Experimental Report

09/01/2014

Proposal: **5-42-327** **Council:** 4/2012

Title: Selection of multiferroic monodomains in Mn2GeO4

This proposal is a new proposal

Research Area: Physics

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Samples: Mn2GeO4

Instrument	Req. Days	All. Days	From	To
D3 CPA	6	11	09/11/2012	15/11/2012
			30/07/2013	05/08/2013

Abstract:

Mn2GeO4 has recently emerged as a rare example of a magnetically-driven multiferroic (MF) material that exhibits spontaneous ferromagnetic and ferroelectric orders. Current experimental evidence suggests that these two orders are directly coupled, and we recently proposed a model for which the coupling is mediated by microscopic Dzyaloshinskii-Moriya interactions. Here we propose to test our proposed model by determining the relationship between the sign of the magnetization and that of electric polarization under various poling-field conditions. Monodomain MF states will be selectively created by using proper poling procedures involving both magnetic and electric fields, and subsequently be characterized by spherical neutron polarimetry using CRYOPAD installed onto either D3 or IN20. We expect that our results will provide a unique demonstration of the complete control of a MF state that stems from the rich magnetic structure underpinning the MF phase.

Experimental Report 5-42-327: Selection of multiferroic monodomains in $\mathbf{Mn_2GeO_4}$

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Introduction

Mn_2GeO_4 is a rare example of a bulk material that, below 5.5 K, displays ferromagnetic and ferroelectric orders that are both spontaneous and point along the **c**-axis [1, 2]. Bulk measurements show the magnetic field-dependence of both the ferroelectric polarisation and ferromagnetic magnetisation within the MF phase, i.e. the $P - \mu_0 H$ and $M - \mu_0 H$ hysteresis loops, to display very similar coercive fields [1]. These results already imply a non-trivial relation between the two ferroic orders when thinking in terms of the magnetic domain structures. Single crystal neutron diffraction was employed to determine the origin of the ferroic properties, and it was discovered that the magnetism underlying the MF state is multicomponent; the ferromagnetism arises from the canting of a simple commensurate **Q**=(0,0,0) antiferromagnetic component, while the ferroelectricity is generated by an incommensurate spin spiral with **Q**=(0.14(1),0.21(1),0) in zero magnetic field. All of our experimental evidence suggests that these two magnetic structure components may be superposed to form a multi-**Q** fan-like spin structure. Moreover, the superposition of the two magnetic structure components provides a means for the coupling between commensurate and incommensurate domains, and hence ferromagnetism and ferroelectricity. To describe how the domains of the commensurate and incommensurate parts of the magnetic structure may combine, we proposed a simple model where the coupling is mediated by microscopic Dzyaloshinskii-Moriya interactions [1].

In this experiment on D3, the aim was to test the proposed coupling model by determining the relationship between the sign of the ferromagnetic magnetization and that of electric polarization under various poling-field conditions. According to bulk measurements [3], proper poling procedures involving both magnetic and electric fields can be implemented to create multiferroic monodomain states in Mn_2GeO_4. The experimental goal was to provide a hitherto unique demonstration of the complete control of a rare type of MF state that stems from a rich underlying magnetic structure.

Experimental Method

Large single crystal samples of Mn_2GeO_4 are grown using the floating zone method [2]. For the present experiments, we prepared a single crystal sample of thickness 1 mm along the ferromagnetic and ferroelectric **c**-axis, and cross-section $\sim$ 20 mm^2 in the **a-b** plane. A horizontal **a-b** scattering plane was chosen to provide simultaneous access to magnetic Bragg peaks of both the commensurate and incommensurate orders.

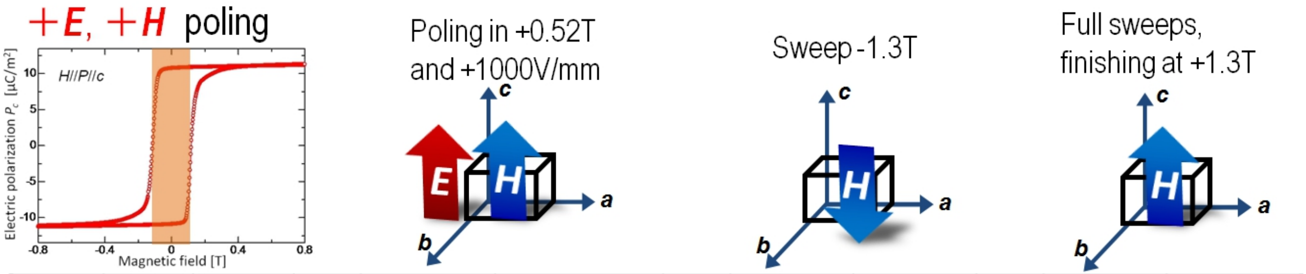
Until now, our experiment was done over two separate beamtimes, and each made use of a different sample stick to apply electric fields across the sample. For the first experiment, the voltage was applied across the sample using a high voltage cable silver-pasted to the top of the sample, and with the ground electrode in direct contact with the sample stick. For the second experiment, a stick was used where the plate-like sample was placed between two parallel plates across which the voltage was applied. For both of these sample sticks, the sample was under high vacuum to allow the application of electric fields at liquid helium temperatures without electrical breakdown. Each of the electric field setups was loaded into the D3 thin-tail cryostat. To apply magnetic fields, the cryostat could be installed into a 1.3 T electromagnet with the magnetic field direction vertical, and also along the **c**-axis.

