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Nature of the Magnetic Order and Origin of Induced Ferroelectricity in TbMnO₃


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The magnetic structures which endow TbMnO₃ with its multiferroic properties have been reassessed on the basis of a comprehensive soft x-ray resonant scattering (XRS) study. The selectivity of XRS facilitated separation of the various contributions (Mn L₂ edge, Mn 3d moments; Tb M₄ edge, Tb 4f moments), while its variation with azimuth provided information on the moment direction of distinct Fourier components. When the data are combined with a detailed group theory analysis, a new picture emerges from the work of Kajimoto et al. [11], magnetic superlattice reflections were observed at (0, τ, l) and (0, 1 − τ, l) type positions with l integer and τ = 0.27. At T₉₂ = 28 K there is a second magnetic transition which coincides with the appearance of a spontaneous electric polarization along the c axis. Finally, the Tb ions order below a third transition at T₉₂ = 7 K. Kenzelmann et al. [4], developed an appealing model of the magnetic structure whereby above T₉₂ the magnetic moments on the Mn ions are polarized along the b axis in an incommensurate, collinear fashion, and argued that at T₉₂ the magnetic moments on the Mn sites rotate to form an elliptical cycloid in the bc plane. This noncollinear structure causes a finite ferroelectric polarization along the c axis. Hard x-ray scattering experiments have been performed on TbMnO₃ [13–15], and report both nonresonant and resonant magnetic satellites at (0, τ, l), (0, 1 − τ, l) type locations. However, for these experiments the resonances used do not provide direct information on the localized Mn 3d or Tb 4f states which are of principal interest for understanding the magnetic order [16–18]. The soft x-ray resonant scattering experiments reported here overcome this limitation by probing these states directly [19–23].

In previous work, neutron diffraction measurements [4,11,12] have shown three magnetic transitions. Below T₉₁ = 42.5 K the Mn³⁺ ions develop long range order. In the work of Kajimoto et al. [11], magnetic superlattice reflections were observed at (0, τ, l) and (0, 1 − τ, l) type positions with l integer and τ = 0.27. At T₉₂ = 28 K there is a second magnetic transition which coincides with the appearance of a spontaneous electric polarization along the c axis. Finally, the Tb ions order below a third transition at T₉₂ = 7 K. Kenzelmann et al. [4], developed an appealing model of the magnetic structure whereby above T₉₂ the magnetic moments on the Mn ions are polarized along the b axis in an incommensurate, collinear fashion, and argued that at T₉₂ the magnetic moments on the Mn sites rotate to form an elliptical cycloid in the bc plane. This noncollinear structure causes a finite ferroelectric polarization along the c axis. Hard x-ray scattering experiments have been performed on TbMnO₃ [13–15], and report both nonresonant and resonant magnetic satellites at (0, τ, l), (0, 1 − τ, l) type locations. However, for these experiments the resonances used do not provide direct information on the localized Mn 3d or Tb 4f states which are of principal interest for understanding the magnetic order [16–18]. The soft x-ray resonant scattering experiments reported here overcome this limitation by probing these states directly [19–23].

Experiments were carried out on beam lines 5U1 at the SRS, Daresbury Laboratory, U.K. and ID08, European Synchrotron Radiation Facility, France. Two crystals with the (0, 1, 0) and (0, 0.28, 1) surface normal were used, cut from the same boule as used previously [13,24]. Unless otherwise noted, the incident photon energy was tuned to the L₂ edge of Mn, to select the magnetic scattering from

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the manganese. The polarization of the incident x rays was chosen to be perpendicular to the scattering plane ($\sigma$ polarization).

Figure 1 shows a scan taken at 20 K along the (0, 1, 0) direction in reciprocal space from the crystal with (0, 1, 0) surface normal. Three superlattice reflections are visible at, (0, $\tau$, 0), (0, 2$\tau$, 0), and (0, 1 - $2\tau$, 0) with $\tau = 0.28$. All three reflections were found to resonate at the $L_2$ and $L_3$ edges of Mn and were not visible off resonance. We assign the (0, $\tau$, 0) reflection to incommensurate ordering of the magnetic moments on the Mn sites and the (0, 2$\tau$, 0) to be the second harmonic from the resonant x-ray cross section \cite{25,26}. The (0, 1 - $2\tau$, 0) reflection corresponds to the second harmonic from the (0, 1, 0) reflection. Upon cooling the sample with the (0, 0.28, 1) reflection surface normal, and tuning the photon energy to the Tb edge, a superlattice reflection was observed at (0, $\tau$, 1) with $\tau = 0.28$ below 28 K. This reflection is not accessible at the Mn $L$ edges, but was visible at the Tb $M_3$ and $M_4$ edges with no intensity observed off resonance.

