Inversion symmetry breaking magnetic structures in multiferroic oxides

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Abstract

We review the recent determination of magnetic structures in two multiferroic materials – $Ni_3V_2O_8$ and $TbMnO_3$ – where magnetic ordering is directly coupled to ferroelectric polarization. In both materials, the magnetic structures in the para- and ferroelectric phases have distinctly different symmetries, described by one and two irreducible representations respectively. Ferroelectricity arises when the magnetic structure breaks inversion symmetry. Through magneto-elastic effects such structures act as an effective electric field leading to electric polarization of the insulating material.

Introduction

Materials with ferroelectric and magnetically ordered ground states have been known for more than forty years [1]. Most of these materials are either (1) perovskite-type structures, (2) hexagonal rare-earth manganites, (3) boracite compounds or (4) barium fluorides in which the onset of ferroelectricity and magnetic order occurs at vastly different temperatures. In these materials, the redistribution of charge, which leads to ferroelectric polarization, is unrelated to the subsequent development of magnetic order at lower temperatures.

Large magnetoelectric coupling effects were recently discovered in $TbMnO_3$ [2] and $Ni_3V_2O_8$ [3]. These materials are different from previously known multiferroics in that their field-temperature phase diagrams consist of several magnetically ordered phases, some of which feature a ferroelectric polarization that vanishes at magnetic phase boundaries. By applying a magnetic field and traversing such phase boundaries, it is possible to change the direction of the electric polarization in $TbMnO_3$ [2], or to completely suppress it in $Ni_3V_2O_8$ [3].

Magnetic structures in $TbMnO_3$

$TbMnO_3$ has a distorted perovskite structure (Fig. 1) and is structurally similar to the prototype ferroelectric $BaTiO_3$ and other insulating pervoskites with non-linear magnetoelectric effects. $TbMnO_3$ however displays a sequence of phase transitions between incommensurate magnetically ordered phases as a function of temperature. Following an initial transition at 42 K to incommensurate order, there is a second transition at 27 K where the temperature dependence of the ordering wave-vector becomes so weak that it was initially interpreted as a lock-in transition. More recent experiments show that the distinguishing characteristic of the low temperature phase is transverse polarization, which leads to inversion symmetry breaking and ferroelectricity [1].

Following the discovery of magneto-electric coupling in $TbMnO_3$, neutron diffraction experiments revealed a sequence of incommensurate phases and provided evidence for competing interactions along the crystallographic **b-**direction [3,4,5]. To understand the origin of magneto-electric coupling in $TbMnO_3$, a comprehensive magnetic structure determination for the para-electric and ferro-electric phases was carried out using the four circle diffractometer TriCS at PSI. The goal of this work was to understand why only one of the two incommensurate phases is ferroelectric.

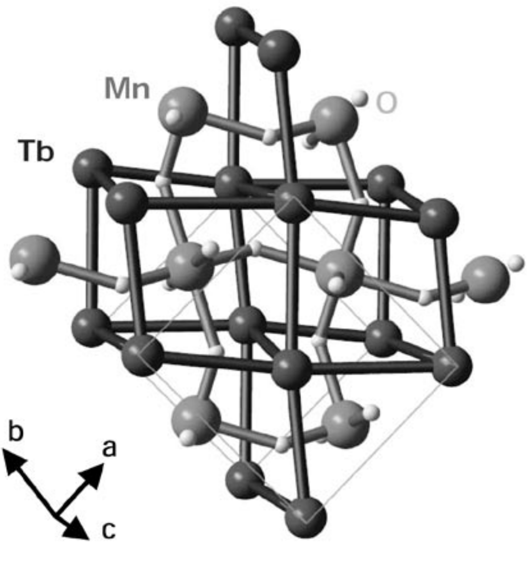

Fig. 1: Chemical structure of $TbMnO_3$, tilted to show the distorted perovskite structure

