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Ordering of localized electronic states in multiferroic TbMnO$_3$: a soft x-ray resonant scattering study

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Abstract

Soft x-ray resonant scattering (XRS) has been used to observe directly, for the first time, the ordering of localized electronic states on both the Mn and the Tb sites in multiferroic TbMnO$_3$. Large resonant enhancements of the x-ray scattering cross-section were observed when the incident photon energy was tuned to either the Mn L or Tb M edges which provide information on the Mn 3d and Tb 4f electronic states, respectively. The temperature dependence of the XRS signal establishes, in a model independent way, that in the high-temperature phase (28 K \( \leq T \leq 42 \) K) the Mn 3d sublattice displays long-range order. The Tb 4f sublattices are found to order only on entering the combined ferroelectric/magnetic state below 28 K. Our results are discussed with respect to recent hard XRS experiments (sensitive to spatially extended orbitals) and neutron scattering.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Magnetoelectric multiferroics are materials that simultaneously display ferroelectric and magnetic long-range order [1]. Consequently, they are of considerable interest both from a fundamental point of view, and for the potential that they offer in the field of spintronics [2, 3]. Of particular importance has been the recent discovery of multiferroic behavior in a diverse range of compounds where the multiferroic state takes the form of the coexistence of ferroelectricity and antiferromagnetism, often with a large coupling between the two [4, 5]. Indeed the burgeoning interest in multiferroics can be traced to the pioneering work by Kimura et al who demonstrated a giant magnetoelectric effect in TbMnO$_3$ where the electric polarization may be switched by applying a magnetic field [6]. More recently it has been shown how an applied electric field can be used to manipulate the magnetic domain distribution [7].

For TbMnO$_3$ (space group $Pbnm$) the Mn$^{3+}$ magnetic moments first order below $T_M = 42$ K. It has been reported,
based on recent neutron diffraction data, that below this temperature the moments are polarized along the b direction with a modulation wavevector \((0 \ q_{\text{Mn}} \ 0)\) in TbMnO₃, \(q_{\text{Mn}} \approx 0.29 b^*\). Below \(T_{N2} = 28\ \text{K}\) the magnetic structure adopted by the Mn sublattice becomes non-collinear, forming a cycloid in the b-c plane [8] and, at exactly the same temperature, a ferroelectric polarization along the c direction is observed. By comparing the magnetic structures above and below \(T_{N2}\), an elegant and appealing model was proposed whereby the ferroelectric transition is driven by a loss of inversion symmetry at the Mn sites as the magnetic structure changes from collinear to non-collinear. The same study also proposed that the Tb magnetic moments are disordered in the collinear phase, and become polarized along the a direction on cooling into the cycloidal phase.

X-ray resonant scattering (XRS) has much to offer the study of multiferroics in general [9–12], and TbMnO₃ in particular. It is an element and electron shell specific technique, which in the case of TbMnO₃ makes it possible to study any ordering of the Mn and Tb sublattices separately. Neutron diffraction by contrast measures the scattering from the sum of the separate contributions. Moreover, XRS is capable of providing information on the presence of any multipolar order [13]. This includes multipoles with time-odd, parity-odd symmetry that may characterize the combined magnetic and ferroelectric state displayed by TbMnO₃ and other related multiferroics [14]. Recently the results of a number of XRS studies of TbMnO₃ have been reported, all performed in the hard part of the x-ray spectrum above 3 keV [15, 16]. The edges accessed in this part of the spectrum are the Mn K and Tb L₂ edges which, for the dominant electric dipole resonances observed, provide information on the ordering of the 4p and 5d extended band states at the Mn and Tb sites, respectively. Here we highlight two of the main results of this x-ray work [15].

The first is the surprising observation of a large polarization of the Tb 5d states in the collinear phase, where according to the former beamline was used for its superior flux and high incident photon energy resolution to determine the energy dependence of the scattering. These measurements were conducted in a similar fashion to that of Wilkins et al [20–22] on both beamlines. The samples were mounted on the diffractometer with the surface normal and [001] direction lying within the scattering plane. In both cases, the diffraction plane was vertical. At 5U1 and ID08 the base temperatures achievable were 22 K and 19 K respectively. Due to experimental apparatus limitations it was not possible to measure the polarization of the scattered x-rays.

