

Resonant X-ray Emission Spectroscopy of Multiferroic TbMnO_3

The Mn 3d valence states in single-crystalline TbMnO_3 along three crystallographic axes were investigated by spin-selective X-ray absorption spectrum (XAS) and resonant X-ray emission spectrum (RXES). The polarized Mn K-edge X-ray absorption spectra show strong polarization dependence, particularly for the white line region. An energy shift ~ 2.4 eV is observed for the maximum of the white line of the Mn K-edge spectra obtained along $E // b$ relative to $E // a$ and $E // c$, indicating the highly anisotropic Mn-O bonding within the ab plane in TbMnO_3 . The $1s3p$ -RXES spectra obtained at the Mn K edge clearly reveal that unoccupied Mn 3d states exhibit a relatively delocalized character, as a consequence of the hybridization of the unoccupied Mn 3d states with the neighboring Mn 4p orbitals. We demonstrated that resonant X-ray emission spectroscopy is able to characterize the degree of localization of the unoccupied states or hole carriers in magnetics.

Multiferroic materials, in which two or more properties among (anti-)ferroelectricity, (anti-)ferromagnetism, and (anti-)ferroelasticity coexist, have recently sparked a surge of interest due to their potential applications in novel magnetoelectric and magneto-optical devices using magnetoelectric (ME) effect. The multiferroicity has been observed recently in manganites such as TbMnO_3 , DyMnO_3 and TbMn_2O_5 . TbMnO_3 exhibits the orthorhombically distorted perovskite structure at room temperature, and shows an incommensurate (IC) lattice modulation at the Néel temperature ($T_N = 42$ K) corresponding to a sinusoidal antiferromagnetic (AF) ordering along the b axis. A second transition into a noncollinear spin arrangement in the spiral phase ($T \sim 28$ K) is accompanied by ferroelectric ordering with an electric polarization $P // c$. The ME phase diagram of TbMnO_3 differs substantially according to the crystallographic axis along which the magnetic field is applied. The quest to understand the origin of multiferroicity has stimulated great interest in the magnetic, structural and dielectric properties of the multiferroic materials.

The appearance of the ferroelectricity at the transition into the spiral structure of RMnO_3 with $R = \text{Tb, Dy, Gd}$ was microscopically explained in terms of the spin supercurrent by $\mathbf{P} = \eta \mathbf{e}_{ij} \mathbf{x}(\mathbf{S}_i \times \mathbf{S}_j)$, where \mathbf{P} is the electric polarization, \mathbf{S}_i and \mathbf{S}_j are the magnetic moment, \mathbf{e}_{ij} is the unit vector connecting the sites i and j , and η is a factor proportional to the transfer integral and is thus related to the hybridization of the Mn 3d states. Based on band structure calculations, Elfimov et al. proposed the hybridization of extended Mn 4p states with neighboring Mn 3d orbitals to be a major factor in the anomalous X-ray scattering at the Mn K-edge in manganites. Moreover, on-site Mn 4p-3d

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hybridization in manganites was artificially introduced to account for an increased intensity in the Mn K -edge pre-edge region for Mn in a tetrahedral coordination site relative to an octahedral coordination site. The Mn $4p$ -Mn $3d$ hybridization is expected to be correlated to the relatively delocalized character of the unoccupied Mn $3d$ states in RMnO_3 , due to the large radial extent of the Mn $4p$ states. However, no clear-cut experimental evidence of the delocalization of the unoccupied Mn $3d$ states nor of the hybridization of the unoccupied Mn $3d$ states with the Mn $4p$ orbitals in manganites has been provided.

Although numerous studies can be found on the structural, magnetic, and dielectric properties of TbMnO_3 , the electronic structure and especially the degree of localization of the Mn $3d$ states in TbMnO_3 has not been investigated in detail. In this study, we investigated the hybridization of Mn $3d$ states in TbMnO_3 using X-ray absorption spectroscopy and resonant X-ray emission spectroscopy.

Untwined high-quality TbMnO_3 single crystals were grown by the high-temperature solution growth method with the use of PbF_2 flux in a Pt crucible. The crystal surfaces of the crystallographic directions of (001), (010), and (100) were prepared using an X-ray diffractometer. The Mn K -edge X-ray absorption spectra and Mn $1s3p$ -RXES spectra were performed at the Taiwan Beamline BL12XU at SPring-8 in Japan. The emitted X-ray fluorescence was analyzed using a Si (440) spherically bent analyzer of 1 m radius. Energy analysis was performed in reflection geometry by moving simultaneously the analyzer and the detector in accordance with the Rowland condition. The overall resolution was estimated to be ~ 0.9 eV from the full width at half maximum (FWHM) of the elastic peak measured at the Mn $K\beta_{13}$ emission energy, ~ 6492 eV.