The complexity of magnetic structures in $TbMnO_3$ arises from the

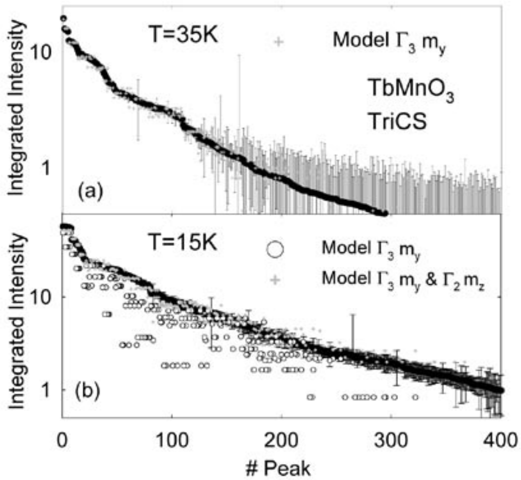

Fig. 2: Integrated intensities of magnetic Bragg peaks at T=15 K and T=35 K compared to various magnetic model structures. Peaks are sorted by decreasing measured intensity.

presence of two magnetic ions, Tb^{3+} and Mn^{3+}, and competing spin interactions. A unique determination of these ordered structures required over 900 magnetic Bragg intensities for each temperature and the use of magnetic representation theory to classify the possible structures.

Fig. 2 shows the intensity of the 400 strongest magnetic Bragg peaks of $TbMnO_3$ at T=15 K and 35 K, in the ferroelectric and paraelectric phases, respectively. The T=35 K structure is described by a single irreducible representation, Γ_3, with ordered magnetic moments along the **b-**axis.

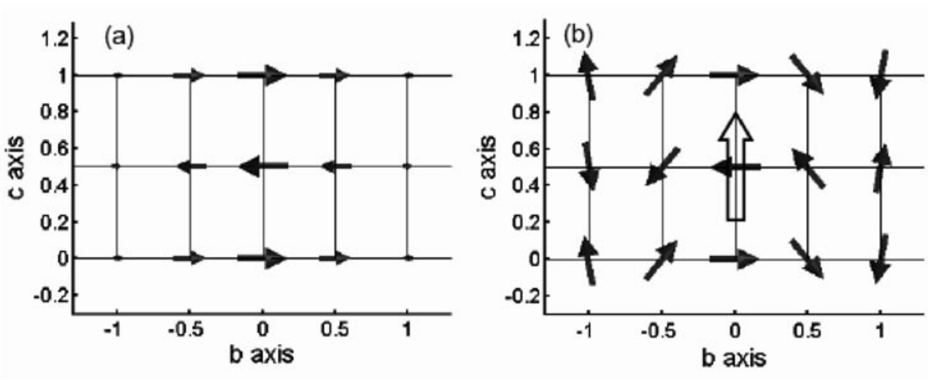

Fig. 3: Schematic of the magnetic structure of $TbMnO_3$ at (a) T=35 K and (b) T=15 K, projected onto the ***b-c*** plane. Filled arrows indicate direction and magnitude of Mn moments. The longitudinally-modulated phase (a) has a point of inversion while the spiral phase (b) does not. Electric polarization indicated by the unfilled arrow is hence allowed in (b) but not in (a).

The T=15 K magnetic structure on the other hand is a spiral described by a *y*-component of Γ_3 and an *x*-component of Γ_2 with a $\pi/2$ phase shift.

The structure at T=35 K, which is consistent with an earlier study [4], is illustrated in Fig. 3a. The absence of observable higher order magnetic diffraction peaks indicates a sinusoidal amplitude modulated structure. The low-temperature incommensurate phase at T=15 K is illustrated in Fig. 3b. Mn moments in this phase form an elliptical spiral.

Magnetic structures in $Ni_3V_2O_8$

$Ni_3V_2O_8$ contains anisotropic S=1 Kagomé planes [3] that can be described as dense magnetic spines running along the a-axis separated by cross-tie sites (Fig. 4a). The anisotropy of the lattice breaks the degeneracy of the Kagomé antiferromagnet and leads to long-range order at low temperatures. Due to the near degeneracy of different spin structures, small perturbations such as a magnetic field, spin-orbit interactions, and possibly magneto-elastic effects lead to qualitative changes in the spin structure. Indeed, $Ni_3V_2O_8$ adopts two different incommensurate magnetic structures – one of them ferroelectric – and at least one commensurate structure as a function of temperature at zero magnetic field [5].

