Experimental report

16/09/2019

Proposal: **CRG-2573** **Council:** 4/2018

Title: Domain relaxation times in the exclusive molecular multiferroic (NH4)2[FeCl5(H2O)]

Research area: Physics

This proposal is a new proposal

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Samples: (NH4)2[FeCl5(H2O)]

Instrument	Requested days	Allocated days	From	To
IN12	5	5	26/07/2019	31/07/2019
			27/09/2019	30/09/2019
IN3	1	1	27/09/2019	30/09/2019

Abstract:

The controllability of magnetic domains by external electric-fields opens the path to possible future applications of multiferroic materials. In addition there is fundamental interest in the switchability and relaxation processes of magnetic domains in multiferroic (and antiferromagnetic) materials as so far only ferromagnetic domain switching could be studied. (NH4)2[FeCl5(H2O)] possesses qualitatively the same sequence of phase transitions as the prototype multiferroic material TbMnO3 but it is the only known partially molecular multiferroic compound. We propose to study the multiferroic relaxation times in (NH4)2[FeCl5(H2O)] as a function of electric-field amplitude and temperature by using our own stroboscopic setup for time-resolved neutron scattering measurements.

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The aim of the allocated beamtime on IN12 was to study the relaxation behavior of multiferroic domain inversion in $(NH_4)_2[FeCl_5(H_2O)]$. It had been already documented for other materials that the temperature and electric-field dependent relaxation process can be described by a simple activation and Merz's law respectively (report CRG-2290, CRG-2439, [1]), but it was unclear, whether the exclusive molecular multiferroic compound $(NH_4)_2[FeCl_5(H_2O)]$ behaves similar. For corresponding measurements of the relaxation processes, 5 days of beamtime had been allocated and the instrument has been operated in the full-polarized mode with a helmholtz-coil setup for longitudinal polarization analysis. All time-resolved data has been recorded with our own time-resolved setup, containing a high-voltage switch and a multichannel data collector.

The exclusive molecular multiferroic erythrosiderite $(NH_4)_2[FeCl_5(H_2O)]$ crystallizes in the orthorhombic spacegroup $Pnma$ with $a = 13.5221(9)\,\text{Å}$, $b = 9.9305(6)\,\text{Å}$ and $c = 6.9219(6)\,\text{Å}$ [2]. The system exhibits two subsequent magnetic phase transitions [3]. First at $T_N = 7.3\,\text{K}$ an incommensurate antiferromagentic ordering with moments pointing along a and $k_{ic} = (0\,0\,0.22)$ evolves [2,4]. At $T_{MF} = 6.9\,\text{K}$ the system undergoes a transition to a spiral arrangement with moments lying in the ac-plane but the incommensurate propagation vector remains the same. Corresponding to the inverse Dzyaloshinskii-Moriya interaction, a ferrolelectric polarization along a develops in this multiferroic phase [3]. The handedness of the spin spiral can be controlled by external electric fields. In order to sense the handedness experimentally, the chiral ratio can be measured by recording the longitudinal spin-flip channels in x direction. It corresponds to the amount of chiral signal with respect to the overall magnetic scattering signal and its sign depends on the sense of rotation of the spin spiral.

