2D ferromagnetic fluctuation above T_N in orbital-ordered $LaMnO_3$

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Abstract

Onset of two-dimensional (2D) ferromagnetic (FM) short range order with $T_{2D} \simeq 150$ K above A-type antiferromagnetic (AF) Néel temperature $T_N = 139$ K was observed in 100-G low field for orbital-ordered $LaMnO_3$. The A-type AF long range order is stabilized through strong 2D basal plane FM superexchange coupling of orbital-ordered e_g electrons and weak c-axis AF coupling. Both T_{2D} and T_N are field dependent, and merge in 1-T high field around 130 K. Mn K-edge X-ray absorption near-edge spectrum (XANES) for orbital-ordered $LaMnO_3$ at room temperature indicates a pre-edge splitting of 2.0 eV due to weakly allowed $1s$-$3d$ dipole transition.

Key words: A-type AF order; orbital order; 2D FM short range fluctuation

$LaMnO_{3+\delta}$ is the parent compound of colossal magnetoresistance (CMR) materials $La_{1-x}A_xMnO_{3+\delta}$ [1-9]. In the stoichiometric $LaMnO_3$ Mott insulator, all the Mn ions are trivalent with four $3d$ electrons with configuration $t_{2g}^3 e_g^1$, due to MnO_6 octahedral crystal field and strong Hund's rule coupling. The three t_{2g} electrons are well localized, while the lone e_g electron occupies one of the doubly degenerate e_g orbitals which are strongly hybridized with the oxygen $2p$ orbitals. The Mn^{3+} ion has both spin and orbital degrees of freedom. The orbital degree of freedom is spontaneous frozen by the real space ordering of e_g orbitals accompanied by the cooperative Jahn-Teller lattice distortion with an orbital ordering temperature $T_{OO} \simeq 780$ K [3-5]. The spin and orbital degrees of freedom are strongly coupled and the Mn spins are ordered antiferromagnetically (A-type AF order) through anisotropic superexchange interaction below $T_N \simeq 140$ K. The A-type AF structure is stabilized by the strong 2D basal plane ferromagnetic (FM) superexchange coupling, and by the weak c-axis AF coupling [1-9].

In order to check the possibility of 2D FM short range fluctuation with T_{2D} above T_N, the $LaMnO_{3+\delta}$ samples ($\delta = 0, 0.07, 0.1$) were synthesized by standard solid-state reaction. The oxygen stoichiometric parameter δ is controlled by annealing samples at 1000^oC in flowing Ar with 5% H_2, in air or in O_2. The structural studies indicate that there are no interstitial oxygen sites for $LaMnO_{3+\delta}$. With fully occupied oxygen sublattice and La/Mn vacancies, the correct composition is $La_zMn_zO_3$ with z = 3/(3+δ), and maximum formula unit volume $V_{f.u.}$ (= $V_o/4$ for orthorhombic phase (Pbnm) and = $V_r/6$ for rhombohedral ($R\bar{3}c$) phase) is achieved at the stoichiometric $LaMnO_3$ [1,2]. By comparing with reported data, the $\delta \simeq 0$ is achieved for Ar/H_2 sample with $V_{f.u.} = 61.24$ $\mathring{A}^3$, $\delta \simeq 0.07$ for air sample with $V_{f.u.} = 59.55$ $\mathring{A}^3$, and $\delta \simeq 0.1$ for O_2 sample with $V_{f.u.} = 58.90$ $\mathring{A}^3$ [9].

The XANES for the $LaMnO_{3+\delta}$ samples are shown in Fig. 1. 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+}), M_2O_3 (Mn^{3+}) and MnO_2 (Mn^{4+}) indicates a substantial shift of E_0 with increasing Mn formal valence. Since the spectra of three $LaMnO_{3+\delta}$ samples show a substantial shift of the edge energy which agree well with previously reported $LaMnO_{3+\delta}$ data [6-8], this indicates that the sample annealed in Ar/H_2 is very close to $\delta = 0$ with Mn^{3+}.

The molar magnetic susceptibility χ_m(T) in low 100-

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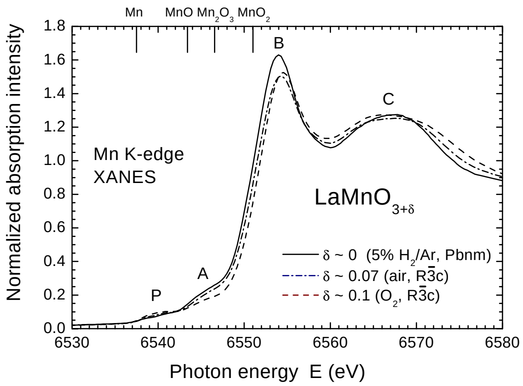

Fig. 1. Mn K-edge XANES for $LaMnO_{3+\delta}$. The threshold edge energy of three standards and Mn metal foil are indicated.

