Field-induced linear magnetoelastic coupling in multiferroic TbMnO$_3$

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We have used in-field neutron and x-ray single-crystal diffraction to measure the incommensurability $\delta$ of the crystal and magnetic structures of multiferroic TbMnO$_3$. We show that the flop in the electric polarization at the critical field $H_C$, for field $H$ along the $a$ and $b$ axes, coincides with a first-order transition to a commensurate phase with propagation vector $k=(0,\frac{1}{2},0)$. In-field x-ray diffraction measurements show that the quadratic magnetoelastic coupling breaks down with applied field as shown by the observation of the first harmonic lattice reflections above and below $H_C$. This indicates that magnetic field induces a linear magnetoelastic coupling.

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Control of the spontaneous ferroelectric polarization ($P_s$) with an external magnetic field ($H$) in a material opens the opportunity for new types of magnetoelectric devices. The realization of such devices is based on multiferroic materials in which magnetism and ferroelectricity are strongly coupled. While available multiferroics are limited, it has been shown that frustrated spin materials may offer a unique class of enhanced multiferroics.\textsuperscript{1–3} In one of these materials, TbMnO$_3$, we find that multiferroic behavior arises as a consequence of the release of frustration with $H$. Here ferroelectricity arises below the Néel temperature ($T_N$) from a coupling to the lattice of an incommensurate (IC) modulation of the magnetic structure [Fig. 1(a)] that is caused from frustration in the ordering of the Mn $d$ orbitals.\textsuperscript{1,3} In this communication we show that magnetic field releases this frustration, inducing a linear magnetoelastic coupling, so that ferroelectricity is no longer a secondary effect. The linear magnetoelastic coupling drives a magnetostructural transition from an IC phase, which has $P_s$ along the $c$ axis ($P_c$), to a commensurate (C) phase with $P_s$ along the $a$ axis ($P_a$).

In TbMnO$_3$, when a magnetic field is applied along the $b$ axis ($H||b$) at 2 K, parallel to the direction of the IC magnetic modulation [see Fig. 1(a)], the electric polarization of the lattice flops from $P||c$ to $P||a$ at the critical field $H_C^{\perp} \approx 4.5$ T [Fig. 2(d)]. When field is applied along the $a$ axis ($H||a$), perpendicular to the magnetic modulation, a similar flop is found but at a higher critical field, $H_C^{\perp} \approx 9$ T [Fig. 2(a)]. Recently there have been a number of examples of magnetoelastic coupling in complex multiferroic oxides such as TbMn$_2$O$_5$, which exhibit a reversible polarization switch with applied field,\textsuperscript{4} and hexagonal HoMnO$_3$, where one magnetic phase is selected over another by applying an electric field.\textsuperscript{5} However, TbMnO$_3$ is unique as it is the only known example of a material that exhibits a field-induced flop of its polarization.

In TbMnO$_3$ the staggered ordering of Mn$^{3+}$ 3$d_{x^2-y^2}$/3$d_{3z^2-r^2}$ orbitals as found in LaMnO$_3$ is frustrated partly due to the small ionic size of Tb$^{3+}$. This leads to an IC spin ordering which drives a ferroelectric lattice modulation.\textsuperscript{3,6} The wave vector for the modulation of the Mn spins is $\kappa_{Mn}=(0,k\pm \delta_{m},0)$, with incommensurability $\delta_{m} \approx 0.29$ at $T_N$ (first harmonic).\textsuperscript{7,8} Accompanying the magnetic ordering there is a lattice modulation with $\delta_{c}=2\delta_{m}$ (second harmonic)\textsuperscript{1–3} consistent with a quadratic magnetoelastic coupling between the lattice and the spin-density wave.\textsuperscript{9,10} Below $T_N=7$ K, sinusoidal Tb spin order is also found [$\kappa_{Tb}=(0,k\pm \delta_{m},0)$, $\delta_{m}=0.42$] (Ref. 8) and is expected to produce a similar coupling to the lattice with $\delta_{Tb}=2\delta_{m}^{Tb}$.

