Origin of incommensurate satellite reflections on TbMnO$_3$ by resonant x-ray scattering

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Abstract. We have performed a deep spectroscopic study of incommensurate satellite reflections ($h, k, l$) $\pm (0, 0.278, 0)$ on a TbMnO$_3$ single crystal in order to shed light on its physical origin. Resonant x-ray scattering experiments at the Mn K-edge and Tb L$_3$-edge have been performed at different temperatures and azimuthal angles, analyzing the outgoing light polarization. Our experimental results agree with a magnetic origin for A and C-type reflections, while F and G-type have the hallmarks of anisotropic tensor susceptibility (ATS) reflections, so that they come purely from the structural modulation.

1. Introduction.
The characterization of the complex magnetoelectric phase diagram of TbMnO$_3$ has become a great challenge in the recent years [1-4]. This multiferroic material shows a collinear antiferromagnetic (AFM) ordering (A-type) of Mn sublattice below $T_N^{1} \approx 41$K [1]. The amplitude of the moments of this magnetic structure is sinusoidally modulated, being the modulation vector $q \approx 0.278b^*$ incommensurate (ICM). Below $T_N^{2} \approx 27$K Mn moments develop a new component along $c$ resulting in a cycloidal magnetic structure [3]. A net electric polarization along $c$ axis appears at $T_N^{2}$ due to the inversion symmetry breaking caused by this non-collinear magnetic structure. In addition, Tb sublattice orders AFM below $T_{TB} \approx 8$K.

Under this complex scenario many attempts to characterize the ICM reflections have been performed [2-7], some of them being contradictory. Following Bertaut’s notation [8], the ICM reflections are classified as A-type ($h+k$ even, $l$ odd), F-type ($h+k$ even, $l$ even), C-type ($h+k$ odd, $l$ even) and G-type ($h+k$ odd, $l$ odd), independently of its origin: (i) structural (ATS, from atomic environment anisotropy) or (ii) magnetic (magnetic moment modulations on magnetic ordered phases). Neutron diffraction experiments on single crystals mainly detected A and G-type reflections on the collinear phase [2, 3]. Some authors ascribe the appearance of G-type reflections on the non-collinear ($T_N^{2}$) phase to Tb ordering coupled to Mn [2], while some others also detect C and F-type reflections arising from this coupling as well [3].

Resonant x-ray scattering (RXS) is a very powerful technique to separate Tb and Mn contributions due to its chemical selectivity, but it can also provide information on the nature of the reflections. Magnetic reflections are much weaker than Thomson (standard diffraction) reflections. When tuning
the photons out of the absorption edge, both magnetic and Thomson reflections can be detected in the \(\sigma-\sigma'\) and \(\pi-\pi'\) polarization channels (being \(\sigma\) and \(\pi\) polarizations perpendicular and parallel to the scattering plane, respectively). However, Thomson reflections are not seen in the \(\sigma-\pi'\) channel, so reflections that are observed out of resonance in the \(\sigma-\pi'\) channel correspond to magnetic reflections [8]. On the other hand, when tuning the photon energy across the absorption edge, both ATS and magnetic reflections can be detected in the \(\sigma-\pi'\) channel.

Regarding RXS experiments on TbMnO\(_3\) single crystals, some authors claim that only A-type reflections are due to magnetic modulations while F and C reflections do not come from the magnetic modulation [4]. However, other authors claim that F-type reflections are magnetic when appearing in the non-collinear phase [5-7].

We have performed a deep spectroscopic study both at Mn K-edge and Tb L\(_3\)-edge of ICM satellite reflections such as \((h, k, l) \pm (0, q, 0)\), being \(q=q_{\text{Mn}}=0.278\), in order to solve the controversy on the physical origin of these modulations.

2. Experimental section.

TbMnO\(_3\) single crystals were grown by the floating zone method at University of Zaragoza. The untwined crystal was cut and polished with faces perpendicular to [100]/[010]/[001] directions. It was characterized by x-ray powder diffraction and magnetic susceptibility measurements, being the lattice parameters \(a=5.316\ \text{Å},\ b=5.831\ \text{Å},\ c=7.375\ \text{Å}\).

RXS experiments were carried out at ID20 beam line on the ESRF (Grenoble, France). A double crystal Si (111) monochromator was used to select the energy of the beam, which is 99% linearly polarized perpendicular (\(\sigma\)) to the scattering plane. A closed-cycle helium refrigerator was used to study the temperature dependence of the reflections down to 12 K. Azimuthal dependence was also tested by rotating the sample around the scattering vector \(Q\). The scattered beam polarization (\(\sigma'\) or \(\pi'\)) was analysed putting a Cu (220) crystal between the sample and the detector. All reflections were studied off and on resonance at the Mn K-edge and Tb L\(_3\)-edge.