For both experiments, once the sample was poled through the MF transition temperature for a certain magnetic and electric field condition, the cryostat was removed from the electromagnet and installed into CryoPAD on D3. This manipulation of the cryostat could be done without disturbing the base temperature of the sample, which was typically between 3.3 and 3.8 K. To characterise the magnetic order in the sample, a standard set of polarimetry matrices and magnetic intensities, were recorded for both commensurate and incommensurate reflections. The results of these measurements shed light on both the commensurate and incommensurate domains in the sample, the populations of which are expected to display a clear dependence on the poling conditions.

Results

Since the incommensurate wavevector of the MF spin spiral is in general **Q**=(q_h,q_k,0), there are two k-domains and Bragg peaks also exist for **Q**=(q_h,-q_k,0) wavevectors. Therefore, for a certain poling condition, a series of polarimetry matrices were recorded for peaks within in each k-domain. Many of the measurements in the two experiments were aimed at determining the magnetic domain structures at different points of the $P - \mu_0 H$ and $M - \mu_0 H$ hysteresis loops, and after different signs of the initial poling fields.

Here, we must point out that we found poling below 5.5 K in simultaneously applied electric and magnetic fields to



q_h	q_k	q_l		P_{yx}	P_{zx}		P_{yx}	P_{zx}		P_{yx}	P_{zx}
1.86	0.79	0		-0.26(1)	-0.31(1)		0.49(1)	0.49(1)		-0.41(1)	-0.43(1)
0.14	1.21	0		0.42(1)	0.41(1)		-0.39(1)	-0.39(1)		0.53(1)	0.51(1)
0.14	0.79	0		0.45(1)	0.39(1)		-0.41(1)	-0.38(1)		0.55(2)	0.51(2)
-0.14	1.21	0		-0.29(1)	-0.31(1)		0.47(1)	0.48(1)		-0.39(1)	-0.43(1)

Figure 1: Experimental results obtained from D3 with CryoPAD. The top row shows the $P - \mu_0 H$ loop explored by our experiments, and then the sequence of measurement conditions (explained in more detail in the text). The table shows the measured P_{yx} and P_{zx} polarisation matrix elements for two incommensurate Bragg peaks from each k-domain, and for each measurement condition. After the initial poling, the measurement temperature remained at 3.4 K.

be experimentally challenging. Consequently, a significant portion of the first beamtime was spent determining how the poling should be done, to both avoid electrical breakdown, and so that each of the applied fields was sufficiently large so as to create a measurable change in the magnetic domain populations. The time spent optimising the poling procedure somewhat limited the final volume of data that we could obtain in this first experiment, but nonetheless the data that we did obtain showed the experiment to be feasible, and that our main questions can be tackled experimentally.

Below we outline an important result achieved during the first beamtime, and which is summarised by Fig. 1. In the top half of the figure, the $P - \mu_0 H$ hysteresis loop is shown, followed by the experimental sequence of the applied fields for each measurement. In detail this sequence was:
i) the sample was initially poled to 3.5 K in $\mu_0 H = +0.52$ T and $E = +1000$ V.mm^{-1}. Once this was done, both fields were removed and the cryostat installed into CryoPAD for the polarimetry measurements.
ii) The cryostat was then re-installed into the magnet and, whilst always remaining at base temperature, the $\mu_0 H$ was swept to -1.3 T then back to zero. The cryostat was then installed back into CryoPAD for further measurements.
iii) The cryostat was installed again into the electromagnet, and $\mu_0 H$ was swept between +1.3 T and -1.3 T four times, finishing on +1.3 T and then going to zero. Subsequently, the cryostat was re-installed back into CryoPAD for the measurements.

The bottom half of Fig. 1 shows measurements of the polarization matrix elements P_{yx} and P_{zx} done at two incommensurate Bragg peaks within each k-domain. These particular matrix elements, P_{yx} and P_{zx}, are sensitive to chiral scattering from the spin spiral magnetic structures. The elements are non-zero when there is unequal population of spiral-handedness domains within each k-domain; our measurements shown in Fig. 1 reveal that the spiral-handedness populations for the initial poled state can indeed be controlled. Furthermore, P_{yx} and P_{zx} are shown to change sign upon sweeping the magnetic field, which amounts to the magnetic field control of the IC spiral-handedness within each k-domain.