Figure 1 shows polarized Mn K -edge high-resolution X-ray absorption spectra of single-crystalline TbMnO_3 measured at ~ 10 K for the polarizations $E // a$, $E // b$, and $E // c$. The absorption spectra were obtained in the partial-fluorescence-yield mode, with the spectrometer energy fixed at the maximum of the Mn $K\beta_{13}$ line. The Mn K -edge X-ray absorption spectra consist of two well resolved peaks in the pre-edge region (P1 and P2 in Fig. 1) and an intense white line on the site of greater photon energy (B in Fig. 1). As noted, three pseudo-Voigt functions were required to properly model the pre-edge structures.

These pre-edge features are generally ascribed to quadrupole $1s$ - $3d$ and/or modifications of the dipole transition probability due to the hybridization between $3d$ and $4p$ states. In the case of the Mn oxide systems, the latter are assumed to be dominant. However, there has been no direct evidence to elucidate this controversial issue. There

have been a large number of papers in addressing these issues for many transition metals, not all of which are in agreement. The interpretation of the pre-edge features remains controversial. The present work reveals the nature of the pre-edge peaks P1 and P2, as discussed in the following paragraphs. The main line (peak B in Fig. 1) is related to the $1s$ to $4p$ transitions. The feature C gains intensity from the multiple scattering contribution of MnO_6 surrounded by eight Tb. As shown in Fig. 1, the Mn K -edge X-ray absorption spectra exhibit a significant anisotropy along the three crystallographic directions, particularly for the main line region (peak B). As noted, a substantial difference in the spectral shape and energy of the main line is observed among the polarizations, especially for $E // b$ compared with $E // a$ and $E // c$. An energy shift ~ 2.4 eV is measured for the maximum of the main line of the spectrum obtained along $E // b$ relative to $E // a$ and $E // c$. This implies the strong anisotropic Mn-O bonding within the ab plane in TbMnO_3 and relatively weak covalency along the b axis. The origin of this energy difference is reminiscent of the Jahn-Teller distortion of the MnO_6 octahedra and the Coulomb repulsion between the occupied $3d$ orbital and the $4p$ orbitals.

The MnO_6 octahedra of TbMnO_3 is highly distorted and tilted with an average in-plane Mn-O-Mn bond angle of $\sim 145^\circ$ to be compared with a much larger value of $\sim 155^\circ$ in LaMnO_3 . Through the large tilting in TbMnO_3 , the relatively weak overlap between the Mn $3d$ e_g and the O $2p$ orbitals along the b axis, as shown in Fig. 1, is too small to provide a strongly FM superexchange between Mn cations. This distorted octahedra in TbMnO_3 leads to the highly anisotropic Mn-O bonding within the ab plane as

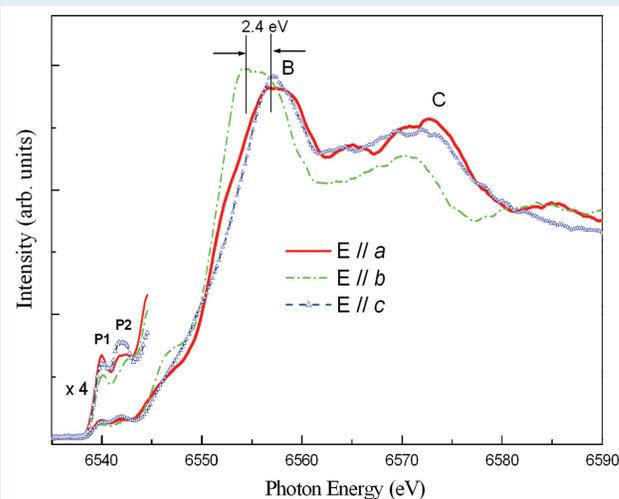


Fig. 1: Polarization-dependent Mn K -edge X-ray absorption spectra of single-crystalline TbMnO_3 for polarizations $E // a$, $E // b$; and $E // c$ at ~ 10 K measured by partial-fluorescence-yield at the $K\beta_{13}$ line. The pre-edge peaks P1 and P2 are shown enlarged.

evident in Fig. 1, and in turn to the frustrated magnetic ordering caused by the competitions of the ferromagnetic superexchange nearest-neighbor (nn) Mn-Mn interactions and the antiferromagnetic superexchange next-nearest-neighbor (nnn) Mn-Mn interactions along the diagonal in Mn-O plaquette (along *b*-direction), in particular spiral spin structures, responsible for their multiferroic behaviour in TbMnO₃.