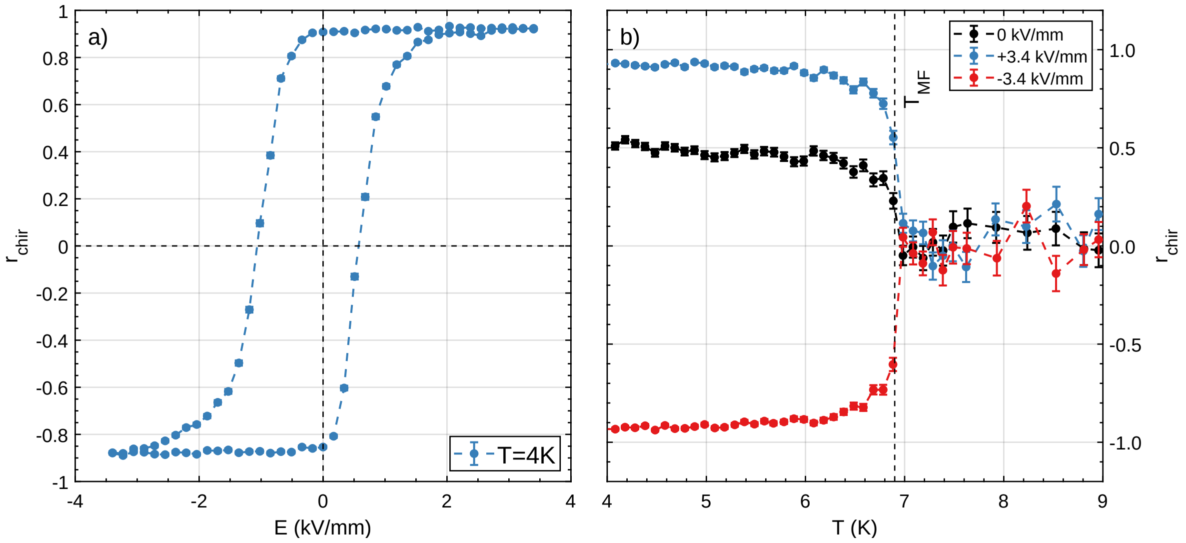

Figure 1.1: Hysteresis loop and poled chirality
The electric field dependent chiral ratio, which is displayed in both figures a) and b) has been measured at $\mathbf{Q} = (0\,1\,0.22)$. For all three sequences that are show in figure b), the system had been heated up first to $T = 9\,\text{K}$ and then the data has been recorded, while cooling the system.

$$r_{\text{chir}} = \frac{I_{x\bar{x}} - I_{\bar{x}x}}{I_{x\bar{x}} + I_{\bar{x}x}} = \frac{-i\left(\mathbf{M}_\perp \times \mathbf{M}_\perp^*\right)_x}{|\mathbf{M}_\perp|^2} \tag{1.1}$$

From equation 1.1 it becomes obvious that for maximum chiral ratios of ±1, the scattering vector has to be perpendicular to the spiral. Due to the chosen scattering plane (010)/(001), this condition cannot be fulfilled and thus, chiral ratios below the maximum values ±1 are expected even for a monodomain state. The sample itself was squeezed between two aluminum capacitor plates in order to apply high voltage to the system. For recording the time-resolved switching curves of the chiral ratio, it is essential to know the temperature dependence of the coercive field and this requires the measurement of hysteresis loops for different temperatures. Several hysteresis loops have have been recorded within the multiferroic phase and above the transition. Due to a too high coercive field, the chirality couldn't be reversed below $T = 2.5\,\text{K}$ for $E = 3.5\,\text{kV}\,\text{mm}^{-1}$ and above the transition the enclosed area of the loop is zero as expected. Figure 1.1 a) displays exemplary a recorded loop at $T = 4\,\text{K}$. One significant feature is the fact that the system possesses a preferred chiral handedness, as it can be seen by the asymmetric coercive fields of the hysteresis loop. This property is also visible for the poling sequences, visible in figure 1.1 b). It is obvious that even in zero field, the chiral signal is non-zero, while cooling the system into the multiferroic phase. Before each sequence, the sample had been heated up above T_N but it didn't affect the preference of a certain handedness during the cooling sequence. The main part of the experiment was about recording time-resolved switching curves of the chiral ratio. Figure 1.2 a) and b) display two curves for two different temperatures. It can be seen that the relaxation time in the millisecond range varies with temperature. Also visible is the asymmetric switching behavior, which was already expected from the previous recorded asymmetric hysteresis loops.