Using neutron diffraction, it was found that as for $TbMnO_3$ the high-temperature incommensurate (HTI) magnetic structure is longitudinally modulated and can be described by a single irreducible representation [5]. In the low-temperature incommensurate (LTI) phase, which is ferroelectric, the magnetic structure is again a spiral with two spin components that belong to different irreducible representations. The LTI structure breaks inversion symmetry, which in an insulator implies that there will also be a finite electric polarization [1,3]. Below T=4 K, $Ni_3V_2O_8$ adopts commensurate (C and C') magnetic structures that restore inversion symmetry and are not ferroelectric.

Trilinear Coupling Theory

Harris et al. [3,6] recently showed that insulators with axial-non-axial parity breaking magnetic phase transitions must also be electrically polarized. The theory is based on a trilinear coupling of the magnetic and electric order parameters of the form

$$V = -\sum_{ij\gamma}\left(a_{ij\gamma}\sigma_{\Gamma_1 i}(q)\sigma_{\Gamma_2 j}(-q) + a^*_{ij\gamma}\sigma_{\Gamma_1 i}(q)\sigma_{\Gamma_2 j}(-q)\right)P_\gamma .$$

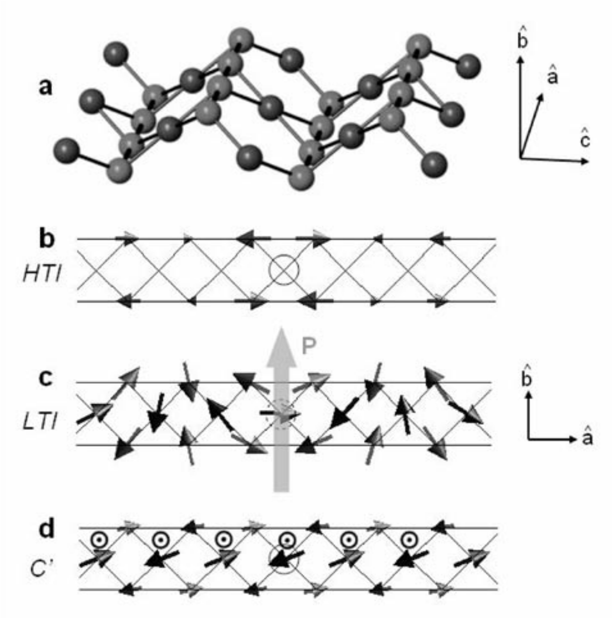

Fig. 4: Crystal and magnetic structures of $Ni_3V_2O_8$. (a) The crystal structure includes spin-1 Ni^{2+} spine sites forming chains and cross tie sites between the chains. (b-d) Simplified schematic representation of spin arrangement in the antiferromagnetic HTI, LTI, and C' phases [5]. The dotted circles in (d) indicate a small ferromagnetic moment. Only the HTI and C' phases have inversion symmetry relative to the indicated central lattice point.

Here $\sigma_{\Gamma_1 i}(q)$ is component i of the magnetic order parameter belonging to irreducible representation Γ_1, P_γ is the electric polarization along the γ crystallographic direction and $a_{ij\gamma}$ parametrizes the strength of the interaction between the electric and magnetic order parameters. This interaction is discussed in detail in Ref. 3, 6, and 7, where it is shown that at least two irreducible representations, Γ_1 and Γ_2, are needed to allow for a finite electric polarization. The direction of the electric polarization depends on the symmetry of the irreducible representations, making their experimental determination a crucial step in testing the theory. On the basis of the observed magnetic structures in $TbMnO_3$, the trilinear coupling theory predicts that there is no ferroelectric polarization at 35 K, but that there is an electric polarization along the c-axis in the low T phase. This is fully consistent with the electric polarization data. Likewise the tri-linear term for $Ni_3V_2O_8$ when combined with the observed magnetic structures correctly predicts the measured direction of the ferro-electric polarization. Taken together these results point to an interesting new class of multi-ferroics where inversion symmetry breaking magnetism induces electric polarization through a tri-linear magneto-electric interaction.

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