Magnetic phase diagram and ordered ground state of GdMn$_2$O$_5$ multiferroic studied by x-ray magnetic scattering

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Abstract. The magnetic structure of multiferroic GdMn$_2$O$_5$ is studied by x-ray magnetic scattering, both off resonance and in resonant conditions at the Gd L$_{III}$ edge. Temperature dependence of magnetic Bragg reflections shows an initial incommensurate (ICM) ordering appearing at $T \sim 40$K with magnetic propagation vector $\mathbf{k}_{ICM} \sim (0.49, 0, 0.18)$ which condenses at $T \sim 33$K in a commensurate (CM) wave vector $\mathbf{k}_{CM} = (\frac{1}{2}, 0, 0)$. In the CM phase Gd$^{3+}$ ions appear to order spontaneously at the same temperature as Mn ions. Azimuthal scans allowed for the precise determination, from x-ray magnetic scattering only, of the orientation and magnitude of the Gd$^{3+}$ magnetic moments. The Gd$^{3+}$ magnetic isotropy allows for the Gd ions to mimic the Mn$^{4+}$ magnetic sublattice via Gd-Mn-Gd superexchange interactions.

1. Introduction

Spin-driven ferroelectrics have attracted much interest due to the possibility of controlling their electric (magnetic) polarization by applying a magnetic (electric) field[1, 2]. Over the last few years, the experimental and theoretical studies of very diverse materials allowed to identify several magnetoelectric coupling mechanisms at play, driven for example by symmetric and antisymmetric magnetic exchange terms or single-ion effects. In the so-called symmetric exchange-striction model, polar displacements are due to a structural relaxation induced by competing Heisenberg terms ($J_{ij} S_i \cdot S_j$) in the magnetic Hamiltonian. This mechanism can lead to large electrical polarization ($\mathbf{P}$) in type-II multiferroics (compared with that of proper ferroelectrics such as BaTiO$_3$ is still minuscule) and has been proposed in the case of the RMn$_2$O$_5$ compounds (R=rare-earth, Y,Bi)[3], Ca$_3$CoMnO$_6$[4] and the manganite E-phase[5]. Of importance here is that this model maximizes $\mathbf{P}$ for commensurate magnetic order and collinear spins.

The RMn$_2$O$_5$ compounds have been extensively studied since the seminal work on the Tb analogue showing that $\mathbf{P}$ can be reversed by an applied magnetic field[6]. For this class of
In the present article, we report on the detailed magnetic structure of GdMn₂O₅ and on the use of x-ray magnetic scattering to fully determine the magnetic structure in this compound. This work is also motivated by the absence of spin-orbit coupling at first-order for Gd³⁺, (4f⁷ electronic configuration) and its larger ionic radius with respect to known members (Tb, Ho, Er, Dy, Tm) and by the reported observation of ferroelectric behaviour together with a large spontaneous polarization (Pₐ >3600 μC/m²) [8, 9] at low temperature. By combining x-ray magnetic scattering (XMS) data, collected off-resonance and at the Gd L_{III}-edge, we derive the complete magnetic phase diagram. We show that an incommensurate phase with wave-vector \( \mathbf{k} = (0.486, 0, 0.18) \) below \( T_{N1} \sim 40\text{K} \) uniquely collapses to a commensurate phase \( \mathbf{k} = (\frac{1}{2}, 0, 0) \) below \( T_{N2} \sim 33\text{K} \), without any further change of wave-vector below \( T_{N2} \). Unlike any compounds of the same series, magnetic ordering of the Gd site follows a proper order parameter below \( T_N = 33\text{K} \), without any further change of wave-vector below \( T_{N2} \). Unlike any compounds of the same series, magnetic ordering of the Gd site follows a proper order parameter below \( T_N = 33\text{K} \), without any further change of wave-vector below \( T_{N2} \). Under any related compounds. In addition we report the investigation of the magnetic domain topology of GdMn₂O₅ as function of electric field. We show maps of the crystal’s surface in the \( ac \) plane on electric field switching along the \( b \) crystallographic direction. These maps evidence the evolution of the magneto-electric domains as function of the applied electric field.

