X-ray diffraction studies on multiferroic $TbMnO_3$ and $DyMnO_3$ compounds in high magnetic fields

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Multiferroic compounds are materials that exhibit two or more switchable states such as polarization, magnetization or strain, which are again interdependent from each other. Magneto-electric multiferroics have recently attracted a lot of interest due to the exceptional properties, which allow the control of spontaneous ferroelectric polarization by applied magnetic fields, ultimately leading to new types of magneto-electric devices. Unlike in conventional ferroelectrics, in the manganite perovskites, such as $TbMnO_3$ and $DyMnO_3$, ferroelectricity arises from a peculiar coupling of the lattice to a spiral ordering of Mn-spins. A strong anisotropic dependence of the spontaneous electric polarization on the direction of the magnetic field is found, which can be related to the spiral ordering of the magnetic moments. The work presented here is a joint effort both from neutron diffraction studies at HMI and x-ray diffraction at HASYLAB, where the two methods very nicely complement each other.

At zero field, $TbMnO_3$ undergoes a magnetic phase transition into an antiferromagnetic (AF) phase with sinusoidal modulation of the magnetic moments at the Néel temperature T_N=41K. In the AF-phase, the Mn moments are aligned along the b-axis. The propagation vector is (0 δ_m 0) with δ_m = 0.29rlu at T_N. This means that the magnetic wave vector is incommensurate to the structural unit cell of the compound. The incommensurability δ_m decreases with decreasing temperature and stabilizes at the critical temperature T_C = 28K at a value of δ_m = 0.28rlu. At T_C, spontaneous ferroelectric polarization along the c-axis (P||c) arises [2]. As found by neutron diffraction studies, the magnetic order changes at this temperature from sinusoidal to helicoidal with no change in wave vector. In Figure 1a, the magnetic structure below T_N is depicted in the ab-plane.

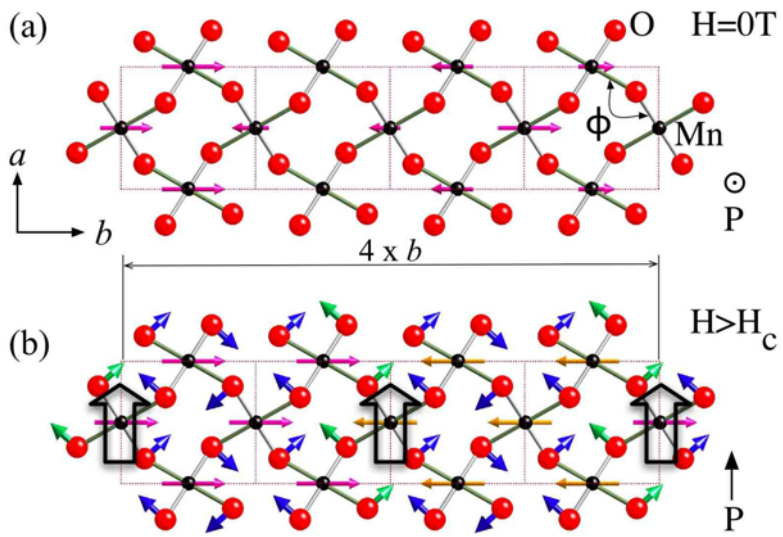

Figure 1. Crystal and magnetic structure of $TbMnO_3$ in the ab-plane. (a) A model of the IC magnetic structure below T_N. (b) A model of the Mn spin structure for $H>H_C$. The large arrows on ferroelectrically active octahedra indicate the direction of polarization predicted from these displacements.

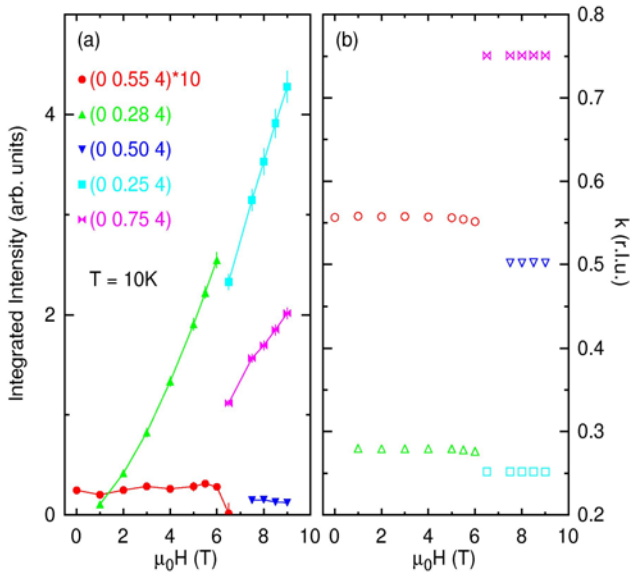

Figure 2. (a) Intensity and (b) wave vector (0 k 4) of the structural first and second harmonic reflections of $TbMnO_3$ as function of magnetic field H||b, measured at a sample temperature of 10K.