To uncover the nature of the coupling between $P$ and $H$ we have used in-field neutron and synchrotron x-ray single-crystal diffraction to measure the field response of $\delta$ with $H||a$ and $H||b$, up to 14 T. Single crystals were obtained by recrystallizing a ceramic rod of TbMnO$_3$ under Ar atmosphere.

FIG. 1. (Color online) Crystal and magnetic structures of TbMnO$_3$ (Pbnm, $a=5.302$, $b=5.857$, $c=7.402$ Å) in the $ab$ plane. Long (darker) and short (lighter) Mn-O bond ordering arises from staggered $3d_{x^2-y^2}$/3$d_{3z^2-r^2}$ orbital ordering found above $T_N$. (a) A model of the IC magnetic structure of TbMnO$_3$ below $T_N$ (Ref. 7). The arrows through Mn atoms indicate the direction of Mn spins. (b) A model of the Mn spin structure for TbMnO$_3$ for $H>H_C$. Here arrows from O atoms indicate the direction of displacement from the average structure as to increase (decrease) the angle $\phi$ on the basis of FM (AFM) coupling between adjacent Mn ions. The large arrows on ferroelectrically active octahedra indicate the direction of the predicted polarization from these displacements.
sphere using an optical floating zone furnace. Small pieces of our crystal were characterized using magnetization and specific heat in good agreement with published measurements.\textsuperscript{1,11} Synchrotron x-ray diffraction measurements were carried out on beamline X21 ($E_i=9.5$ keV) at the NSLS, Brookhaven National Laboratory, using a vertical 13-T superconducting magnet with the sample aligned with $\parallel a$, and at the BW5 beamline at HASYLAB ($E_i=100.5$ keV), using a horizontal 10-T superconducting magnet and the sample aligned with $\parallel b$. Neutron-diffraction experiments were made on a single crystal of TbMnO$\textsubscript{3}$ at the BENS facility of the Hahn-Heinrich Institut, Berlin. For measurements with $\parallel a$ we used the FLEX cold triple-axis spectrometer with a collimation of $40'\times40'\times40'$, $L_0=1.5$ Å$^{-1}$, and a cooled Be filter on the scattered beam, while a magnetic field was applied using the vertical 14.5-T superconducting magnet VM1. For measurements with $\parallel b$ we used the two-axis diffractometer E4 ($\lambda=2.2$ Å) with a $60'\times40'$ collimation while field was applied using the 4-T horizontal field magnet HM1. In all cases diffraction measurements were made in the $bc$ plane. Our neutron-diffraction measurements are sensitive to magnetic ordering whereas x-ray diffraction experiments probe the lattice.

With $\parallel a$ we measured characteristic reflections using neutron diffraction by cooling our crystal from 50 to 2 K in fields of 0, 2, 4, 6, 10, and 14 T. The variation of $\delta$ for Mn and Tb spin ordering as a function of field at 2 K, compiled from these measurements, is shown in Fig. 2(b), while the variation of the intensity of the same reflections is shown in Fig. 2(c).

In Fig. 3(b) we show neutron-diffraction scans through the first harmonic reflection ($0,\delta_{\text{Mn}}^a,1$) as a function of $\parallel a$. The intensity of this reflection is enhanced with $H$ from 2 to 4 T while the magnitude of $\delta_{\text{Mn}}^a$ remains unchanged for fields up to 8 T [Figs. 2(b) and 2(c)]. However, for $H>H_c^a\sim 9$ T we find that $\delta$ of the first harmonic reflection has changed to a C value of $\delta=\frac{1}{2}$ and is accompanied by a second harmonic reflection with $2\delta=\frac{1}{2}$ [Fig. 2(b)]. This transition at $H_c^a$ coincides with the polarization flop from $P_{\parallel c}$ to $P_{\parallel a}$ as shown in Fig. 2(a). The implication of this observation is that the po-

