Antiferromagnetically Spin Polarized Oxygen Observed in Magnetoelectric $TbMn_2O_5$

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We report the direct measurement of antiferromagnetic spin polarization at the oxygen sites in the multiferroic $TbMn_2O_5$, through resonant soft x-ray magnetic scattering. This supports recent theoretical models suggesting that the oxygen spin polarization is key to the magnetoelectric coupling mechanism. The spin polarization is observed through a resonantly enhanced diffraction signal at the oxygen *K* edge at the commensurate antiferromagnetic wave vector. Using the FDMNES code we have accurately reproduced the experimental data. We have established that the resonance arises through the spin polarization on the oxygen sites hybridized with the square based pyramid Mn^{3+} ions. Furthermore we have discovered that the position of the Mn^{3+} ion directly influences the oxygen spin polarization.

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The ability to couple magnetism and ferroelectricity, namely, the control of charges by changing the magnetic state of a material, paves the way to the development of novel multifunctional devices. Recently, the goal of controlling a ferroelectric state by the application of a magnetic field was realized in $TbMnO_3$ [1], and launched a new area of research into magnetoelectric materials. In these materials the coupling is provided through complex magnetic structures. One important class of theory to explain the spontaneous electric polarization in perovskite manganites assumes the presence of an incommensurate cycloidal magnetic structure arising from magnetic frustration [2,3]. Such a magnetic structure breaks global inversion symmetry and allows the development of a ferroelectric moment. It is interesting therefore, that in $TbMn_2O_5$, a material found to have a huge magnetoelectric coupling [4], larger even than that in $TbMnO_3$, the magnetic structure was found to be commensurate and almost collinear [5]. This suggests that an entirely different mechanism drives the magnetoelectric coupling in $TbMn_2O_5$, opening up a possible new route for the development of multiferroic devices. One possible mechanism has been suggested by Moskvin and co-workers [6,7], who show the importance of the charge transfer between the manganese and oxygen, which results in a spin polarization of the oxygen sites.

In this Letter we report the direct observation of a long range, correlated spin polarization at the oxygen sites in $TbMn_2O_5$, by resonant soft x-ray scattering at the oxygen *K* edge. A resonance was measured at the (0.5,0,0.25) antiferromagnetic wave vector corresponding to the commensurate magnetic order. Through *ab initio* calculations of the incident x-ray energy dependence of the diffraction intensity we show that the ordered spin polarization arises from the oxygen sites hybridized with the Mn^{3+} ions. The temperature dependence of the oxygen spin polarization and the manganese ordering confirms that the oxygen spin polarization appears at the high temperature commensurate transition, simultaneous to the onset of the ferroelectric dipole moment. We suggest that the oxygen spin polariza-

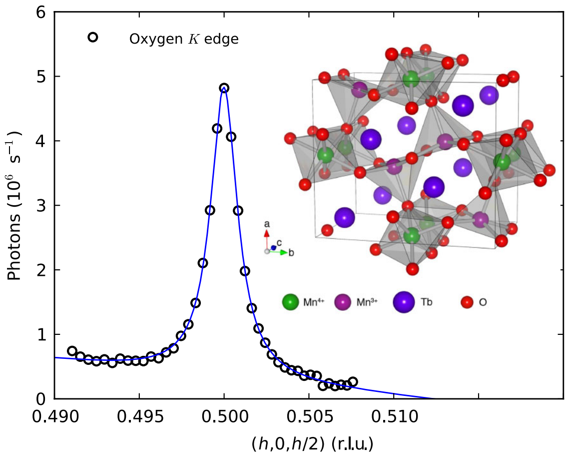

FIG. 1 (color online). **Q** scan of intensity in the (2,0,1) direction in reciprocal space at the oxygen *K* edge at 529.3 eV. The solid blue line is a fit of a Lorentzian line shape with a linear background. The inset represents the *Pbam* crystal structure of $TbMn_2O_5$, highlighting the two different positions of the manganese ions. The grey polyhedra show the octahedra centered on the Mn^{4+} ions (green), and the square based pyramids around the Mn^{3+} ions (purple).

tion is a key factor in the magnetoelectric mechanism of $TbMn_2O_5$, and more generally in multiferroic materials.