In addition to the magnetic first harmonic superlattice reflection, a second harmonic reflection with $\delta_l = 2\delta_m$ is present, which is of purely structural nature. This can be investigated by non-resonant x-ray scattering due to its high sensitivity to structural distortions. If a magnetic field is applied along the a- or b-axis, at fields of ~ 1T, first harmonic structural superlattice reflections start to appear on top of the magnetic superlattice reflections as found by both, neutron diffraction and resonant x-ray scattering experiments. These structural first harmonic reflections show a linear increase of intensity with the applied field (Figure 2a). As an explanation, we here suggest that as the field destroys the spin spiral ordering, a linear magneto-electric effect arises. Indeed, a linear behavior in the relation between the spontaneous polarization P and the applied magnetic field H is evident from polarization data, which is also reflected in the linear increase of the superlattice reflection intensities.

At the critical field, the polarization flops from P||c to P||a with increasing magnetic field, and a shift of the wave vector from the incommensurate (IC) to a commensurate (CM) position is observed for both first and second harmonic reflections (δ_m = 0.25rlu. and $2\delta_m$ = 0.5rlu), as is shown in Figure 2b. This IC to CM transition implies a simplification of the magnetic spiral order

present below H_C by a magnetic moment arrangement, which agrees with the CM reflections. Here we propose a simple ↑↑↓↓-arrangement of the magnetic moments along the b-axis with a magnetic unit cell four times the size of the structural unit cell in this direction. An exchange striction mechanism from competing ferromagnetic and antiferromagnetic super-exchange interactions in this scenario predicts a P||a phase for CM ordering with $\delta_m = 1/4$rlu, valid in the absence of a spiral magnetic ordering and consistent with our data (Figure 1b).

$DyMnO_3$ shows a very similar behavior to $TbMnO_3$ of electric polarization in the temperature-field phase diagram. The Néel temperature and the onset of spontaneous polarization are $T_N = 39$K and $T_C = 19$K, respectively. The critical fields for H||a and H||b occur already at lower fields in the H-T-phase diagram. The compound shows incommensurate magnetic and corresponding structural reflections but with different values of δ_m as compared to $TbMnO_3$. The incommensurability in $DyMnO_3$ is $\delta_m = 0.38$rlu at T_C compared to $\delta_m = 0.28$rlu for $TbMnO_3$. With all these similarities between the two compounds, it is striking that an incommensurate to commensurate transition of the wave-vector is not observed in $DyMnO_3$ at the critical field where the polarization flop P||c to P||a occurs. Instead, the wave-vector varies continuously through the flop transition (Figures 3c-d). Also, the hysteresis effects, present in both the wave vector and the intensity, are very similar for measurements performed without field and in an applied field of 10T (Figures 3a-b).

