times M_{L}^\dagger \rangle_x}{|M_L|^2}. $$

The chiral ratio can amount to $\pm 1$ in the case of an ideal helix and scattering vector parallel to the propagation vector, but in general it will be smaller even for the ideal helix. The chiral ratio for a mono-domain sample can easily be calculated from the magnetic structure $\langle S_i \rangle$. The deviation with the experiment then directly gives the distribution of the chiral domains.

With spherical polarization analysis it is possible to measure the scattering intensity $I_{ij}$ for any directions of the incoming, index $i$, and outgoing, index $j$, neutron polarization. Over-bars indicate antiparallel neutron polarization. Therefore also the rotation of neutron polarization can be analyzed. The chiral ratio can be measured equally well in several channels of the neutron polarization matrix. It can be detected in the spin-flip scattering with polarization parallel to the scattering vector: $I_{xx} = |M_L|^2 - i\langle M_L \times M_{L}^\dagger \rangle_x$ and $I_{zx} = |M_L|^2 + i\langle M_L \times M_{L}^\dagger \rangle_x$ yielding

$$ r_{\text{chir}} = \frac{I_{xx} - I_{zx}}{I_{xx} + I_{zx}}, $$

as well as in transverse polarization channel.

B. Polarized neutron scattering experiments on MnWO$_4$

Neutron scattering experiments were performed on the two cold triple-axis spectrometers IN12 and IN14 at the Institut Laue Langevin (ILL). On both instruments a bender was set between the monochromator (pyrolitic graphite) and the sample in order to polarize the incoming neutron beam. The polarization analysis of the scattered neutrons was performed with a Heusler crystal. For the control of the neutron spin at the sample position a Cryopad III was installed on the IN12 spectrometer. In total a high degree of polarization was achieved. The flipping ratios measured on nuclear Bragg reflections $(0\ 2\ 0)$ and $(1\ 0\ -2)$ amount to 26 and 41, respectively. The slightly lower precision of the polarization at lower scattering angle most likely arises from perturbations in the guide fields. For the second experiment on IN14 a Helmholtz-coil setup was used to control the neutron polarization which only allows longitudinal polarization analysis. For analyzing the chiral domains longitudinal polarization is sufficient, as the chiral contribution can be isolated in the $xx$ channel.

FIG. 2: Time dependent measurement of the magnetoelectric switching at different temperatures for $Q = (-0.241, \frac{1}{2}, 0.457)$. The electric field is switched with a frequency of 8 Hz and an amplitude of $\pm 1.2$ kV/mm, rise time 0.2 ms. The chirality can approximately be switched in the same range as in the quasistatic hysteresis loop. The rise times differ for the two states. Before recording the time dependencies the sample was cooled from 20 K in an electric field of $+1.2$ kV/mm.

FIG. 3: Characteristics of the switching behavior for field cooling the sample with $E = +1.2$ kV/mm. The left and right panels give the amplitudes and the relaxation times, respectively, that were obtained by fitting the stretched exponential function, equation (3), to the stroboscopic data. 1 and 2 denote the relaxation in positive and negative external fields (first and second half of the time profile), respectively. The electric field is switched with a frequency of 8 Hz and an amplitude of $\pm 1.2$ kV/mm. The exponents $b_1$ and $b_2$ were fitted globally for the whole temperature range: $b_1 = 1.21(1)$, $b_2 = 1.63(2)$. The temperature was decreased during the measurement.
C. Stroboscopic technique for neutron scattering

The idea of our measurement was to reverse an electric field and to detect the response of the magnetic structure as a function of time. Typical count rates in neutron scattering experiments range in the time-scale of seconds (elastic) to minutes (inelastic scattering). Therefore studying the time dependence of a single process would not yield enough counting statistics. To overcome this challenge stroboscopic neutron-scattering techniques were developed. With this method it is possible to synchronize a periodical perturbation at the sample with the count rate of the neutron detector. The signal from the detector is recorded in time slots by a multichannel scaler. In order to gain sufficient count rates for each time slot the measurement is repeated periodically while the count rates of the individual time slots are accumulated. This technique was installed on the cold triple-axis spectrometer IN12 at the Institut Laue-Langevin using the CryopadIII setup for spherical polarization analysis. For the study of the multiferroic domain switching in MnWO$_4$ we applied a periodic electric field with rectangular time shape of amplitudes of about ±1.5 kV/mm and half periods of typically 67.5 ms. The electric field was applied by setting the flat single crystals (thickness of the order of 1-2 mm) between two aluminium plates, which were connected with the switchable high-voltage generator. The time slots were in the range of ms. With the fast electronics and with the signal strength of about 1000 cnts/s, it is possible to get sufficient statistics for the entire time dependence within several minutes to an hour.