The *1s3p*-RXES spectra obtained for single-crystalline TbMnO₃ at ~ 10 K are shown in Fig. 2(a), 2(b) and 2(c), respectively for *E* // *a*, *E* // *b*, and *E* // *c* polarizations. The RXES spectra are plotted as a function of transfer energy, and ordered from bottom to top in increasing incident photon energies. Ticks in the Mn *K*-edge X-ray absorption spectrum indicate the excitation energies at which the RXES spectra were recorded. We analyzed the RXES data in terms of quadrupolar transitions to $1s^{-1}3d^{n+1}$ intermediate states or dipolar-assisted transitions to $1s^{-1}3d^n4p^1$ intermediate states, which are primarily assigned to the pre-edge and white-line spectral regions. The final states are reached by decay of a *3p* electron, leading to the $3p^{-1}3d^{n+1}$ or $3p^{-1}3d^n4p^1$ configuration. For simplicity we here neglect multielectronic effects and configuration interaction.

As clearly seen in Fig. 2(a)-2(c), the features related to transitions to the localized intermediate $1s^{-1}3d^{n+1}$ states appear at a constant transfer energy, characteristic of the so-called Raman regime.¹³ Fluorescence-like features,

corresponding to the delocalized $3p^{-1}3d^n4p^1$ final states, appear at a linearly dispersed transfer energy with the incident energy. The whole series of RXES spectra was fitted with a sum of Voigt functions. The emission energy of the fluorescence line provided by the fitting of the RXES spectra is plotted as a function of the incident energy in the top panels of Fig. 2(a)-2(c) (crosses, right scale). The inclined line indicates the Raman region, whereas the horizontal one corresponds to the fluorescence regime. Especially noteworthy from Fig. 2(a)-2(c) is that the Raman regime is only limited to below the pre-edge. The fluorescence regime starts from the first pre-peak of $1s \rightarrow 3d$ transitions, indicating the delocalization of intermediate $1s^{-1}3d^{n+1}$ states and thus a relatively delocalized character of unoccupied Mn *3d* states.

A reasonable explanation for the delocalization of intermediate $1s^{-1}3d^{n+1}$ states via $1s \rightarrow 3d$ transitions originates from the hybridization between Mn *3d* and Mn *4p* orbitals, of which the later belongs to the photon-absorbing Mn atom or to a neighboring Mn atom. We found that the relatively delocalized character of the unoccupied Mn *3d* states was observed even in nearly octahedral structure of Tb_{0.15}Ca_{0.85}MnO₃, for which the contribution of on-site Mn *3d*-*4p* hybridization is negligible. Accordingly, it is expected that hybridization between Mn *3d* orbitals and neighboring Mn *4p* states in TbMnO₃ makes a major contribution to pre-edge structures in Mn *K*-edge x-ray absorption spectrum. Based on the calculations of band structure in LaMnO₃,