$TbMn_2O_5$ crystallizes into the orthorhombic *Pbam* space group [8], with Mn^{3+} and Mn^{4+} ions occupying Wyckoff 4*h* and 4*f* positions respectively [8] (Fig. 1). This places the Mn^{3+} ions in the square based pyramids, and the Mn^{4+} ions at the center of the octahedra. A commensurate magnetic structure is observed between 24 and 33 K, where both Mn^{3+} and Mn^{4+} ions form antiferromagnetic chains in the *ab* plane alternately coupling ferro- and antiferromagnetically (↑↑↓↓) along the *c* axis [5,9]. Incommensurate magnetic phases occur above and below this commensurate phase, and the system is paramagnetic above 43 K. Below 10 K the rare earth ions order antiferromagnetically, although recent resonant x-ray studies have shown a spin polarized terbium 5*d* band in all magnetically ordered phases [10–12]. At 38 K, a large peak in the dielectric constant is observed [4], due to the formation of a spontaneous ferroelectric polarization along the *b* axis. A dramatic drop in the electric polarization is observed upon further cooling below 24 K, concomitant with the low temperature commensurate to incommensurate magnetic transition.

Soft x-ray scattering provides unique insights into the physics of strongly correlated transition metal oxides, and multiferroic materials [13,14], partly due to the great advantage of performing an element specific magnetic measurement. By tuning to a particular absorption edge, it is possible to resonantly enhance scattering from specific ions in a material [15]. Our scattering experiments were undertaken at ID08, ESRF and 5U.1, SRS Daresbury. A single crystal sample of $TbMn_2O_5$ was prepared though prealignment and polishing such that the (2,0,1) direction was surface normal. Figure 1 shows the (0.5,0,0.25) antiferromagnetic signal at the oxygen *K* edge observed upon cooling below 38 K. Figure 2 shows the incident photon energy dependence of the integrated intensity of the (0.5,0,0.25) reflection, and the fluorescence yield (inset), in the vicinity of the oxygen *K* absorption edge. Such strong resonant enhancements were also observed at the manganese $L_{2,3}$ and terbium $M_{4,5}$ edges, and will be discussed in a future paper. The data presented in Fig. 2 were collected by performing a **Q** scan at each energy, to obtain the integrated intensity and exclude the fluorescence background. The **Q** scan of the diffraction peak (Fig. 1) shows that the peak width is limited by the attenuation of the beam by the sample, providing a lower bound on the correlation length of ~2000 Å. The intensity of the reflection was $5 \times 10^6\ s^{-1}$, compared to $4 \times 10^8\ s^{-1}$ at the manganese L_3 edge.

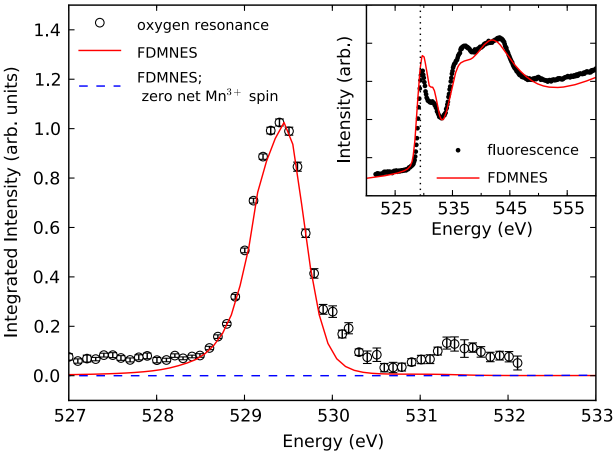

FIG. 2 (color online). Integrated intensity of **Q** scans in the (2,0,1) direction through the (0.5,0,0.25) reflection, at energies from 527 eV to 532 eV through the oxygen *K* edge. (Inset) Fluorescence measurement at the oxygen *K* absorption edge, with a dotted line indicating the peak of the resonant signal. The solid red lines in both panels display the FDMNES calculations, the dashed blue line in the main panel shows the result from a simulation with zero net spin on the Mn^{3+} ions.