III. KINETICS OF MULTIFERROIC DOMAINS STUDIED BY NEUTRON SCATTERING

A. Temperature dependence of the multiferroic rise times

1. First set of experiments on the IN12 spectrometer

In the first experiment the domain kinetics was analyzed on the IN12 spectrometer. By putting the sample between two large aluminium plates the electric field was applied along the crystallographic b-axis, which is the direction of the spontaneous electric polarization. The sample thickness amounts to 1.98 mm in this direction. The sample was mounted in the (0, 1, 0)/(-0.214, 0, 0.457) scattering-plane in order to reach the incommensurate magnetic Bragg peaks. First we recorded static hysteresis loops in order to determine the field strength needed to reverse chiral domains and the chirality saturation that could be achieved, see Fig. [1]. At the magnetic Bragg peak (-0.241, 1/3, 0.457) the hysteresis loops were recorded after cooling the sample from 20 K to 10 K in an applied electric field of ±1 kV/mm. The maximal chirality is ±0.48 and can be fully reversed. We find that the crystal develops a preferred chirality depending on the field direction which is applied during cooling from the paramagnetic phase. A higher field is needed to force the sample in the not-preferred state and a lower field can reverse it into its preferred state. This is in accordance with previous results on the control of multiferroic domains by varying an electric field at constant temperature.

We started studying the time dependence of the multiferroic domain inversion by switching an electric field of ±1.2 kV/mm with a frequency of 8 Hz and by registering the $I_{xx}$ and $I_{xx}$ intensities at the same magnetic Bragg peak as for the hysteresis loops. We observed the domain relaxation in the temperature range from 12.5 K to 7.5 K. The sample was first cooled from 20 K to 12.5 K in a field of +1.2 kV/mm. Three time-resolved curves at different temperatures are shown in Fig. [2]. We see that it is possible to switch the magnetic chirality frequently between the two saturation values and we reach the same amplitude as for the static hysteresis loop. No evidence for a change in the domain response was seen in these runs. Inspection of Fig. [2] immediately shows that the rise time is shorter when the system goes into its preferred state and longer when it is forced to the other state. At the temperatures closer to the upper and the lower boundaries of the ferroelectric phase the domains switch faster (i.e. the rise times of the chiral ratios are smaller). This qualitative analysis agrees with that obtained from other techniques studying the reversal of the ferroelectric domains. Second harmonic generation experiments also find a rather slow domain inversion at T=12 K as well as the comprehensive study by means of dielectric spectroscopy. The dielectric response and this neutron diffraction study show faster response near the upper and the lower transitions. While this behavior is expected for approaching the upper continuous transition, it is quite unexpected for the lower first-order transition.

In order to quantitatively analyze the dynamics of the domain inversion, the following function was fitted to the data:

$$y(t) = \frac{1}{2} \left[ 1 - \tanh \left( \frac{t - t_0}{0.001 \text{ ms}} \right) \right] \left[ A_2 + (A_1 - A_2) e^{-\left( \frac{t - t_0}{t_1} \right)^{b_1}} \right] + \frac{1}{2} \left[ 1 + \tanh \left( \frac{t - t_0}{0.001 \text{ ms}} \right) \right] \left[ A_2 + (A_1 - A_2) \left( 1 - e^{-\left( \frac{t - t_0}{t_2} \right)^{b_2}} \right) \right]$$

The hyperbolic tangent yields a continuous approximation of the heaviside step function which describes the instantaneous reversal of the electric field. $t_0$ is half the period. $t_{1,2}$ are the characteristic rise times for the two field directions (positive and negative, respectively). $A_1$ and $A_2$ describe the minimal and maximal chiralities that are obtained for the two field directions, respectively. We discuss the relaxation on the basis of the Avrami model, which corresponds to a simple domain growth. For the two directions of the field inversion, the exponents $b_1$ and $b_2$ can be globally fitted for the whole temperature range yielding values of 1.21 and 1.63 for the faster and for the slower switching, respectively. The characteristic time constants and the maximal chiral ratios recorded...
FIG. 4: Time dependent measurements of the multiferroic switching at different temperatures. The sample was cooled from 20 K in an electric field of \(-1.2 \text{ kV/mm}\). Frequency: 8 Hz, amplitude: \(\pm 1.2 \text{ kV/mm}\). The switching behavior is highly asymmetric.