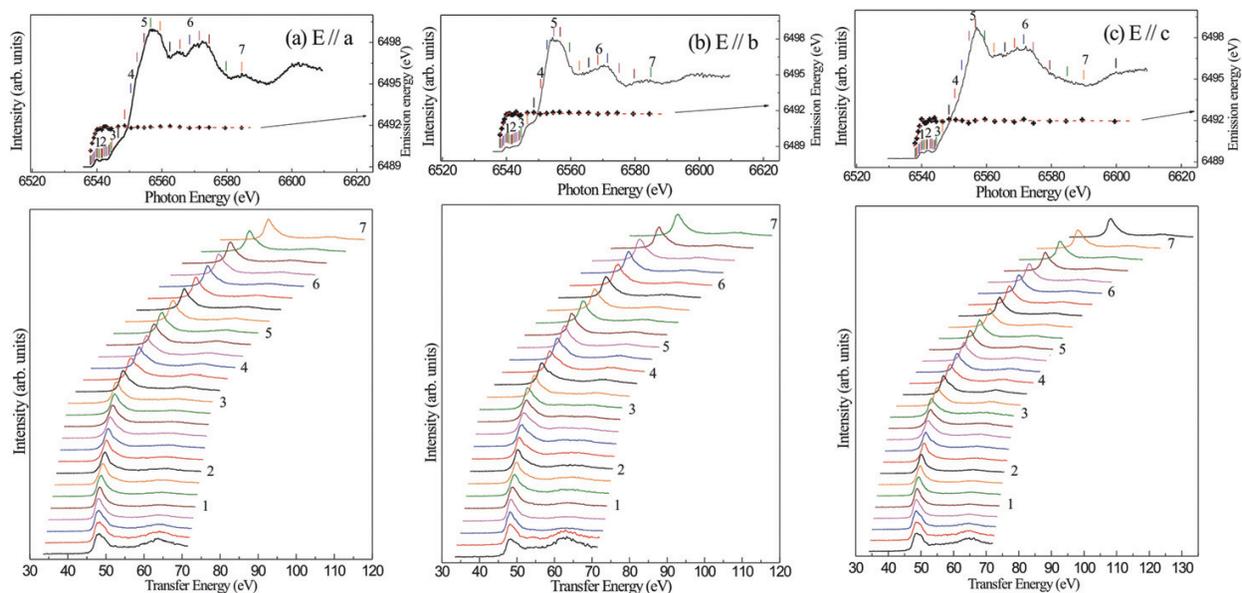


Fig. 2: *1s3p*-resonant X-ray emission spectra of single-crystalline TbMnO₃ measured at ~ 10 K as a function of transfer energy for polarizations (a) *E* // *a*, (b) *E* // *b*, and (c) *E* // *c*. The resonant X-ray emission spectra are plotted from bottom to top in increasing incident photon energies. Ticks in the Mn *K*-edge absorption spectrum shown in the top panels indicate the excitation energies at which the resonant X-ray emission spectra were recorded. The number indicated in the emission spectra corresponds to the excitation energy marked in the Mn *K*-edge X-ray absorption spectra. The emission energy at the $K\beta_{13}$ line in the emission spectra as a function of the incident energy along three crystallographic directions is plotted in the top panels (crosses, right scale).

Elfimov *et al.* proposed that the central Mn $4p$ orbitals hybridize either directly or via the intervening O $2p$ orbitals with the neighboring Mn $3d$ orbitals. The present RXES fully agrees with this hypothesis. Similar phenomenon for the Mn $3d$ -Mn $4p$ hybridization has been found for other manganites, such as DyMnO_3 , TbMn_2O_5 , $\text{Dy}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x = 0 - 0.85$), $\text{Tb}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x = 0 - 0.85$), *etc.* The hybridization of the unoccupied Mn $3d$ states with the neighboring Mn $4p$ orbitals is thus not specific to TbMnO_3 . It is therefore believed that the present experimental finding is of a general nature in manganites.

To ensure a proper assignment of the preedge features P1 and P2 in Fig. 1, we performed local density approximation plus on-site Coulomb interaction U (LDA+U) band structure calculations for hypothetical A-type AF, E-type AF-, and ferromagnetic (FM) structure of TbMnO_3 . P1 in Fig. 1 is ascribed to the transition into unoccupied majority-spin $e_g \uparrow$ states hybridized with the Mn $4p$ states. The direct coupling strength of the off-axis t_{2g} states with the $4p$ orbitals is proposed to be negligible. However, based on polarized O K -edge X-ray absorption spectra of TbMnO_3 single crystals, strong hybridization of the Mn $t_{2g} \downarrow$ and the O $2p$ orbitals was observed particularly for $E // c$. As shown in Fig. 1, the intensity of the P2 peak is stronger for $E // c$ relative to $E // a$ and $E // b$. It appears that the $t_{2g} \downarrow$ orbitals, hybridized indirectly with the neighboring Mn $4p$ states through the O $2p$ states, contribute to the P2 peak. We therefore suggest that P2 in Fig. 1 is assigned as a superposition of the transition into empty minority-spin $t_{2g} \downarrow$ and $e_g \downarrow$ states hybridized with the $4p$ states.

In conclusion, we investigated the Mn $3d$ valence states of single-crystalline TbMnO_3 by combining XAS and RXES. The polarized Mn K -edge X-ray absorption spectra show strong a polarization dependence, particularly for the white line region. The RXES spectra obtained at the Mn K -edge clearly reveal that the unoccupied Mn $3d$ states exhibit a relatively delocalized character as a consequence of the hybridization of the unoccupied Mn $3d$ states with the neighboring Mn $4p$ orbitals. We clearly demonstrated that with resonant X-ray emission spectroscopy one can characterize successfully the degree of localization of the unoccupied states or hole carries in manganites. ■

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Publication

- J. M. Chen, C. K. Chen, T. L. Chou, I. Jarrige, H. Ishii, K. T. Lu, Y. Q. Cai, K. S. Ling, J. M. Lee, S. W. Huang, T. J. Yang, C. C. Shen, R. S. Liu, J. Y. Lin, H. T. Jeng, and C. C. Kao, *Appl. Phys. Lett.* **91**, 054108 (2007).

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