This surprising observation of a diffraction signal at the oxygen *K* edge indicates an antiferromagnetically ordered spin polarization on the oxygen sites. To confirm that the scattering observed at the oxygen *K* edge is indeed magnetic, we measured the azimuthal dependence, at both the oxygen *K* edge and manganese L_3 edge. The resonant x-ray scattering cross section is dependent on the incident x-ray energy, the polarization of the incident and outgoing x rays, and the Fourier component of the magnetic structure. The energy dependence gives us the resonant profile as shown in Fig. 2, while the polarization dependence indicates the direction of the Fourier component. It is possible to take a measurement sensitive to such a direction by rotating the sample around the scattering vector, thereby changing the projection of the electric field of the incident x rays on the magnetic moment. Figure 3 shows the azimuthal dependence measured with vertically (π) polarized incident x rays at the manganese L_3 and oxygen *K* edge sensitive to the direction of the Fourier components on the manganese and oxygen sites, respectively. The dashed lines superimposed on these data are calculations based on the magnetic structure as reported by Blake [9], and the resonant x-ray cross section [16]. The oxygen *K* and manganese L_3 edge data show exactly the same anisotropy with the differences between the curves arising solely due to geometrical differences due to the different photon energies. It is apparent therefore, that both the spin polarized oxygen and the manganese possess a common magnetic structure.

The temperature dependence of the commensurate magnetic reflection shown in the inset of Fig. 3, displays a transition at both the oxygen and manganese edges at 38 K. The identical temperature dependencies at both the manganese and oxygen edges further confirm the link between the spin polarization on the oxygen and the magnetic structure on the manganese ions. There has been some confusion over the coexistence of the magnetic and electric polarization transitions. Neutron diffraction studies have reported a magnetic transition at 33 K [5], some 5 K lower

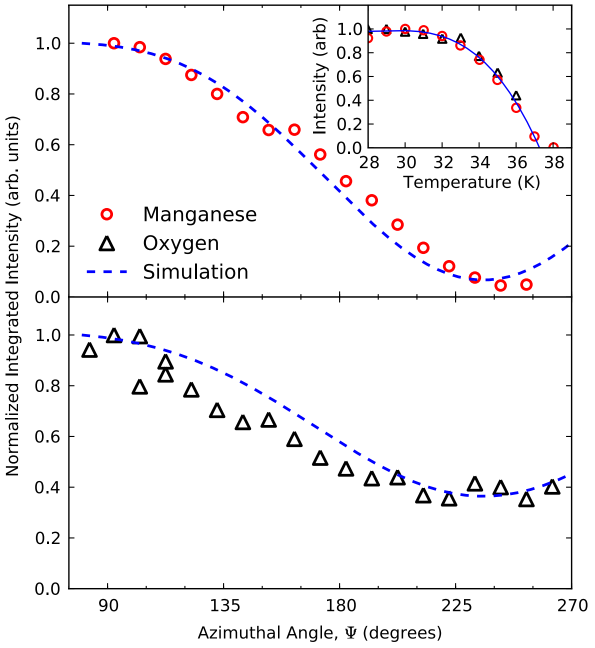

FIG. 3 (color online). Variation of intensity of the diffraction signal at the manganese L_3 and oxygen K edges with azimuthal rotation of the sample around the scattering vector, with vertically (π) polarized incident x rays. The dashed lines show simulations of the azimuthal dependence as calculated from the manganese moments determined by Blake *et al.* [9]. $\Psi = 0$ corresponds to the c axis in the scattering plane, the fitting errors for the azimuth are within the size of the data points. (Inset) Temperature dependence of the (0.5,0,0.25) reflection at the manganese L_3 edge (644.1 eV) and oxygen K edge (529.4 eV). The solid line shows a guide to the eye.

than the electric polarization transition. This has caused difficulty in the analysis of transitions between the magnetic point groups of incommensurate and commensurate magnetic structures [17]. Our data, in agreement with earlier x-ray [18] and neutron diffraction studies [19], strongly suggest a simultaneous magnetic and ferroelectric transition, simplifying the phase diagram. We also observed an incommensurate magnetic reflection at both the oxygen and manganese absorption edges between 37 and 42 K.