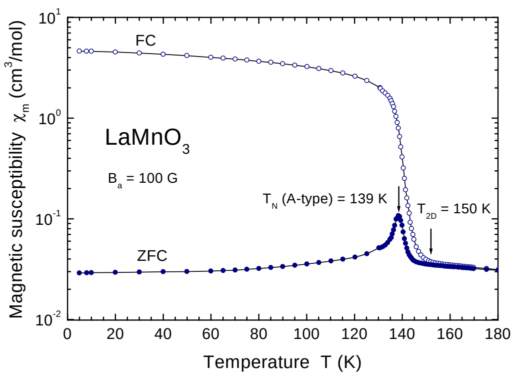

Fig. 2. Molar magnetic susceptibility χ_m(T) in 100-G field (ZFC and FC modes) for $LaMnO_3$. 2D FM short-range order T_{2D} is defined as the merging point of ZFC and FC curves.

G zero-field-cooled (ZFC) and field-cooled (FC) mode for the stoichiometric, orthorhombic $LaMnO_3$ sample are shown in Fig. 2. Sharp A-type AF transition in ZFC curve with T_N of 139 K is observed with small peak value. A 2D FM short range order is observed from the merging point of ZFC and FC curves with $T_{2D} \simeq 150$ K. Both T_{2D} and T_N are field-dependent, with $T_{2D} \simeq 142$ K, $T_N = 137$ K in 1-kG field, and $T_{2D} \simeq T_N \simeq 130$ K in high field of 1 T. The FC data in Fig. 2 indicates a weak ferromagnetic (WFM) contribution for $LaMnO_3$. The hysteresis loop at 5 K for $LaMnO_3$ [9] shows a soft, WFM behavior with small residual magnetic moment of m_r of 0.11 μ_B/Mn for $LaMnO_3$, which is smaller than the aligned magnetic moment of 3.49 μ_B/Mn for A-type AF order in $LaMnO_3$ [1]. The WFM contribution may originate from weak but non-perfect c-axis AF coupling of t_{2g} electrons between two ferromagnetic planes. However, the possibility of double exchange Mn^{4+}/Mn^{3+} contribution cannot be excluded.

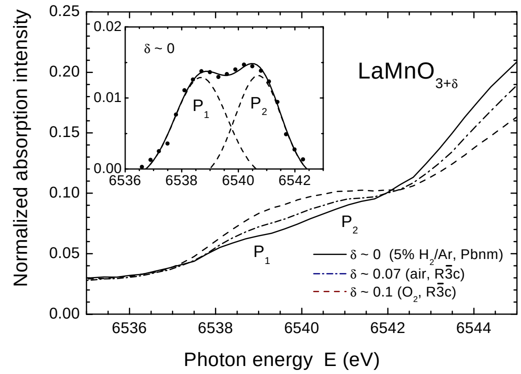

Fig. 3. Low intensity pre-edge region of Mn K-edge XANES for $LaMnO_{3+\delta}$. The pre-edge P for $LaMnO_3$ (inset for $\delta \simeq 0$) can be fitted with two peaks P_1 and P_2.

The room temperature K-edge XANES data shown in Fig. 1 is sharp with a long, low energy tail. The main edge is attributed to $1s$-$4p$ dipole transition to Mn $4p$ states. The shape of the edge with features A, B, C can be explained by the $4p$ partial density of states from LSDA+U calculation, which is broaden by the finite lifetime of $1s$ core hole [6]. The calculation indicates that the $4p$ states are highly delocalized and extend over several Mn atoms. The small pre-edge feature P (Fig. 3) is corresponding to $1s$-$3d$ dipole transition, which is weakly allowed through the hybridization of $4p$ states with $3d$ states of neighboring Mn atoms [6,7]. The low intensity pre-edge P feature for the orbital-ordered $LaMnO_3$ at 300 K can be fitted with two peaks P_1 and P_2 after subtracting the smooth background, with P_2-P_1 energy separation of 2.0 eV [9]. P_1 is corresponding to a transition to empty majority spin $e_{g\uparrow}$ states on the neighboring Mn ions and P_2 is a transition to $e_{g\downarrow}$ and $t_{2g\downarrow}$ minority spin states [6-9].

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