FIG. 5: Characteristics of the switching behavior for field cooling \(-1.2 \text{ kV/mm}\). Frequency: 8 Hz, amplitude: \(\pm 1.2 \text{ kV/mm}\). The exponents \(b_1\) and \(b_2\) were fitted globally for the whole temperature range: \(b_1 = 1.63(1), b_2 = 1.29(1)\). The temperature was decreased during the measurement.

at all temperatures are shown in Fig. 5. The properties, which were already discussed at the three example runs (Fig. 2), are confirmed by the whole temperature dependence.

As reported previously, the multiferroic domain inversion in MnWO\(_4\) is rather slow, of the order of milliseconds to a few tens of milliseconds indicating that the domains in the multiferroic state are well pinned. This is in accordance with the large coercive fields found in the quasi-static experiments. The slow multiferroic rise times underline the importance of the lattice in the control of domains. For a purely structural domain the finite sound velocity can limit the speed of domain inversion to below the quotient of thickness to sound velocity (of the order of \(\mu s\) for a mm sized crystal), but this is not the limiting factor in MnWO\(_4\). That we observe three orders of magnitude larger rise times indicates effective pinning. Our neutron experiment senses the chiral magnetic component that could in principle be decoupled from the total ferroelectric polarization during the domain inversion. The good agreement between the magnetic response and the dielectric one clearly excludes such decoupling. Furthermore we always find a single relaxation; there is no indication for some faster magnetic relaxation preceding slower ferroelectric domains. This documents once more, that magnetism and ferroelectric polarization are strongly coupled in MnWO\(_4\).

The precise reason for the slow domain inversion remains unclear. Since only tiny atomic displacements can be associated with the observed small ferroelectric polarization, it seems unlikely that strong pinning arises due to these purely ferroelectric displacements. Instead higher-order modulations appear more likely to be at the origin of the strong pinning. For a magnetic modulation one can always expect a coupling with a structural modulation of half the magnetic period. In reference it was shown, that this half-period structural modulation is sizeable in MnWO\(_4\) and that it is accompanied by a second-order modulation of the magnetic structure. The two modulations exhibit coherent interference underlining their tight coupling. This structural distortion can possess a higher pinning potential than the weak ferroelectric distortion itself. It is quite astonishing that domains switch again much faster when approaching the lower boundary of the multiferroic phase. Since this transition is of clear first order, one would not expect any slowing down of excitations, which could melt the pinning. Instead the lower transition is related to the anharmonic distortions of the magnetic modulation, which increase upon cooling in the multiferroic phase. This increase is relatively stronger than that of the first-order magnetic modulation. Increasing anharmonicity may result in some depinning.

After this first series of experiments we tried to investigate whether we could change the preferred chirality by reversing the field during cooling. We heated the sample to 20 K and cooled it in a field of \(-1.2 \text{ kV/mm}\). Then we recorded the switching behavior in a temperature range from 12.5 K to 7.5 K. Three curves at different temperatures are shown in Fig. 4. As expected the sample now has a preference to negative chirality what is in accordance with the field applied during cooling. Comparing the fit parameters of the two temperature runs (Fig. 3 with Fig. 5) reveals reversed behavior. Now the negative chirality exceeds the positive chirality. However the positive (not preferred) chirality shows a less smooth curve than before because the full saturation is not reached at all temperatures. The behavior of the time constants is also reversed. Now the time needed to switch to the positive chirality exceeds the time needed to switch to the negative chirality. We also observe that the rise time to switch to not preferred chirality became longer than that observed in the first series.

The reversal of the preferred orientation agrees with the pronounced memory effects reported in reference. Most likely the cooling with a large electric field freezes in some local fields which determine the preferential orientation of the multiferroic domains. This leads to the strong asymmetries in the hysteresis cycles as well as in the time dependence of domain reversion.

2. Second set of experiments on the IN14 spectrometer using a different crystal

The time-resolved measurement was repeated at the IN14 spectrometer at the ILL with a crystal grown in a different batch, in order to investigate which properties
were specific to the sample and which ones are general. The second sample was 0.89 mm thick. For this experiment we used a conventional Helmholtz setup for the polarization analysis as it provides a higher scattering intensity, and as the chiral component can be studied in the longitudinal \( xx \) channel. The intensity of the magnetic reflection \((-0.214, 0.5, 0.457)\) amounts to 1400 cnts/s, i.e. comparable to the first experiment in spite of the smaller sample volume. First, we recorded a hysteresis loop after zero-field cooling the sample and thereby avoiding a freezing-in of electric fields, see Fig. 6 a). At 10 K a negative field of \(-1.25 \) kV/mm was applied yielding a saturation value of the chiral ratio of 0.85 which is significantly higher than that for the first sample and indicates an almost perfect monodomain state (95\%, comparable to earlier studies\(^{12}\)). Nevertheless, the hysteresis loop is not perfectly symmetric but shows a clear preference for negative electric polarization which corresponds to the first field the crystal sensed after cooling. \( \text{MnWO}_4 \) crystals thus possess some intrinsic preference for the multiferroic state, whose origin requires further clarification. For the time-dependent studies we chose a field of \( \pm 1.35 \) kV/mm, which is sufficiently above the coercive field in both directions.