From these measurements, using our model for the spiral magnetic structure we were able to deduce the population of spiral-handedness domains in each k-domain, and for each measurement condition. Polarization matrices were also measured for a few commensurate peaks but, as expected from the projection of magnetic interaction vector in the (h,k,0) plane, it was not possible to determine the change in domain populations. The commensurate domain populations can be in fact be determined with a sample aligned in the (0,k,l) plane, but there was insufficient time available to do this in the first beamtime. Nonetheless, a short survey of the magnetic Bragg intensities in (h,k,0) plane clearly evidenced the domain populations for both commensurate and incommensurate magnetic structure components to be sensitive to the poling and field sweeping protocol, and thus that further measurements should be carried out.

Indeed, the study of the commensurate magnetism in an alternative scattering plane was a particular goal of the second beamtime conducted using the alternative sample stick. We began this second experiment again with the sample in the (h,k,0) horizontal plane, to take some overlap/base-line measurements that could be compared with the previous experiment. Unfortunately however, shortly after the experiment began, the power supply for the electromagnet failed and we were left only able to apply electric fields to the sample (which for electric fields up to ~ 3 kV.mm^{-1}

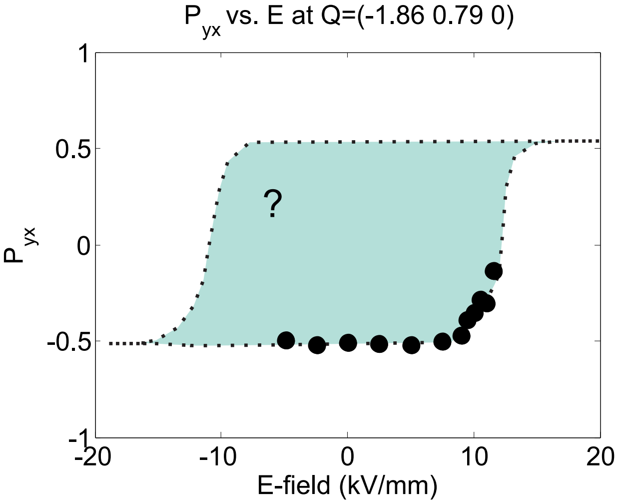


Figure 2: The electric field dependence of the polarization matrix element P_{yx} at the incommensurate Bragg peak **Q**=(-1.86,0.79,0). The experimental data are shown as filled symbols. The dashed line perhaps indicates the possible hysteresis loop.

has been done in detail by us before previously at PSI [3]). This unfortunate equipment failure meant that we were not able to explore further the response of the sample under simultaneously applied electric and magnetic fields.

Nonetheless, we used the remaining time in an effort to determine the necessary experimental conditions for measuring the ferroelectric hysteresis loop, i.e. the $P-E$ loop. This has yet to be done for $\mathrm{Mn_2GeO_4}$ due to the huge electric fields seemingly necessary, which likely arises due to a combination of the low temperature and the complex multicomponent magnetic structure. The measurement of the $P-E$ loop by polarimetry is well-known to be done by obtaining the size and sign of either P_{yx} or P_{zx} at incommensurate Bragg position as a function of electric field.

Using the present experimental apparatus and sample, voltages up to 12 kV could be applied and so electric fields of $\sim$ 12 kV.mm^{-1}. A lot of effort was made in determining the optimum approach for measuring the $P-E$ loop. Finally, we poled to base temperature in a large negative electric field of -4.9 kV.mm^{-1}, then heated until just below the multiferroic transition temperature. Subsequently, we measured the P_{yx} polarisation matrix element as a function of sweeping positive electric field, and at the incommensurate position **Q**=(-1.86,0.79,0). The resulting curve is shown in Fig. 2, where it can be seen that only part of the expected loop could be measured. Nonetheless, this preliminary result provides tantalising evidence that the ferroelectric domains in the sample are indeed switchable using just the electric field. Following on from this, the consequence of the switching behaviour on the commensurate component of the magnetic structure remains an important open question that needs to be addressed.

Summary

To summarize our project thus far, we have used D3 with CryoPAD to study the detailed magnetic and electric field dependence of the magnetic domain structures in the ferromagnetic ferroelectric phase of $\mathrm{Mn_2GeO_4}$. In our first experiment, we finalised a protocol to successfully pole a sample in simultaneously applied magnetic and electric fields. Our measurements revealed that the spiral-handedness in the k-domains of the incommensurate order can be controlled by sweeping the magnetic field at low temperature. However, further measurements are required to discover the effect on the commensurate domain populations, which will allow us to unambiguously identify the response of the multicomponent magnetism in each magnetoelectric domain to both magnetic and electric fields.

In our second experiment, due to a failure of the electromagnet we were unable to explore the open questions remaining from the first experiment. Nonetheless, we were able to get a handle on the experimental conditions that will be necessary to measure the first $P-E$ hysteresis loop in this material. By doing so, further questions arise concerning the behaviour of the commensurate part of the magnetism, and so the ferromagnetism, and which we aim to address by similar experiments in the near future.

References

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[3] T. Honda *et al.* (in preparation) (2014)