To establish the origin of the resonant x-ray scattering signal we performed calculations with the FDMNES code [20]. FDMNES is an *ab initio* cluster based monoelectronic code, written for calculating x-ray absorption and x-ray resonant diffraction signals. Figure 2 shows the results of the FDMNES calculations based on the crystal structure of Blake *et al.* [9], with the oxygen positions corresponding to the room temperature neutron diffraction data [8], the only data currently available. The calculation used a magnetic unit cell of size $2a \times b \times 4c$ containing 160 oxygen atoms at 40 inequivalent sites, calculated over a cluster radius of 4 Å, with an average of 23 atoms per cluster. The simulated intensity arose entirely from the $E1$-$E1$ electric dipole terms. A successful fit to the data was achieved using the FDMNES code, with a Fermi energy of 527.7 eV. The simulation of the fluorescence yield, based upon absorption calculations, is in excellent agreement with the experimentally measured curve as shown in the inset of Fig. 2. The FDMNES simulation of the resonance not only correctly predicts the energy corresponding to the maximum intensity, but also reproduces the main spectral feature. It is interesting however that there are further small resonances at 531.5 eV and possibly 530 eV, that are not reproduced by FDMNES. It is possible that these correspond to mixing of the unoccupied manganese t_{2g} and e_g spin bands with the oxygen $2p$ states [21]. The presence of these further unoccupied states in the resonant diffraction signal show that these states are also antiferromagnetically ordered.

Calculations of the density of states of the manganese ions show that at the energy corresponding to the oxygen K edge resonance, the only available final states correspond to the Mn^{3+} ions. By contrast the nearest available Mn^{4+} states are ~10 eV higher in energy, suggesting that the resonant signal observed at the oxygen K edge arises purely from long range order of the spin polarization of the oxygen sites through the hybridization with the Mn^{3+} ions. A second FDMNES simulation was performed with zero net spin on the Mn^{3+} ion, shown by a dashed line in Fig. 2. This shows no calculated intensity at the (0.5,0,0.25) wave vector confirming this hypothesis.

The *Pbam* symmetry of $TbMn_2O_5$ allows freedom of the position of the Mn^{3+} ion along the axis of the pyramid. Such movement alters the Mn-O bonds, and thus the hybridization between the manganese $3d$ and oxygen $2p$ states. We investigated the effect of the position of the Mn^{3+} within the square based pyramid, and how this affects the antiferromagnetic spin polarization of the oxygen sites, through calculating the intensity of the (0.5,0,0.25) reflection at the oxygen K edge. Figure 4 shows how the simulated resonant scattering intensity varies as a function of the position of the Mn^{3+} ion as it is moved out of the basal plane of the pyramid toward the apical oxygen. The zero position corresponds to the manganese ion sitting in the basal plane, and the arrow shows the experimentally determined position of the Mn^{3+} in $TbMn_2O_5$ [9]. The structure factor corrected result shows that as the Mn^{3+} ion is moved out of the basal plane, the degree of antiferromagnetic spin polarization increases, shown by the increasing intensity of the (0.5,0,0.25) signal. The calculation indicates that when the manganese is in the basal plane there is minimal long range ordered spin polarization with the magnetic wave vector. However, the antiferromagnetically ordered spin polarization is close to the maximum when the Mn^{3+} ions are at the empirically measured position.