The first set of time-dependent measurements was taken after field-cooling the sample from 20 K to 12 K with an electric field of \( \pm 1.35 \) kV/mm. The electric field was modulated with a frequency of 8 Hz and an amplitude of \( \pm 1.35 \) kV/mm, and time-resolved data were recorded every 0.5 K down to 7.5 K. Three characteristic time scans are shown in Fig. 6 b)-d). The reproducibility of the results was verified by raising the temperature to 20 K and field-cooling the sample again and by taking data with 1 K steps. The obtained data are perfectly reproducible in these two runs indicating in particular the absence of fatigue, see Fig. 7.

The entire procedure was repeated with this second crystal but starting with field-cooling in a negative field of \(-1.35 \) kV/mm. Characteristic time scans are shown in Fig. 6 e)-g) and the results of the relaxation description are given in Fig. 7. In this run the sample develops a clear preference for negative fields and shows more asymmetric behavior. The sign of the asymmetry agrees with the one observed after zero-field cooling of the virgin crystal and therefore seems to be intrinsic to this crystal. The rise times in the favorable negative field direction of this run are faster than those in the previous run, and the rise times in the unfavorable positive field direction are even slower than the previous ones. So, the field-cooling in negative fields seems to enhance the natural asymmetry of this crystal, while field-cooling in the opposite field seems to reduce it thereby yielding an almost symmetric state. However, all the general aspects of the rise times with maximum times near 10 K are again observed. In this last run the rise times in the unfavorable direction became too long to reach saturation, therefore the amplitude in the unfavorable direction diminishes towards low temperatures and exhibits a minimum around 10 K.

The time-resolved data were again analyzed with the relaxation formula (2). The exponents \( b \) of the stretched exponentials could be fitted globally for all temperatures or individually without significant differences in the rise times: they amount to 1.67/1.32 and 1.43/1.36 in the slow/fast switching processes in the first and second sequence, respectively, so that it actually is a compressed exponential behavior. Although the stretching exponent clearly depends on sample history and on the direction of the field switch the average value agrees for the two samples and the various histories studied. The average stretching exponent is found at 1.4. This exponent can be interpreted within the frame-work proposed by Ishibashi and Takagi\(^{31}\). The exponent corresponds to the dimensionality of the domain growth enhanced by one for the case of constant continuous nucleation. Therefore our data suggests a low-dimensional domain growth as it is typically observed in ferroelectrics. A distribution of pinning properties and of local rise times will decrease the fitted exponent thereby weakening the conclusion of one-dimensional domain growth, but a large exponent that is reduced by severe spread of rise times is inconsistent with our time domain data.

In Fig. 7 the rise times and amplitudes of all measurements with the second setup are combined as function.
of temperature. Qualitatively, these values agree with the results of the first experiment, see Fig. 3 and 5 but there is less difference between the up and down field directions and the rise times are slightly shorter in general. The controlled chiral component remains close to the ideal value over the entire temperature range in the second sample. Also this sample shows the faster domain response when approaching the upper and the lower boundaries of the ferroelectric phase. Additionally, the second sample displays a weak long-time-scale relaxation process which can be observed at 8 K and 10 K in Fig. 6. The main part of the chiral ration adapts to the new field in less than 10 ms, but then the chiral ratio still increases with a much lower time scale. This behavior was not observed with the other sample studied on IN12, which, however, could be switched to a lesser extent.

Due to the different initial poling (parallel and antiparallel to the intrinsic preference of the crystal) and due to the two field directions there are in total four different configurations to be considered for each of the two crystals, see the combined plot in the right panel of Fig. 7. If we average these four curves we determine rise times of 2.5, 10.5 and 3.6 ms at 12, 9.5 and 7.5 K, respectively, for the second crystal, while the rise times of the first crystal amount to 3.6, 15, and 4.5 ms at the same temperatures. The slightly slower domain reversion (roughly a factor 1.5) in the first crystal can be attributed to the lower applied field (see discussion below) so that the two sets of measurements agree quite well with each other. By averaging the four possible configurations one finds the intrinsic domain properties for this type of crystals. Note, that the two crystals were obtained from different growth processes but using the same technique.