3. Results and discussion

We first consider the results for the Mn L edges taken using the [0 1 0] orientated sample. On cooling below \(T_{N1} \approx 42\ \text{K}\) an F-type satellite diffraction peak was observed at \((0 \ q \ 0)\), with \(q \approx 0.295 b^*\) just below \(T_{N1}\). The peak was present at both the L₂ and L₃ edges, and was found to increase in intensity and move to lower \(q\) as the temperature was decreased (figures 1(a) and (b) peak). By fitting this satellite peak to a Lorentzian line shape, the correlation lengths (defined as \(\xi = \frac{\kappa}{q}\)) were determined to exceed 200 Å in both the L₂ and L₃ edges, and in both the cycloidal and collinear phases. This result demonstrates that the x-rays probe a significant number of unit cells within the crystal and hence, these measurements are not particularly surface sensitive.

A scan of the incident photon energy at fixed wavevector transfer in the high-temperature collinear phase revealed strong enhancements of the scattering cross-section at the Mn L₂ and L₃ edges (figure 1(c)). While a simple, single resonant response is evident at the L₂ edge, the energy line shape displays much more structure in the vicinity of the L₃ edge. Notwithstanding these important details, the strong electric dipole resonances, combined with the sharpness of the peaks in reciprocal space, establishes the fact that the Mn 3d electronic states display long-range order in the collinear phase. In figure 1(c) the results of an energy scan in the cycloidal phase
Figure 1. \(\theta-2\theta\) scan of the (0 \(q\) 0) reflection in the cycloidal (25.5 K) and collinear (32 K) phases collected with incident x-ray photon energies equal to (a) the Mn L3 resonance (639 eV) and (b) the Mn L2 resonance (652 eV) as determined from (c) an energy scan at fixed wavevector of the (0 \(q\) 0) reflection in the two phases. The vertical arrows indicate the energies at which a temperature dependence was recorded. Apart from an overall increase in intensity, the response in this phase is indistinguishable from that in the collinear one.

It should be noted that a number of soft x-ray resonant scattering studies have been made of related rare-earth manganite compounds, which are not multiferroic [20–23]. Results from all of these studies have shown that, for both the magnetic and orbital reflections, the resonant feature at the Mn L3 edge is always strongest. This is clearly not the case for the (0 \(q\) 0) reflection observed in this study. However, to obtain further information from this fixed wavevector energy scan, detailed modeling of the electronic structure is required, which is beyond the scope of the present work.

Figure 2. Temperature dependence of the (0 \(q\) 0) superlattice reflection: (a) the position and (b) the integrated intensity of the Mn L2 (652.3 eV) and L3 (643.1 eV) edges. (c) the integrated intensity of the (0 \(q\) 1) superlattice reflection at the Tb M5 edge (1240 eV), (an offset of −2 K has been applied to this data). Finally (d) is the integrated intensity of the (0 1 – \(q\) 0) superlattice reflection, again this was recorded with photons equal in energy to the Tb M5 edge (1240 eV).

at 19 K are also shown. Apart from an overall increase in intensity, the response in this phase is indistinguishable from that in the collinear one.

It should be noted that a number of soft x-ray resonant scattering studies have been made of related rare-earth manganite compounds, which are not multiferroic [20–23]. Results from all of these studies have shown that, for both the magnetic and orbital reflections, the resonant feature at the Mn L3 edge is always strongest. This is clearly not the case for the (0 \(q\) 0) reflection observed in this study. However, to obtain further information from this fixed wavevector energy scan, detailed modeling of the electronic structure is required, which is beyond the scope of the present work.

Scans parallel to \(b^*\), across the (0 \(q\) 0) reflection were performed as a function of temperature at incident photon energies equal to the main features of the Mn L2 and L3 edges, which are not multiferroic [20–23]. Results from all of these studies have shown that, for both the magnetic and orbital reflections, the resonant feature at the Mn L3 edge is always strongest. This is clearly not the case for the (0 \(q\) 0) reflection observed in this study. However, to obtain further information from this fixed wavevector energy scan, detailed modeling of the electronic structure is required, which is beyond the scope of the present work.