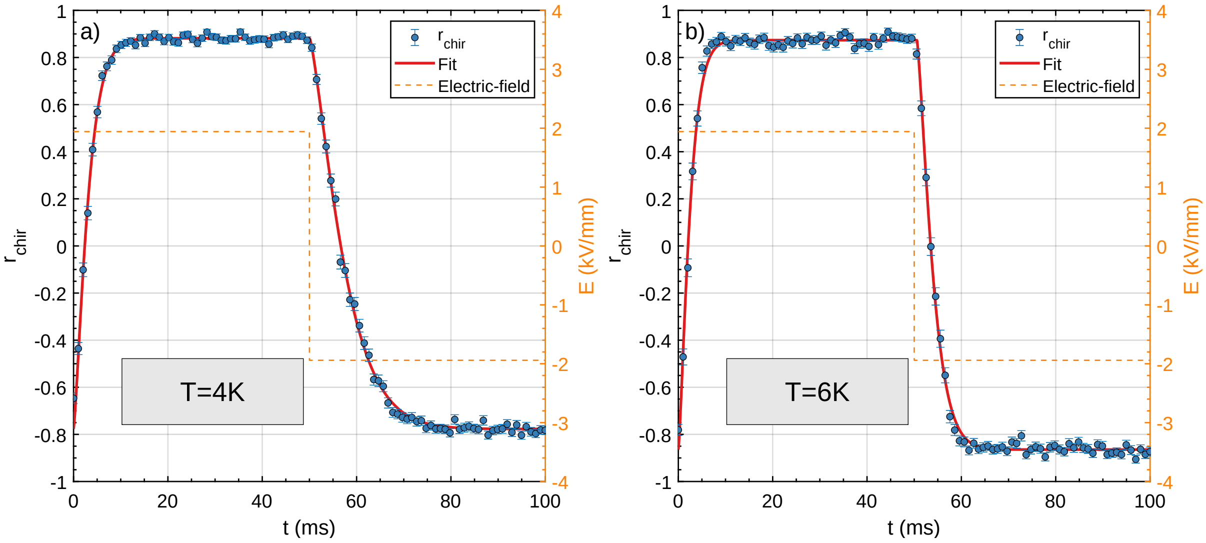

Figure 1.2: Time-resolved switching curves
Both figures display time resolved switching curves of the chiral ratio, which have been recorded at $\mathbf{Q} = (0\,1\,0.22)$ for different temperatures. The red curve corresponds to a fit of the recorded data in blue. A dashed orange line visualizes the applied electric field.

All curves can be fitted by a hyperbolic approximation of the heavyside function from which the relaxation time for both directions can be extracted. The analysis of the recorded temperature and electric field dependent relaxation times is subject of current work and will answer the question, whether the relaxation follows also a simple activation description or not. Up to this point, one astonishing feature is the tiny time range of evaluated relaxation times. Where in other systems (report CRG-2290, CRG-2439, [1]) the relaxation can be followed over several decades in time, the relaxation in $(NH_4)_2[FeCl_5(H_2O)]$ varies only in the millisecond range for different temperatures and electric field amplitudes. During the last part of the experiment, time-resolved scans over a magnetic Bragg peak have been recorded, while switching the electric field periodically. Figure 1.3 shows the resulting three dimensional plot for one single spin-flip channel along x.

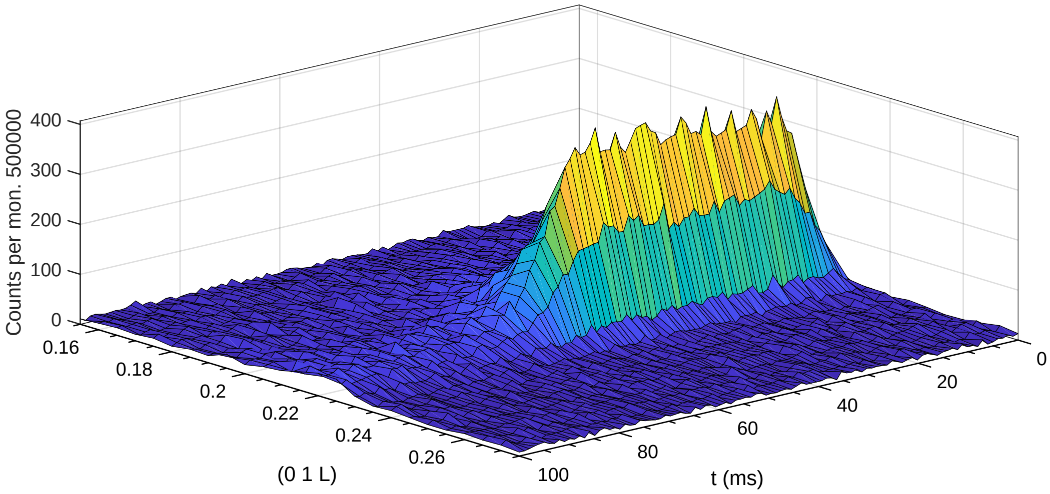

Figure 1.3: Time-resolved scan over magnetic Bragg peak
This figure illustrates a time-resolved $\mathbf{Q}$-scan over the magnetic reflection $\mathbf{Q} = (0\,1\,0.22)$ while switching the applied electric field periodically between its field amplitudes of $\pm 1.94\,\mathrm{kV\,mm^{-1}}$

We would like to thank for the allocation of this beamtime and especially we would like to thank our local contact Karin Schmalzl for on-site support. We were able to collect a sufficient amount of data in order to analyze and investigate further the dynamics of multiferroic switching.

References

[1] M. Baum, et al. *Phys. Rev. B*, 89:144406, Apr 2014. doi:10.1103/PhysRevB.89.144406.
[2] J. Rodriguez-Velamazán, et al. *Scientific Reports*, 5, 03 2015. doi:10.1038/srep14475.
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