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However, for the first harmonic HC indicates that for lattice reflection at the wave vector of the first harmonic of magnitude between 0 and 2 T in Fig. 2 the metamagnetic transition of Tb spins magnetic scattering is allowed for this reflection, and indeed in the intensity of the ferromagnetic magnitude of the IC-spin component. The FM ordering of Tb magnetic field parallel to the b axis in the direction of the magnetic modulation, occurs at a lower critical field of HC,~4 T [Fig. 2(d)]. Here we applied a magnetic field parallel to the b axis after the sample was cooled to 2 K in zero field, and characteristic superlattice reflections, such as the (0,2δMn,3), were measured using x-ray diffraction (see Fig. 4). When a magnetic field is applied, the incommensurability of the second harmonic reflection remains invariant [Fig. 2(e)] but its intensity rapidly decreases with field from 0 to 2 T and remains low up to ~4 T [Fig. 2(f)]. Increasing field clearly destabilizes the lattice modulation and leads to a discontinuous transition to the C phase with 2δ=1/2 at HC=4.5 T [Figs. 2(e), 2(f), and 4(a)]. We find C and IC reflections coexisting over the field range of 4–5.5 T, while for H>5.5 T only the 2δ=1/2 superlattice reflection is visible [Fig. 4(a)]. Coincident to this magnetostuctural transition is the polarization flop from P∥c to P∥a at about 4.5 T as shown in Fig. 2(d).

As with the previous field configuration, here our x-ray measurements also revealed superlattice reflections with δ = 1/2 above HC [Figs. 2(e), 2(f), and 4(b)]. The linear increase in the intensity of this reflection with H∥b above HC is particularly striking, as it mirrors a linear increase in P∥a [Fig. 2(d)] between 4 and 10 T. This linear increase in P∥a is indicative of a linear magnetoelectric coupling in the C phase. The variation of intensity with field of the second harmonic reflection is different in that it increases rapidly above HC and shows a constant variation with H above ~6 T [Fig. 2(f)].

For this field configuration we find, using neutron diffraction, that at 2 K Tb spins undergo an additional discontinuous transition to a C phase with δTb=1/2 at H∥b=1.25 T, as shown in Fig. 2(e). From symmetry analysis Tb spins for this phase are both sign and amplitude modulated. This transition is reflected in an anomaly in P∥c at the same field value [Fig. 2(d)], and a significant increase in the magnetization at this temperature is also reported. However, unlike the H∥a case, here field neither suppresses the intensity of the IC Tb reflections nor does it enhance the FM component [Fig. 2(f)]. Above HC we find no evidence of IC ordering of Tb spins while the FM intensity appears to decrease.

In zero field TbMnO3 is an improper ferroelectric where the lattice polarization arises from a quadratic magnetoelastic coupling to a spin-density wave, as indicated by the observation of second harmonic structural reflections. Here we...
demonstrate that this picture of improper ferroelectricity in TbMnO$_3$ breaks down with $H$ even below $H_C$ for the case of $H\parallel a$ and most likely for $H\parallel b$. The identical periodicity of the magnetic and crystal structures indicates that $H$ switches on a linear magnetoelastic coupling which is maintained into the C phase. This would suggest that the IC–C phase transition we report on, and consequently the polarization flop at $H_C$, are driven by field-induced linear magnetoelastic coupling. Our measurements clarify the role of Tb spins on the polarization flop at $H_C$. For $H\parallel a$ Tb spins show a FM alignment well below $H_C$ and only a smaller IC component, and thus are not expected to contribute to the polarization flop strongly. For $H\parallel b$, however, the situation is more complex as Tb spins exhibit an additional transition to the $\delta_m^{1b}=\frac{1}{2}$ phase, while a strong FM enhancement is not observed. Together with the lower critical field for $H\parallel b$ the polarization flop here may be driven by an interplay between Mn and Tb spin ordering as suggested by Kimura et al.\textsuperscript{1}