Two theories currently compete to explain the origin of the spontaneous polarization in $TbMn_2O_5$. The first, ''ionic polarization'' model, requires a displacement of ions from their centrosymmetric positions thereby generating an electric polarization. This ionic displacement is extremely small, with calculated displacements in the order of

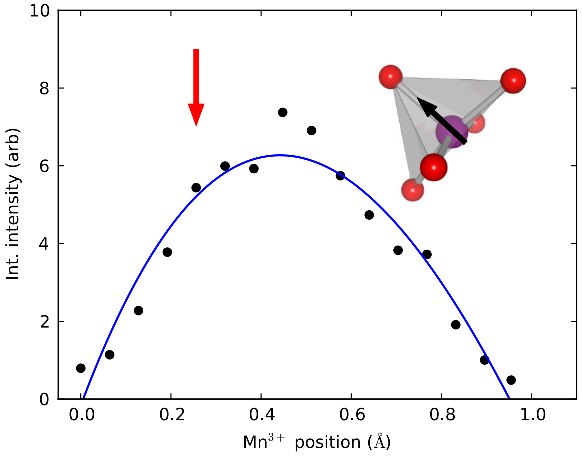

FIG. 4 (color online). Calculated integrated intensity of the K edge resonance line shape at $\mathbf{Q} = (0.5, 0, 0.25)$ as a function of Mn position on the axis of the MnO_5 pyramid (see inset). The solid line is a guide to the eye and the vertical (red) arrow indicates the experimentally determined position [9].

10^{-3} Å [22], and has not yet been measured, although an experimental method has been suggested [23]. In the second model; the spin configuration induces a charge redistribution around the ion nucleus, thus supporting an electric polarization. This model is supported by optical second harmonic generation results [24], and requires a strong Mn-O hybridization and spin polarization of the oxygen ligands [6].

A strong electric polarization is produced from this parity breaking exchange mechanism where the electric polarization on the oxygen ($\mathbf{P}_O$) can be written [7]:

$$\mathbf{P}_O = \sum_n \Pi_n (\langle \mathbf{S}_O \rangle \cdot \mathbf{S}_n) \tag{1}$$

where Π_n is the effective dipole moment of the manganese orbital states, $\mathbf{S}_n$ are the spins of the manganese, and $\langle \mathbf{S}_O \rangle$ is the spin polarization of the oxygen ligands. It is reasonable to assume that $\langle \mathbf{S}_O \rangle \cdot \mathbf{S}_n$ is maximized by the common structure of the ordered spin moment on the manganese and the oxygen spin polarization, demonstrated here through the common $\mathbf{Q}$ and azimuthal dependencies. Our data, clearly showing a long range order of the spin polarization of the oxygen sites induced by the hybridization with the Mn^{3+} ions, reinforce previous work showing that the MnO_5 pyramid contributes particularly strongly to the electric polarization [6].

In conclusion, the presence of a resonantly enhanced soft x-ray diffraction signal at the oxygen K edge at the (0.5,0,0.25) wave vector proves the existence of a significant, long range correlated order of the spin polarization of the oxygen sites. The temperature dependence reveals a common transition temperature, coinciding with the high temperature commensurate transition, confirming the magnetic origin of both reflections. Comparing the azimuthal dependencies of the signals observed at the manganese L_3 and oxygen K edge we establish a common magnetic structure for both elemental sites, that of the previously refined manganese magnetic structure. Through simulating the resonance using the FDMNES code we have shown that the resonance arises from the order of the spin polarization on the oxygen sites hybridized by the Mn^{3+} ion. While not ruling out the ionic polarization model, such a spin polarization of the oxygen is a crucial component in the model of Moskvin and Pisarev [6] to explain the magnetoelectric coupling in $TbMn_2O_5$. Furthermore we show that the position of the manganese within the square based pyramid in $TbMn_2O_5$ is such that the ordered spin polarization is dramatically increased when compared to the basal plane ion position. We believe that further studies of oxygen spin polarization in multiferroics will lead to great insights in the understanding of the magnetoelectric coupling mechanism.

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