Mn K-edge XANES of hexagonal manganites $RMnO_3$ (R = Sc, Y)

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Abstract

Mn K-edge X-ray absorption near-edge spectra (XANES) and magnetic studies for ferroelectromagnetic compounds $RMnO_3$ (R = Sc, Y) are reported. $ScMnO_3$ shows stronger $d-p$ hybridization with a triangular antiferromagnetic (AF) order of $T_N = 133$ K and a spin reorientation $T_{sr} = 23$ K, as compared to $T_N = 74$ K for $YMnO_3$. The identical main threshold edge energy of 6545 eV indicates Mn^{3+} character. Small pre-edge features with energy separation P_2 - P_1 of 2.27 eV for $ScMnO_3$ and 2.72 eV for $YMnO_3$ is from the 1*s*-3*d* dipole transition, which is weakly allowed through the hybridization of Mn 4*p* with 3*d* states of neighboring Mn atoms. The larger P_1 peak is corresponding to transition into empty $e'_\downarrow$ and $e''_\downarrow$ minority states, and the smaller P_2 peak is into leftover $e'_\downarrow$ states.

Key words: ferroelectromagnetic materials; triangular antiferromagnetism; XANES

The rare earth hexagonal $RMnO_3$ manganites ($P6_3cm$) are ferroelectromagnetic materials possessing both ferroelectric (FE) and antiferromagnetic (AF) ordering. The FE transition T_{FE} occurs at high temperature around 600-1000 K, while triangular AF Néel temperature T_N occurs below 70-130 K [1-7]. The Mn^{3+} ion ($3d^4$, S = 2) is subject to a trigonal bipyramidal crystal field where 3*d* levels are splitted into a_1 and two doubly degenerate *e* states (e' and e''), with four *d* electrons in $e_\uparrow$ majority spin states by Hund's rule. The FE polarization is caused by the displacement of ions along the hexagonal c-axis. The AF structure below T_N is a 120° triangular AF configuration which coexists and strongly couples with FE phase. For nonmagnetic rare compounds, $YMnO_3$ shows a simple $T_N \simeq 70$ K [2-6]. On the contrary, complex spin reorientation with confusing reorientation temperature T_{sr} below $T_N \simeq 130$ K were reported for $ScMnO_3$ [1-3,5,7]. Here we report the Mn K-edge XANES for these two interesting compounds.

Samples were synthesized by standard solid-state reaction. The measured hexagonal formula unit volume $V_{f.u.} = V_h/Z$ (Z = 6) of 54.84 Å^3 for $ScMnO_3$ and 61.94 Å^3 for $YMnO_3$ indicate that the samples prepared are close to 113 stoichiometric composition with trivalent Mn^{3+} [7]. The extremely small volume of $ScMnO_3$ indicates stronger MnO_5 crystal field and Mn-O 3*d*-2*p* orbital hybridization.

The molar magnetic susceptibility χ_m(T) in 1-kG field with zero-field-cooled (ZFC) and field-cooled

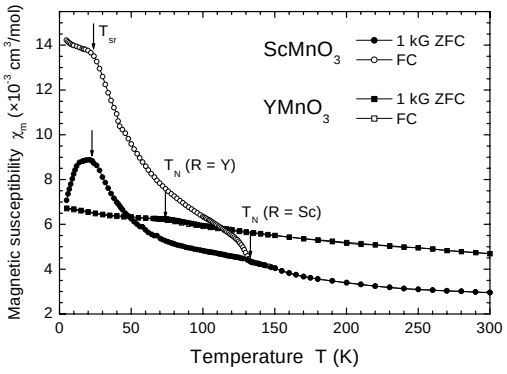

Fig. 1. Molar magnetic susceptibility χ_m(T) in 1-kG field (ZFC and FC modes) for $ScMnO_3$ and $YMnO_3$.

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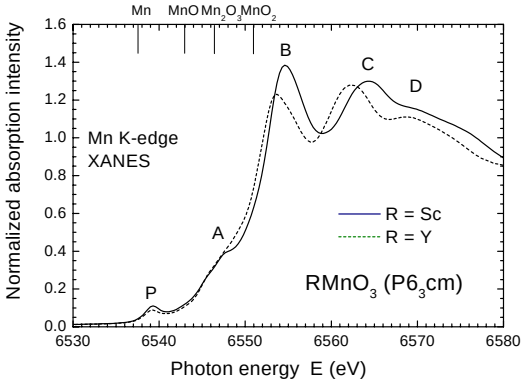

Fig. 2. Mn K-edge XANES for $RMnO_3$ (R = Sc, Y). The threshold edge energy of three standards and Mn metal foil are indicated.