2. Experimental

A high quality single crystal (1.2x0.9x0.5mm³) of GdMn₂O₅ grown using floating zone method [10] was used for the x-ray magnetic scattering experiment, performed at the I16 beamline (Diamond Light Source Ltd.) [11, 12]. The sample was mounted on the beamline Kappa diffractometer in a closed circle refrigerator with base temperature of \( \sim 5\text{K} \). The crystal was oriented with the diffraction face perpendicular to the \((110)\) direction (Fig. 1). The azimuthal angle reference \( (\psi = 0) \) is defined when the \((100)\) reflection is in the scattering plane and its projection onto the incoming beam parallel to it. The diffractometer was operated in the vertical-plane scattering mode with an azimuth setup to allow for a 360° sample rotation about the scattering vectors. In this geometry the natural polarization of the incident beam is perpendicular to the scattering plane \( (\sigma) \). The integrated intensity of the reflections was measured using either a Dectris Pilatus 100K area detector and/or an avalanche photodiode point detector. In the latter case, the polarization of the reflected beam was linearly analyzed by rotating the scattering plane of a mosaic crystal chosen to have a Bragg angle close to 90° at the energy of interest (Al (220) at 6.4 keV, and Au (222) at 7.255 keV). The measured Bragg intensities have been corrected for self-absorption and Lorentz factors, multiplying them by the factor

\[
A(Q, \psi) \cdot L(Q) = \left[ 1 + \frac{\sin \alpha(Q, \psi)}{\sin \beta(Q, \psi)} \right] \cdot \sin 2\theta(Q) \quad \text{where } \alpha(Q, \psi) \text{ and } \beta(Q, \psi) \text{ are the incident and exit angles with respect to the crystal surface. To separate the contribution of the Gd from the Mn one, the photon energy was tuned close to the } E_{\text{res}}(\text{Gd L}_{III}-\text{edge}) = 7.255 \text{ keV. In this condition}
\]
Figure 1. (Color online) A schematic diagram of the experimental layout. Sample mounted with the (110) surface cut in diffraction conditions.

a very large (factor \(\sim 40\)) enhancement (Fig. 2) of the magnetic scattering was observed which allowed to ascribe the observed signal entirely to the Gd magnetic moments. A different experimental configuration has been used to collect magnetic domain maps and apply an electric field along the \(b\) direction. The sample was rotated and mounted on a suitable sample holder with the \(ac\) plane in scattering conditions. Diamond phase plates have been used to select circular right and circular left light polarization of the incident x-ray beam and the beam size of 195x32 \(\mu m^2\) has been reduced, using slits, to a \(\sim 50x50\) \(\mu m^2\) beam footprint on the sample surface. A Cu220 crystal has been used to analyse the scattered light in off-resonant conditions at 6.4 keV.

3. Results and Discussion

GdMn\(_2\)O\(_5\) crystallizes in the centrosymmetric \(Pbam\) space group. Manganese ions are found in two oxidation states, Mn\(^{4+}\) (Wyckoff position 4f, 0,0.5,0.2551) and Mn\(^{3+}\) (Wyckoff position 4h,0.4118,0.3518,0.5), respectively in octahedral and square-pyramidal environments. The octahedra share edges to form chains along the \(c\)-axis. In the \(ab\)-plane, Mn polyhedra share edges and corners to form layers that can be viewed as an alternate stacking along \(b\) of ziz-zag \(...\text{Mn}^{4+}\text{-Mn}^{3+}\text{-Mn}^{3+}\text{-Mn}^{4+}\,...\) chains running along the \(a\)-axis. The Gd\(^{3+}\) cations form GdO\(_8\) polyhedra which are located on position 4g (0.1395,0.1716,0) and separate the adjacent "Mn" \(ab\)-layers.