The temperature dependence of the integrated intensity of the (0, $\tau$, 0), (0, 2$\tau$, 0), and (0, 1 - $2\tau$, 0) reflections at the Mn $L_2$ edge is shown in Fig. 2(a). Here a clear transition is seen at $T_{N1}$, below which the intensity of the (0, $\tau$, 0) grows. At $T_{N2}$, a further transition is observed at which the intensity of the (0, $\tau$, 0) reflection is found to increase more rapidly. Turning to the (0, 2$\tau$, 0) and (0, 1 - $2\tau$, 0) reflections, these are only observed below a temperature of 35 K. On cooling below 35 K their intensities increase, first gradually then more rapidly below $T_{N2}$. Upon cooling below $T_{N1}$, $\tau$ decreases in an almost linear fashion, as shown in Fig. 2(b), until $T_{N2}$ where the value stabilizes at approximately $\tau = 0.287$, although it does not lock in. Identical behavior was seen in $\tau$ from all reflections. Finally, Fig. 2(a) also shows the integrated intensity of the (0, $\tau$, 1) reflection measured at the Tb $M_4$ edge. This reflection is only visible below $T_{N2}$. The presence of the Tb resonant signal is an explicit confirmation of a finite Tb moment in the low $T$ phase, as inferred previously \cite{4,27}.

It is possible to determine the magnetic moment direction by utilizing the fact that the scattered intensity is a function of the projection of the moment along the scattered x-ray direction and the scattering geometry \cite{25}. In a diffraction experiment, one measures the direction of the Fourier component of the magnetic structure as determined by the $Q$ vector chosen. To determine the direction of all Fourier components present, we measured the azimuthal dependence (the rotation of the sample around the $Q$ vector) of all observed Mn wave vectors. No measurement of the scattered polarization was made.

Figure 3 shows the azimuthal dependence of the (0, $\tau$, 0), (0, 2$\tau$, 0), and (0, 1 - $2\tau$, 0) reflections as measured at the Mn $L_2$ edge. In the top panel, the (0, $\tau$, 0) reflection is shown at 26 K (red circles) and 32 K (blue squares). While the integrated intensity changes between these two temperatures, the functional form is identical, indicating that the direction of this Fourier component does not change across $T_{N2}$. This azimuthal dependence can be fitted to the form $I_c(\psi) = A\cos^2\psi$, where $A$ is a proportionality constant and $\psi$ is the azimuthal angle. $\psi = 0$ corresponds to the condition where the [001] direction lies in the scattering plane. We can immediately exclude a $b$-axis direction for this Fourier component, since this is parallel to the $Q$ and thus would be invariant under rotations around $Q$. The zero in intensity at $\psi = 90^\circ$ (corresponding to the case where the $c$ axis is perpendicular to the scattering plane) implies that the magnetic moment has no projection along the outgoing x ray at this azimuth, and

![FIG. 1 (color online). Scan along the [010] direction in reciprocal space at an incident photon energy corresponding to the $L_2$ edge of Mn. r.l.u. denotes reciprocal-lattice units.](image)

![FIG. 2 (color online). (a) Temperature dependence of the integrated intensity of the (0, $\tau$, 0), (0, 2$\tau$, 0), and (0, 1 - $2\tau$, 0) measured at the Mn $L_2$ edge and the (0, $\tau$, 1) measured at the Tb $M_4$ edge. (b) Temperature dependence of the incommensurability $\tau$ measured from the peak position of the (0, $\tau$, 0) measured at the Mn $L_2$ edge.](image)
In summary, we conclude that at 26 K, the magnetic structure possesses Fourier components at \((0, \tau, 0)\) and \((0, 1 - \tau, 0)\) which are along the principal \(c\) and \(a\) axes, respectively, in addition to the to the \(b\)-axis and \(c\)-axis components reported previously at \((0, \tau, 1)\) [4].

To explain the presence of these Fourier components, and the previous neutron results [4] one might turn to a model of magnetic domains in which different parts of the sample have different ordering wave vectors. Instead, we propose that these reflections arise from one coherent magnetic structure which explains all the observed wave vectors. This is because (i) the incommensurability is the same and has the same temperature dependence at all reflections, and is consistent with that measured by neutrons [4,11] and nonresonant x rays [13,15]. This would seem unlikely if the reflections originated from different parts of the sample with different physical characteristics. (ii) The \((0, \tau, 0)\) wave vector shows magnetic transitions at 41 K and at 28 K; that is, it exhibits transitions entirely consistent with those observed at the \((0, \tau, 1)\) wave vector [4] again suggesting they have a common origin. (iii) Such a coherent structure is consistent with the symmetry analysis performed by Kenzelmann et al. [4]. Finally, we note our sample does indeed show the cycloidal ordering below 28 K, which we observe at the \((0, \tau, 1)\) wave vector. We can thus rule out the possibility that this sample somehow differs from others and is not multiferroic.