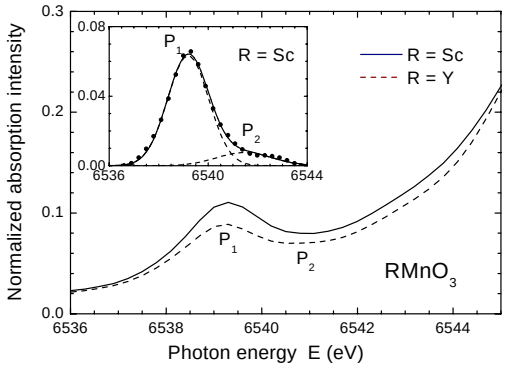

Fig. 3. Low intensity pre-edge region of Mn K-edge XANES for $RMnO_3$ (R = Sc, Y). The pre-edge P can be fitted with two peaks P_1 and P_2 (inset for $ScMnO_3$).

(FC) modes for $ScMnO_3$ and $YMnO_3$ are shown in Fig. 1. The kink near 73 K with almost identical ZFC and FC values indicates AF order with T_N = 74 K for $YMnO_3$. For $ScMnO_3$, the merging point of ZFC and FC curves with larger FC value indicates a T_N = 133 K with weak ferromagnetic (WFM) contribution from non-perfect AF alignment in the hexagonal basal plane. No spin reorientation is observed in $YMnO_3$. For $ScMnO_3$, a spin reorientation $T_{sr} \simeq 23$ K is observed. This T_{sr} value is close to 22 K observed from SHG spectroscopy [2]. More spin reorientations may exist at higher temperature but are difficult to identify in the magnetic measurements [2,3,7]. The neutron diffraction measurement indicates that the ordered Mn moments are aligned along the hexagonal [100] axis for $ScMnO_3$ with a $T_{sr} \simeq 75$ K [3]. The low temperature at T = 5 K magnetization data for $ScMnO_3$ shows a small residual magnetic moment m_r of 3×10^{-3} μ_B/Mn [7]. On the contrary, almost pure AF behavior with negligible m_r of 2×10^{-5} μ_B/Mn was observed for $YMnO_3$ [7]. These values are much smaller than the ordered magnetic moment of 3.54 μ_B/Mn for $ScMnO_3$ and 2.90 μ_B/Mn for $YMnO_3$ [3].

The Mn K-edge XANES at room temperature is shown in Fig. 2. The energy is calibrated by a Mn metal foil with threshold edge energy of $E_0 = 6537.4$ eV. The E_0 for three standards MnO (Mn^{2+}), Mn_2O_3 (Mn^{3+}), and MnO_2 (Mn^{4+}) indicate a substantial shift of E_0 with increasing Mn formal valence. Almost identical $E_0 = 6545$ eV for Sc and Y samples indicate trivalent Mn^{3+}. The XANES is sharp with a long, low energy tail. The main edge is attributed to 1*s*-4*p* dipole transition to Mn 4*p* states. The shape of the edge with features labeled as A, B, C, D can be reasonably explained by the 4*p* partial density of states, which is broaden by the finite lifetime of 1*s* core hole. The 4*p* states are highly delocalized and extend over several Mn atoms and the small pre-edge feature P observed is corresponding to 1*s*-3*d* dipole transition which is weakly allowed through the hybridization of Mn 4*p* states with 3*d* states of neighboring Mn atoms.

Fig. 3 shows the low intensity pre-edge P feature. The pre-edge P can be fitted with two peaks P_1 and P_2 after subtracting the smooth background, with energy separation P_2 - P_1 = 2.27 eV for $ScMnO_3$ and 2.72 eV for $YMnO_3$. Since the Mn *d* levels in MnO_5 crystal field are splitted into a_1 and two doubly degenerate *e* states (e' and e'') with four *d* electrons in $e_\uparrow$ majority spin states. The LSDA+U calculation indicates that the allowed 1*s*-3*d* dipole transition is into unfilled $e_\downarrow$ and a_1 states [4]. The transition into a_1 states is unfavorable from orbital wavefunction overlap point of view, so the larger P_1 peak appears corresponding to transition into empty $e'_\downarrow$ and $e''_\downarrow$ minority states and the smaller P_2 peak from leftover $e'_\downarrow$ states [7]. The smaller peak intensity for $YMnO_3$ is due to larger volume with weaker hybridization of Mn 4*p* states with Mn 3*d* states of neighboring atoms.

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