The magnetoelastic coupling is expected to change in a similar way as the magnetoelastic coupling. Indeed the behavior of TbMnO$_3$ with $H$ is reminiscent of that of BiFeO$_3$, which exhibits a switch to linear magnetoelastic coupling at $\sim$20 T (Refs. 12 and 13). The coupling between $P$ and $H$ is expressed by $P_i=P_{st}+\alpha_i H+i\beta_{ijk} H_j H_k$, where $P_s$ is the spontaneous polarization, $\alpha_{ij}$ is the tensor of the magneto-electric susceptibility, and $\beta_{ijk}$ is a tensor describing the coupling of a spiral and/or cycloid magnetic structure to the lattice.\textsuperscript{12,13} In an analogy to BiFeO$_3$, we suggest that as field destroys the spiral spin ordering ($\beta_{ijk}$ is renormalized), a linear magnetoelastic effect would be expected to arise.\textsuperscript{12,14} Indeed a linear behavior in $P$ versus $H$ is evident for $H\parallel b$ [Fig. 2(d)].

The propagation vector of $\kappa=(0,\frac{1}{2},0)$ uniquely gives a spin structure that is only sign modulated as depicted in Fig. 1(b). It is important to consider the effect of this magnetic ordering on the frustrated orbital ordering. The crystal structure of TbMnO$_3$ ($H=0$ T, $T>T_N$) shows an ordering of long and short bonds as found in LaMnO$_3$, but with a large angle $\phi$ of 144° between MnO$_6$ octahedra (Mn-O-Mn), compared to 165° found in LaMnO$_3$ (Ref. 15). A simple application of Goodenough’s rules would suggest a layered antiferromagnetic (AFM) ordering, inconsistent with the present data.\textsuperscript{16}

We propose here that the structural distortion that is coupled to the $\uparrow\uparrow\downarrow\downarrow$ spin structure arises from the ordering of $\phi$. Small values of $\phi$ would result in AFM interactions between adjacent Mn spins as the influence of superexchange via $t_{2g}$ orbitals would be more significant.\textsuperscript{3,16} On the other hand, a relative larger value of $\phi$ will be less influenced from $t_{2g}$ interactions and would propagate a FM coupling between Mn spins as it does in LaMnO$_3$. Indeed the layered AFM structure is stable to values of $\phi$ as low as 148°, found in SmMnO$_3$ (Ref. 3). Using the magnetic ordering of the high-field C phase as a constraint and displacing O atoms in the paraelastic structure so that $\phi$ should increase (decrease) for FM (AFM) coupling between adjacent Mn spins, one arrives at a structural model show in Fig. 1(b). The result is a structure where ferromagnetically coupled MnO$_6$ octahedra undergo simple rotations (ferroelectrically inactive), while octahedra that are frustrated by AFM coupling in the $ab$ plane show a scissorlike distortion (ferroelectrically active). The combined rotations and scissorlike distortions in the structure lead to antiferroelectric displacements for the O atoms along the $b$ axis but an overall ferroelectric displacement along the $a$ axis, in agreement with polarization measurements. While this simple model predicts the correct polarization for the C phase on the basis of the magnetic structure, the periodicity of the structural distortion suggests displacements of the Mn ions that cannot be accurately predicted in the absence of high-field crystallographic data. Finally, we note here that although in Fig. 1(b) we depict a collinear structure for simplicity, our neutron measurements show that indeed in the C-phase reflection types that arise from spiral components are visible but suppressed by a factor of 6 compared to the zero-field IC phase.

In this Communication we have demonstrated that the polarization flop in TbMnO$_3$ arises from a transition to a C phase with propagation vector $\kappa=(0,\frac{1}{2},0)$. The quadratic magnetoelastic coupling breaks down with field and the high-field phase exhibits linear magnetoelastic and magneto-electric behavior. We argue that field has the effect of releasing the apparent frustration in the orbital ordering in TbMnO$_3$ and leads to a C phase by an ordering of Mn-O-Mn bond angles.

\textit{Note added:} Arima et al.\textsuperscript{17} recently reported some x-ray diffraction measurements for $H\parallel b$ similar to those described here.

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