We now construct these new magnetic structures. For the high-temperature phase above 28 K, we start from the model of Kenzelmann et al. [4], who found a single \(\Gamma_3\) component along the \(b\) axis with a wave vector of \((0, \tau, 1)\). We add to this the \((0, \tau, 0)\) \(c\)-axis Fourier component observed here. This introduces a canting of the spins away from the \(b\) axis. Further, this canting must be ferro ordered along the \(c\) axis, since this Fourier component is observed at even integer \(l\) values. We estimate the canting angle from the neutron intensities of Kajimoto et al. [11], to be approximately 5° away from the \(b\) axis. This new structure is noncollinear and is shown with this canting angle in Fig. 4(a). Note, this structure is consistent with the group theory presented by Kenzelmann et al. [4]. If we examine the \(\Gamma_1\) irreducible representation of the little group \(G_k\) of the wave vector \((0, k, 0)\) from the crystallographic space group \(Pbnm\), we find that the symmetry operation \(m_{z\tau}\) at \(z = \frac{1}{4}\) relates two Mn spins along the \(c\) axis and has a character of 1. For a \(b\)-axis Mn magnetic moment, this symmetry operator flips the spin, resulting in an antiferro arrangement along the \(c\) axis (odd integer \(l\)). On the other hand, for a \(c\)-axis component, this same operator leaves the spin invariant (ferro along \(c\) and peaks at even integer \(l\)). Therefore in a canted structure with Fourier components present at odd and even integer \(l\) values, these must see the \(b\)-axis and \(c\)-axis moment directions, respectively—as is observed.

Turning now to the low temperature structure, we again start from the model of Kenzelmann et al. [4], who found a
single Fourier component of \((0, \tau, 1)\) with both \(\Gamma_2\) and \(\Gamma_3\) components with moment directions along the \(c\) axis and \(b\) axis, respectively. We add to this the \((0, \tau, 0)\) \(c\)-axis component, as in the high-temperature phase, and the \((0, 1 - \tau, 0)\) \(a\)-axis Fourier component. The fact that this latter reflection is a satellite of the \((0, 1, 0)\) forbidden Bragg reflection, implies that this component is arranged antiferromagnetically along the \(b\) axis. Thus this \((0, 1 - \tau, 0)\) \(a\)-axis component causes a canting of the Mn moments towards the \(a\) axis that is antiferro ordered along the \([010]\) direction. From the ratio of the azimuthal maxima of the \((0, 2\tau, 0)\) and \((0, 1 - 2\tau, 0)\) peaks we estimate the ratio of the \(a\)-axis component to the \(c\)-axis component to be \(\sim 0.66\). These \(a\)-axis and \(c\)-axis Fourier components then modify the cycloid of Kenzelmann et al. and the resulting structure is shown in Fig. 4(b).

The addition of the \((0, 1 - \tau, 0)\) component is consistent with a \(\Gamma_2\) representation. The Mn spins along the \(b\) axis are related by the \(b\) glide \((m_{yz})\) and the twofold screw axis \(2_1\). In the \(\Gamma_2\) representation, the characters of these operators are \(-1\) and \(1\), respectively. For an \(a\)-axis spin, then, \(\Gamma_2\) will have an antiparallel alignment to \(b\)-axis neighbors and therefore a wave vector of the \((0, 1 - \tau, 0)\) type. For the \((0, \tau, 0)\) \(c\)-axis component, the same analysis was as discussed above in the high-temperature phase also applies below \(28\) K and it is a \(\Gamma_3\) component. Thus this new low temperature structure is also consistent with Kenzelmann et al. with both \(\Gamma_2\) and \(\Gamma_3\) components. We note that the \((0, 1 - 2\tau, 0)\) reflection is also present in the high-temperature phase. While the intensity is too weak to carry out azimuthal analysis, symmetry arguments suggest that it remains an \(a\)-axis component, in which case it would be a \(\Gamma_2\) component and both representations would be present above \(28\) K too.

In conclusion, we propose new magnetic structures above and below \(28\) K in TbMnO\(_3\). Specifically, our data require the addition of \(a\)-axis and \(c\)-axis components, with Fourier components \((0, 1 - \tau, 0)\) and \((0, \tau, 0)\), respectively.