The sequence of magnetic phase transitions of GdMn\(_2\)O\(_5\) as shown in Fig. 2, has been obtained by sampling a large area of reciprocal space using an area detector. Additional Bragg reflections appear below 40K (red triangles in fig. 2), and can all be indexed by the incommensurate propagation vector \(\mathbf{k}_{ICM} \sim (0.49 0 0.18)\). It is important to note that the observation of two peaks at \((k_x,0,k_z)\) and \((1-k_x,0,k_z)\) confirms that the structure is also incommensurate along \(x\), albeit the deviation from 0.5 is small. Below \(T_{N2} \sim 33K\), \(k\) locks at
the commensurate value \( k_{CM} = (1/2, 0, 0) \). In the commensurate phase in the vicinity of \( T_{N2} \), the temperature dependence of the magnetic peaks intensities, shown in Fig. 2, are adequately fitted with a power law (critical exponent \( 2\beta \) since the intensity is proportional to the square of the magnetization). The critical exponents measured in non resonant and resonant conditions are identical within the experimental error, respectively \( \beta = 0.26 \pm 0.02 \) and \( \beta = 0.29 \pm 0.03 \) [13]. This critical behavior indicates a unique order parameter with contribution from both the Gd and Mn magnetizations. This is in contrast to the observed induced magnetic ordering (secondary coupled order parameter) of Ho, Tb and Er observed in other compounds of the same family [14, 15].

The azimuthal dependence of five magnetic reflections measured in resonant conditions at \( T=5K \) (fig. 3(a)) has been used to derive a model for the magnetic structure of the Gd sublattice. In the dipolar approximation of the resonant case, the scattering is observed only in the rotated channel \((\sigma \pi')\) and the scattering amplitude \( f \) for a magnetic Bragg peak at momentum transfer \( Q \) and azimuth \( \psi \) is given by[16]:

\[
J_{\text{res}}^{\sigma \pi'}(Q, \psi) \propto k' \cdot S_{Gd}(Q, \psi),
\]

considering only the lowest order term, where \( k' \) is the scattered wave-vector and \( S_{Gd} \) the Gd magnetic structure factor. The technique probes indirectly the magnetic order of the f-electrons through the polarized Gd d density of states, as the d-f hybridization is allowed by the absence.
Figure 3. (Color online) Azimuthal dependence of the magnetic Bragg peak intensities at 5 K. The azimuth value is given with respect to a reference in the (1 0 0) direction. Upper panel: magnetic Bragg reflections at resonance (Gd L_{III} edge). The symbols containing the error bars show the experimental data points. The straight lines are fits to the data. Inset: Energy dependence of the magnetic reflection (2.5 3 0) (full circles) and of the fluorescence background (open circles) around the Gd L_{III} resonance energy. Lower panel: (2.5 3 0) reflection in non resonant condition at 6.4keV, in the $\sigma\sigma'$ (open circles) and $\sigma\pi'$ (full circles) channels. Error bars are contained in the spot size.
of inversion symmetry at the Gd site. The azimuthal scans present a two fold periodicity with maxima at positions close to \(\psi=0\) and 180\(^\circ\), which given the azimuthal reference in the (100) direction, indicates that the Gd moments are approximately aligned along the crystallographic a-axis. The Gd sublattice magnetic configuration and its magnetic symmetry were determined empirically by least-square refinements of all azimuthal scans considered simultaneously. There is a unique solution for which the Gd moments (labelled 1-4 in Fig. 5) are oriented in the \(ab\)-plane and related by the time-reversed two-fold rotation axis along \(b\). A further refinement imposing this symmetry restriction lead to excellent results as shown in Fig. 3(a). For the magnetic structure stabilization, given the order parameter in the special direction (a,0), two irreducible representations \((X_1,X_2)\) are allowed. The full magnetic space group found, which corresponds to \(X_2\), is \(P_a b_2 a\) (\(P_{a\!\!c\!a\!2_1}\) in conventional International Tables for Crystallography settings). The proposed symmetry allowed magnetic mode (out of the six allowed ones spanning \(X_1\) and \(X_2\)), is uniquely consistent with Gd moments in the \(ab\)-plane and a ferroelectric axis along \(b\), as observed experimentally. With this symmetry, only the moments on site Gd1 and Gd2, on one hand, and Gd3 and Gd4, on the other, are related by the two-fold rotation, while the two sets are unrelated due to the loss of inversion symmetry. Finally, temperature dependent (T=5, 15, 25, 31K) energy scans of the resonant signal and of the azimuthal scans (not shown) suggested an unchanged Gd magnetic configuration.