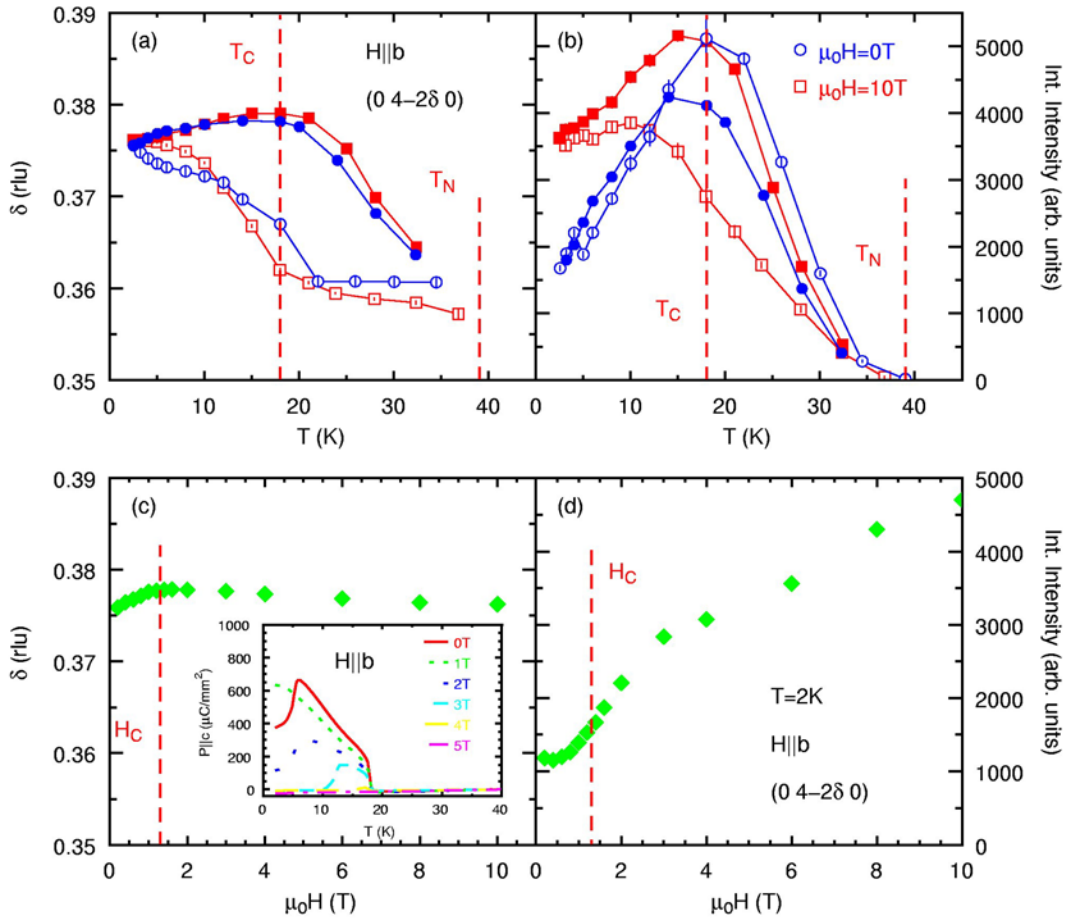

Figure 3. (a) Incommensurability and (b) intensity of the $DyMnO_3$ second harmonic superlattice reflection (0 4-2δ 0) as function of temperature for zero field and 10T. Magnetic field dependence of (c) wave vector and (d) intensity at T = 2K. The inset shows the spontaneous polarization P||a as a function of magnetic field H||b.

In the general case, the polarization flop is driven by a flop of the axis of rotation of the magnetic spiral as was pointed out by Mostovoy et al. [1]. The direction of the spontaneous ferroelectric polarization is determined by magnetic anisotropy terms. From the perspective of symmetry, there is no restriction that the high field spiral must be CM. In this view, the magneto-elastic phase transition to a CM phase in $TbMnO_3$ would be a special case, especially when we did not find such a transition in $DyMnO_3$. The difference in behavior between the two multiferroics is not of fundamental nature but rather lies in the magnitude of the incommensurability. For $TbMnO_3$, δ_m = 0.28rlu lies close to the CM value of 1/4. For this value of the wave vector, the amplitude of the magnetic moment is not modulated as described above, and may thus be energetically more favorable than an IC amplitude modulated phase. For $DyMnO_3$, δ_m = 0.38rlu is further away from a CM value (1/3) and thus such a transition to a CM phase is not as favorable.

This smooth behavior of the spiral wave vector in $DyMnO_3$ at the spin flop transition may explain the large increase of the dielectric constant ε_a, observed in this compound [4,5]. At the critical field, where the spin-flop transition occurs, there is a freedom to rotate the spiral around the b-axis. The corresponding magnetic excitation can be excited by an electric field E||a. Its softening at H_C would result in a divergence of the static dielectric susceptibility ε_a, as is observed in $DyMnO_3$.