B. Electric field and frequency dependence of the rise times

With the first experimental setup on IN12 we investigated the influence of the amplitude of the switching field by applying 1.2, 1.35, and 1.5 kV/mm with a constant repetition rate of 8 Hz, see Fig. 8. The difference for the three applied amplitudes can be easily analyzed: If we switch from the not preferred state to the preferred state (i.e. the rapid process) the field of 1.2 kV/mm already largely exceeds the minimal required field (i.e. the coercive field of the preferred state). The maximal chirality and the stretching exponents stay almost the same for all three fields, but the rise time diminishes with increasing electric field. If we switch into the not-preferred state more drastic changes occur as function of electric field. The domain distribution reaches lower saturation values at smaller fields, and, more importantly, the rise times decrease more rapidly than the inverse of the electric field, see Fig. 8. This E-field dependence of the rise times allows us to overlay the multiferroic domain behavior in the two distinct crystals.

In addition, we investigated the effect of the frequency on the switching behavior. At 10 K we switched at the following frequencies (chronological order): 10, 12, 5, 8, 20, and 40 Hz. The measured curves at 5, 10, 20, and 40 Hz are shown in Fig. 9. The system behaves as expected for a preferred state which is imprinted by the first cooling in strong applied electric fields. When we switch faster than the system is able to respond to, the saturation value of the chiral component is not reached in that field direction. The dielectric studies also observe incomplete domain switching depending on frequency and temperature. The rise times in our experiment, however, do not essentially change within the studied frequency range.

During the entire sequence of experiments with the
first setup we realized that the sample exhibits some fatigue. We compare runs which were done at 10 K and 8 Hz with different histories of the sample. As reference we use the run which was taken in the beginning of the measurement during the first temperature scan of rise-time experiments. At this first time the chirality could be flipped almost as large as in the static cycle (+0.49, −0.48) but the not preferred chirality decreased to −0.28, see Fig. 9 for ν = 5 Hz. After taking the entire frequency dependence, ending with switching at 40 Hz, all parameters stay more or less the same. This indicates a general fatigue mechanism due to the switching and the thermal cycling rather than a destruction of the sample by applying a too high frequency. After the observation of fatigue effects, we heated the sample to 20 K and cooled it again. However, the sample did not restore to its initial behavior. So we heated the sample to 120 K in the hope that such procedure would restore the sample, however, this was not accomplished. The repeated switching seems to induce defects influencing magnetic and polar order which do not heal when going far beyond the magnetic phase transition. With the second setup no fatigue was observed, as described above.

IV. CONCLUSIONS

In conclusion the time scales of controlling the magnetic chiral components by an external electric field have been studied by time-resolved polarized neutron diffraction experiments. By comparing comprehensive measurements with two different samples and with different poling history we can identify the general features of the domain switching and those which depend on the sample and on its thermal history.

In general the rise times to invert the magnetic components are slow, typically of the order of a few to several tens of milliseconds. This agrees with a measurement of second harmonic generation and in particular with a comprehensive study by dielectric spectroscopy. The magnetic response can be described by single relaxation process (only in one case we find evidence for a superposed even slower domain relaxation) and there is no indication for a fast process. We always find a weakly enhanced stretching exponent. The reversal of domains seem to be essentially controlled by a single process type which preserves the tight coupling between magnetic chirality and ferroelectric polarization. The chiral magnetism cannot be reversed faster than the ferroelectric polarization.

The peculiar temperature dependence of the rise times with a maximum around 10 K also is a general feature of the domain kinetics in MnWO$_4$. The faster response is naturally expected when approaching the upper phase transition, where ferroelectricity and the chiral components disappear continuously associated with softer excitations. However, the faster kinetics near the lower first-order phase transition is astonishing and possibly related to the increase of the anharmonic modulations upon cooling in the multiferroic phase. The second- and higher-order modulations of both, the nuclear and the crystal structure can be relevant for the effective pinning of domains in MnWO$_4$. The independent measurement on crystals of two different batches yield good agreement concerning the qualitative temperature dependence and even quantitative agreement when considering the average of the four possibilities of the electric field (relaxation field and initial poling) and taking the field strength into account.

The sign and the size of the asymmetries, which are seen in the rise times, in the saturation chiral component or in the coercive fields, clearly are sample and history dependent. Even after zero-field cooling, a finite asymmetry persists indicating an intrinsic property of the sample. Field cooling from higher temperatures seems to imprint stronger polar preferences, which can be reverted by different thermal cycling.

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While there is perfect agreement concerning the upper two magnetic transition temperatures, the first order transition between AF1 and AF2 phases seems to slightly depend on the sample, see C. Tölzer diploma thesis (University of Cologne 2012, unpublished).