The complete magnetic structure, Mn and Gd magnetic ordering and the relative phase between Gd and Mn modulations, was probed using non-resonant magnetic scattering (NRMS). In this case, the azimuthal dependence of the scattering amplitudes\([16, 17, 18]\) in the \(\sigma\sigma'\) and in the \(\sigma\pi'\) channels used to fit the data are:

\[
\begin{align*}
  f_{\sigma\sigma'}^{\text{nres}}(Q, \psi) &\propto (\mathbf{k} \times \mathbf{k}') \cdot \mathbf{S}(Q, \psi), \\
  f_{\sigma\pi'}^{\text{nres}}(Q, \psi) &\propto (1 - \mathbf{k} \cdot \mathbf{k}') \mathbf{k} \cdot \mathbf{S}(Q, \psi)
\end{align*}
\]

where \(\mathbf{k}\) is the incident wave-vector and \(\mathbf{S}\) is the magnetic structure factor including Gd and Mn contributions. Due to the long collection time, only a single off-resonant azimuthal scan could be collected in the full azimuthal range, preventing to perform an unconstrained refinement including all Mn moments. Instead, the magnetic configuration of the Mn in the \(ab\) plane was fixed to that found for other commensurate structures of the RnMnO\(_5\) compounds, the main difference being caused by the different magnetic periodicity along \(c\). As shown in Fig. 5, Mn\(^{3+}\)-Mn\(^{3+}\)-Mn\(^{3+}\)-Mn\(^{3+}\) form zig-zag AFM chains along the \(a\)-axis, and the moments are tilted by \(\sim 20^\circ\) with respect to the crystallographic \(a\)-direction, pointing along the axis of the pyramidal Mn\(^{3+}\) site. Such configuration on its own does not account well for the observed off-resonance signal, in particular under-calculating the intensities in the \(\sigma\pi'\) channel. However, by including the Gd contribution derived from the RMS work, the off-resonance scan can be adequately fitted, as shown in Fig. 3. Despite the fact that the relative orientation of the Mn moments with respect to the Gd moments could be inferred from the NRMS data since the total magnetic structure factor is sensitive to the relative phase, the lack of available data (only one scanned reflection) does not allow to uniquely discern between a ferromagnetic or antiferromagnetic Gd-Mn alignment. Preliminary neutron scattering performed on a recently isotropically substituted GdMn\(_2\)O\(_5\) crystal confirms, as reported in Fig. 5, the Gd moments are arranged almost antiferromagnetically relative to the neighboring Mn\(^{3+}\) moments (pyramidal sites). By supposing that the Mn ordered moments are saturated at the spin-expected value of 3\(\mu_B\) (octahedral site, \(S=3/2\)) and 4\(\mu_B\) (pyramidal site, \(S=2\)), one obtains, from the NRMS data, an ordered moment for Gd\(^{3+}\) at 5K of \(\sim 5.14(4)\mu_B\) and \(\sim 4.75(4)\mu_B\) for Gd1/Gd2 and Gd3/Gd4 respectively. The Gd ordered moment is much larger than that found for R=Tb or