We now consider the results taken with photon energies close to the Tb M4 and M5 edges. In contrast to the Mn L edges, where only the F-type reflection may be observed, at the Tb M edges, A-and C-type reflections are also accessible. (To observe the A-type reflection, the [0 1 0] was replaced by the [0 0.28 1] orientated sample.) Comprehensive searches in the collinear phase for any of these reflections produced negative results. On cooling into the cycloidal phase, strong, well-
was observed in the cycloidal phase at the Tb M 5-edge, but of the (0 1 1271 eV) as determined from (c) an energy scan at fixed wavevector which a temperature dependence was recorded.

Influenced by the cycloidal magnetic order. Figure 2(c) shows A-type (0 1) reflection. The vertical arrow indicates the energy at which a temperature dependence was recorded.

Figure 3. (a) (b) and (c) a 2θ scan of the (0 q 1) reflection in the cycloidal phase at T = 26 K collected with incident x-ray photon energies equal to (a) the Tb M 5 resonance (1240 eV) and (b) the Tb M 4 resonance (1271 eV) as determined from (c) an energy scan at fixed wavevector of the (0 q 1) reflection. The vertical arrow indicates the energy at which a temperature dependence was recorded.

defined A-type reflections appeared at both the M 4 and M 5 edges. The sharpness of the diffraction profiles (figures 3(b) and (a)) immediately establishes that the electronic states (in this case the Tb 4f states) are long-range ordered. Figure 3(c) shows a energy scan at the fixed wavevector of the (0 q 1) reflection in the cycloidal phase, demonstrating significant resonances at the M 5 edge and M 4 edges. This indicates that for the (0 q 1) reflection, the Tb 4f electronic states are strongly influenced by the cycloidal magnetic order. Figure 2(c) shows the temperature dependence of the scattered intensity for the modulation wavevector of the A-type (0 q 1) reflection at the Tb M 5 edge. As for the F-type peak, where the results were taken at the Mn L edges, the magnitude of the modulation wavevector evolves as a function of temperature. For this crystal orientation, however, the reflection becomes off-specular. Experimental limitations at 5U1 made it impossible to accurately resolve the evolution of peak’s position as the temperature was increased, and hence here we only present the integrated intensity as a function of temperature, determined as for the (0 q 0) reflection. As can be seen, the intensity of the scattering at the M 5 edge drops rapidly and linearly with increasing temperature, with zero intensity being observed for T > 24 K.

In conclusion, we have performed the first direct element specific study of the effect of the magnetic order on the electronic structure of magnetoelectric multiferroic TbMnO 3. We have demonstrated that the Mn 3d localized bands display strong long-range order in both magnetic phases for the F-type domain. The temperature dependence of this (0 q 0) reflection is in good agreement with previously observed trends for both the position of the modulation wavevector (0 qMn 0) and the scattered intensity, with clear changes at the magnetic phase transitions. Mn L edge energy scans at this wavevector show minimal changes in the overall 3d band structure between the collinear and cycloidal phases. The scattered intensity as a function of temperature does differ, however, between measurements performed at the Mn L 2 and L 3 edges. The transition at 28 K into the ferroelectric phase is more significant for the measurements performed at the Mn L 3 edge. The energy scans taken at the Tb M edges clearly show, that for the A-type (0 q 1) reflection, the Tb 4f band is highly influenced by the cyclodial magnetic order, whilst this reflection was absent in the collinear phase, indicating that there is no long-range ordering of the Tb 4f states for this phase. This data supports the neutron diffraction model which states that the Tb 4f states should be disordered in the collinear phase. However the absence of Tb 4f ordering in the collinear phase suggests that ordering of Tb 5d bands as seen with hard x-rays [15] is of a different origin. In addition to strong Tb M edge resonances observed for the A-type peak, much weaker Tb M edge resonance peaks corresponding to the F-type (0 q 0) and C-type (0 1 q 0) reflections were observed in the cycloidal phase. The fact that these two reflections were observed with π-incident x-rays only and are much weaker, suggest a difference between the magnetic structures of the domain states. Finally, the lack of an F-type reflection in the vicinity of the oxygen K edge, shows that for this reflection at least, there is no long-range ordering of the oxygen 2p band.

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