3. Results.

A and F-type reflections are observed at both absorption edges below \(T_{N1}\). The energy dependence of these reflections at the Mn K-edge can be observed at figure 1. Both reflections are resonant in the \(\sigma-\pi'\) channel, while no intensity was observed in the \(\sigma-\sigma'\) one.

![Figure 1](image.png)

Figure 1. Energy dependence at zero azimuthal angle in the \(\sigma-\pi'\) channel and at several temperatures below \(T_{N1}\) of (a) \((0, 4-q, 0)\) F-type reflection and (b) \((0, 4-q, 1)\) A-type reflection.
The (0, 4-q, 0) F-type reflection shows a main resonance at the Mn K-edge, as it is shown in figure 1(a), but there is no diffracted peak at this reflection out of resonance. The spectral dependence of this reflection is very similar to that observed for the (0, 3, 0) reflection [10], which is forbidden by the group symmetry but seen on resonance due to the ATS contribution [11]. However, A-type reflections show a non-resonant contribution (NRXS) below T_{N1}, which is the main feature of magnetic reflections.

The azimuthal evolutions for A and F type reflections have been checked (not shown here): while the first one does not show any significant change along the φ-scan, F-type reflection shows a cos^2θ modulation. Azimuthal evolution of A-type reflections is not expected. The scattering factor (proportional to scalar product $k \cdot m$) is almost constant around $Q$ for this reflection in the non-collinear phase because $m_b$ and $m_c$ show very close values [2].

The same spectroscopic behaviour is found at the Tb L3-edge for F and A-type reflections, as can be observed on figure 2(a). There is a NRXS contribution for A-type, while F-type reflection can be only detected on resonance in the $\sigma^{'}\pi$ channel. The temperature dependence of both reflections on resonance (Tb L3-edge) can be seen on figure 2(b). It is very similar to that observed at Mn K-edge, as both reflections appear below T_{N1} and no changes are noticeable across T_{N2}.

On the other hand, C and G-type reflections appear just below T_{N2} only at Tb L3-edge in the $\sigma^{'}\pi$ channel. Figure 3(a) shows the resonances at Tb L3-edge of both reflections. G-type is less intense than C type reflection, so its signal is normalized to the first. It is noteworthy that the maximum of G-type reflection is shifted to high energies with respect to C-type. C-type reflection is also observed out of resonance (magnetic origin) and its temperature dependence is plotted on the inset of figure 3(a) at E=7.5 keV: it disappears above T_{N2}. The temperature dependence of C and G-type on resonance (Tb L3-edge) is plotted in figure 3(b), both appearing below T_{N2}, in the non-collinear phase.

The azimuthal evolution of (0, 3-q, 0) C-type reflection can be observed on the inset of figure 3 (b) and corresponds to the variation of the c magnetic moment component around the scattering vector in the non-collinear phase.
Figure 3. (a) Energy dependence of C (l=0) and G (l=1) type reflections at the Tb L$_3$-edge and 12 K in the σ-π’ channel. Inset: Temperature evolution of the off-resonance intensity of (0, 3+q, 0) C-type reflection. (b) Temperature evolution of the same reflections on resonance. Inset: Azimuthal evolution of (0, 3-q, 0) C-type on resonance.

4. Conclusions
The experimental results above make it possible to assert that A-type reflections, which are observed below $T_{N1}$ at both Mn K-edge and Tb L$_3$-edge on and off resonance, come from the magnetic modulation. However, F-type reflections are not seen out of resonance, so they cannot be ascribed to the magnetic modulation. On the other hand, its spectral dependence points to an ATS origin, coming from a structural modulation of the out-of-diagonal elements of the Mn and Tb atomic scattering factors, that is, $f_{xy}=f_{xy0}+\delta f_{xy}[2\pi q(R_n+r)]$.

On the other hand, C and G-type reflections are only resonant at the Tb L$_3$-edge and below $T_{N2}$. C-type reflections are also observed off resonance so that they contribute to non-resonant magnetic scattering. G-type reflections, not detected off-resonance, show the hallmarks of ATS reflections, coming from a structural modulation from the Tb sublattice.

Both Mn and Tb magnetic modulations are coupled with $q=q_{Mn}=0.278$ below $T_{N2}$, but also the lattice ones, as F and G-type reflections are showing.

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