\[1\] Note that since the wave-vector doubles the magnetic unit-cell along \(b\), an equivalent solution relates all these moments by a two-fold axis (without time reversal).
In order to observe the magnetic domains and their evolution upon application of an external electric field, the sample was rotated and electrodes were applied close to the crystallographic $b$ direction. The sample has been aligned with the $[0.5, 0, 2]$ reflection in scattering conditions and it has been cooled to 5 K, with electric fields of + and - 1100 V/mm. The $ac$ surface have been mapped by using incident circularly polarised light and by analysing the polarization of the scattered signal[19]. The ratio between circular right and circular left light has been measured in non-resonant conditions and plotted as function of the position on the sample surface. The resulting magnetic domain maps are shown in figure 4(a) and 4(b)). The data show that the magnetic domain populations was partially switched with the reversal of electric field but not fully reversed. We believe the combination of $\sim 25^\circ$ tilt of the sample $b$ axis with respect to the electric field direction and the maximum electric field generated by the Keithley electrometer used during this experiment wasn’t enough to fully control the magnetic domain population in this compound. The domains size appear to be of the order of $\sim 100$ microns and the larger ones (top left and centre right of fig 4, appear to act as pinning domains, blocking the domain population changes in the nearby regions.

4. Conclusions
The magnetic structure stable below $T_{N2}$ of GdMn$_2$O$_5$ is the simplest of the series, and yet supports ferroelectricity along the $b$ crystallographic axis. Although GdMn$_2$O$_5$ shows similarities with respect to other RMn$_2$O$_5$ compounds in the most polar phase, such as a locking of the propagation vector at half along the $x$ direction, with the formation of AFM chains along the $a$-axis with constant moment amplitude, this is the only system for which $k_z=0$. The direct consequence of this periodicity is the production of a FM stacking along $c$ of the adjacent AFM planes. This effect can be explained by two phenomena: firstly, eight-coordinated Gd$^{3+}$ has a
slightly larger ionic size (1.193 Å) than other rare-earth (Tb=1.18 Å, Dy=1.16 Å, Ho=1.15 Å, Er=1.14 Å), which affects the Mn$^{4+}$-Mn$^{4+}$ direct exchange interaction through the Gd layer. Since longer Mn-Mn inter-atomic distances promotes direct exchange (in manganese metals the crossover between AFM and FM is $\sim$2.83 Å), the argument seems to hold for GdMn$_2$O$_5$, where the Mn-Mn distance is 2.89 Å. There is however a notable exception for BiMn$_2$O$_5$ which, despite an even larger ionic radius on the R site, displays antiferromagnetic stacking ($k_z = 1/2$). Secondly, based on the absence of first-order orbital momentum on the Gd site (4f$^7$ electronic configuration), it can be assumed that magnetism on the Gd site is very isotropic, and that the Gd moment direction will simply align along the spin of its strongest interacting neighbor.

Since the Gd moments are nearly collinear with the first neighbor Mn$^{3+}$ spins (Gd-Mn distance $\sim$3.303 Å), the latter explanation is in excellent agreement with experimental observations. The situation is very different in analogues with non-quenched orbital momentum displaying non-collinear arrangements of the R moments[10]. Due to this simple commensurate structure, unlike in any other ferroelectric RMn$_2$O$_5$, in GdMn$_2$O$_5$ the rare earth exhibit a large ordered moment in every layer. This unique magnetic configuration has important consequences for the ferroelectric behavior: since the Gd spin configuration on its own breaks inversion symmetry, one expect a finite contribution to the polarization along $b$ from the coupled polar ionic displacements allowed by symmetry on the Gd site and coordinated oxygens. In the presence of a large ordered moment on Gd, one can anticipate a large contribution to the total polarization, provided that all polar displacements (Mn,O,Gd) are in phase. In this scenario, the Gd-Mn symmetric exchange striction, together with the Mn-Mn exchange striction mechanism, could lead to very large ferroelectric polarizations, as experimentally observed [9]. Ab-initio calculations, that will be facilitated by the small magnetic unit-cell, should shed light on the respective contributions of different ions to the total electric polarization, and separate the part imputable to the Gd magnetic ordering.

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Figure 5. (Color online) Magnetic structure of GdMn$_2$O$_5$ projected in the $ab$ plane. The structure is shown in two unit-cells, marked by thin black lines, along the $a$- and $b$-axis. The green (small and light grey), red (grey) and blue (black) arrows represent magnetic moments on $Mn^{4+}$, $Mn^{3+}$ and $Gd^{3+}$ sites respectively. Corresponding Mn-O polyhedra are shown with the same colors.

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