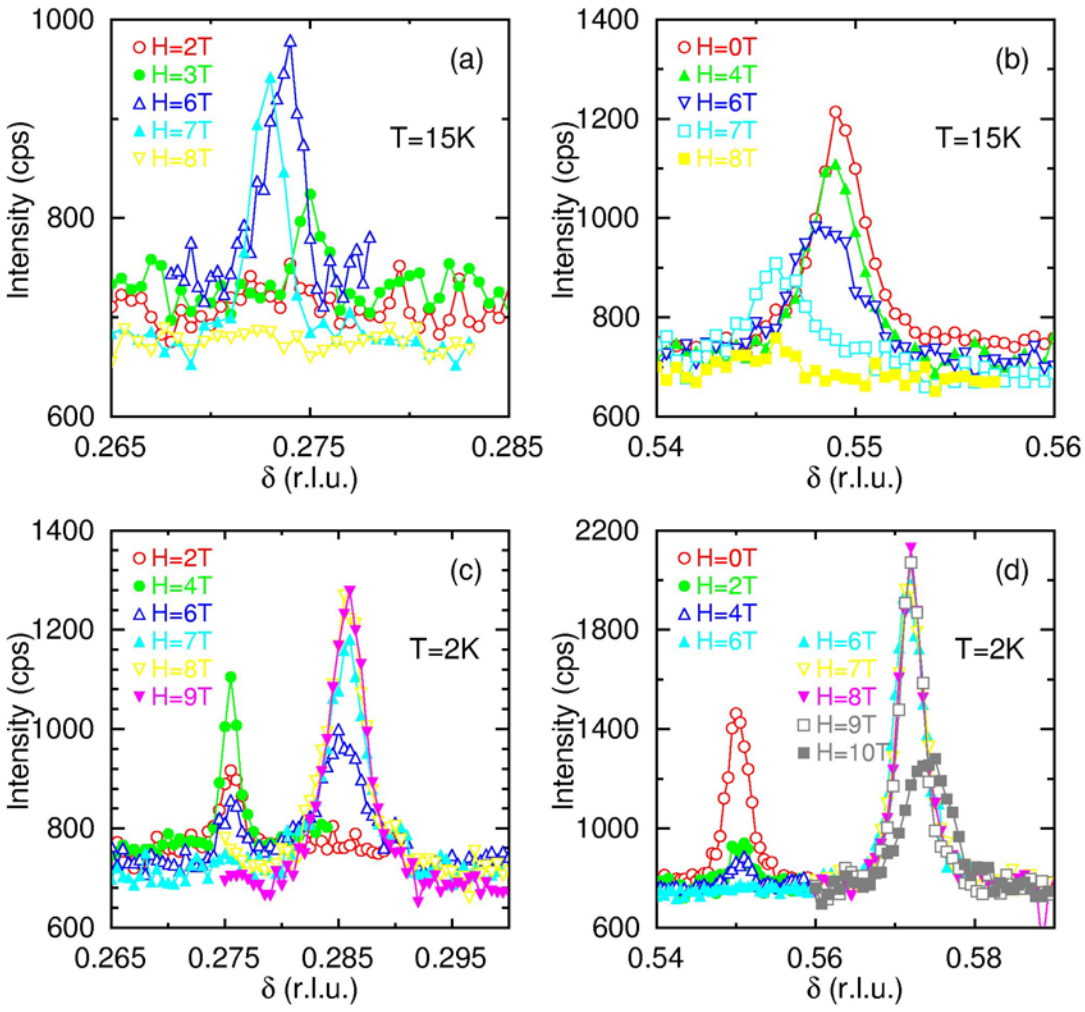

Figure 4. First and second harmonic reflections of $DyMnO_3$ as function of the applied magnetic field H||c for T = 12K (a-b) and T = 2K (c-d).

If a magnetic field is applied along the c-direction (H||c), the system enters, other than for H||a and H||b, into a paraelectric phase at the critical field with a minimum critical field of 7T at around 12K. This high-field phase is characterized by a simple commensurate antiferromagnetic order of the Mn-spins. At lower temperatures, ferroelectricity remains up to high fields. As the temperature is lowered with the system in the paraelectric phase at high fields, re-entrance into the ferroelectric phase is observed that coincides with the development of incommensurate Mn- and Tb-spin ordering. This is illustrated in Figure 4, where the 12K data show the transition into the paraelectric phase with the vanishing of the superlattice reflections at 7T (Figures 4a-b) and the 2K data show the incommensurate reflections up to fields of 10T, which is still below the critical field at this temperature (Figures 4c-d). At 6T, a discontinuous jump of δ is observed for both δ_m and $2\delta_m$. This jump, which is also observed for δ_m^{Tb} at a different field, is due to sharp magneto-elastic transitions in both, the Mn- and Tb-sublattices, which correlate well with measurements of physical properties[3].

Summary

In summary, we find a linear increase of the first harmonic IC and CM reflections in $TbMnO_3$ as well as in $DyMnO_3$, and an IC to CM transition of the wave vector of the superlattice reflections in $TbMnO_3$ for field H||a and H||b. By looking at the results from $DyMnO_3$, where the IC to CM transition is absent, this transition turns out to be a special case due to an energetically favorable spin configuration in the high field phase and it is thus not essential for the polarization flop to occur. On the other hand, the appearance and linear increase of the first order structural reflection is a general feature of both multiferroic compounds. Application of a magnetic field along the c-axis melts the IC magnetic ordering of the Mn spins, which coincides with the suppression of ferroelectricity at the critical field.

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