Indication of Novel Orbital Ordering in Ferromagnetic Insulating $La_{7/8}Sr_{1/8}MnO_3$ by Resonant X-ray Scattering

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Introduction

Lightly doped $La_{1-x}Sr_xMnO_3$ (LSMO) ($0.1 < x < 0.17$) compounds exhibit a very intriguing ferromagnetic insulating (FMI) phase at low temperatures, in which the charge ordering and/or orbital ordering (CO/OO) is believed to play a key role. Despite extensive investigations, the nature of the CO/OO in the FMI phase still remains unknown. The characteristic superstructure reflections in the FMI phase were revealed earlier by a number of neutron and x-ray scattering experiments [1-4], which were usually interpreted in terms of the long-range CO and associated lattice modulations. However, based on a recent resonant x-ray scattering (RXS) experiment [5], the earlier CO scenario was questioned, since none of these superstructure reflections were found to show resonance behavior at the Mn K edge. The investigators concluded that the OO is indeed the main characteristic of the FMI phase. However, an orbital ordered state without CO is expected to be metallic and may not be consistent with the fact that the lightly doped LSMO is insulating. In fact, several stable ferromagnetic charge- and orbital-ordered states were realized in a number of recent theoretical calculations [6-8]. The picture was further complicated by the new observations of lower-symmetry monoclinic and triclinic phases at low temperatures for samples with x of ≈0.11 to 0.125 [9, 10], which may indicate the presence of some novel OO type.

RXS has been playing increasingly important role in studies of the degree of freedom of orbitals in highly correlated transition-metal and rare-earth compounds [11]. The antiferro-distortive OO of the type $(3x^2 - r^2)/(3y^2 - r^2)$ in undoped $LaMnO_3$ was experimentally determined by RXS at the Mn K absorption edge [12]. For such K-edge resonance, 4p states of transition metals are involved in the intermediate state in the electric dipolar (E_1) process, and they have to be modulated in accordance with the orbital order. This modulation was initially considered to come from the anisotropic term of the 4p-3d intra-atomic Coulomb interactions, but subsequent studies based on the band structure calculation have revealed that the modulation of 4p states comes mainly from the crystal distortion via the oxygen potential on the neighboring sites [13, 14]. Therefore, RXS can be very sensitive to lattice distortions (e.g., the Jahn-Teller distortions [JTDs] in manganites). Very recently, it was quantitatively revealed that the cooperative JTD is largely responsible for the resonance observed at forbidden Bragg reflections in thin-film $LaMnO_3$ [15]. In contrast, similar resonance was observed not in the JTD regime but only in the FMI phase, indicating a JTD-frustrated region in lightly doped LSMO [5]. This is clearly a very surprising and controversial observation.

Methods and Materials

To re-examine a number of issues mentioned above, new synchrotron x-ray scattering experiments have been undertaken on a number of high-quality and well-characterized single crystals with lightly doped Sr. In this report, only the results from the $La_{7/8}Sr_{1/8}MnO_3$ sample will be discussed. The x-ray scattering measurements were undertaken at MU-CAT beamline station 6-ID-B at the APS by using a standard, four-circle, vertical scattering geometry. A closed-cycle cryostat was used to cool down the sample. To discriminate the different polarization states of the scattered beam in a resonant scattering experiment, a polarization analyzer set up with a Cu(220) crystal was employed.

Results

The $La_{7/8}Sr_{1/8}MnO_3$ sample transforms to a ferromagnetic insulator below 150K, and the characteristic superstructure reflection $q_1 = (0,0,1/2)$ appearing in the FMI phase was characterized by comprehensive nonresonant x-ray scattering measurements [16]. The temperature dependence of the satellite reflection (0,0,3.5) is shown in Fig. 1, which is reminiscent of a second-order transition into the ferromagnetic insulating phase.

With the polarization analysis, the strong resonance from the forbidden (0,1,0) reflection was observed at the σ-π' channel, as shown in Fig. 2(a). The main resonance is at about 6554 eV; a weaker second resonance takes place 12 eV higher, at 6566 eV. This “double resonance” feature was perfectly predicted from the band structure calculation [14].

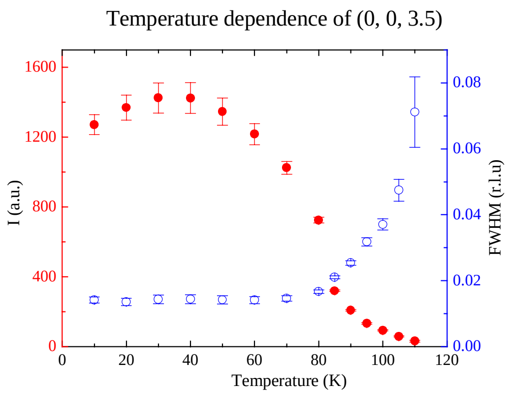

FIG. 1. Temperature dependence of (0,0,3.5).

The temperature dependence of RXS at (0,1,0), as shown in Fig. 2(b), is amazingly matched by the measured orthorhombic strain in the *a*-*b* plane, which is an indication of the cooperative JTD. The azimuthal-angle dependence of the (0,1,0) resonance at all temperatures shows the same characteristic behavior as that observed in $LaMnO_3$. This result clearly does not support the claim that the RXS from the forbidden reflections (0,*k*,0) (*k* = odd) represent the order parameter for the OO in the FMI regime. The RXS reflectors taking place at these forbidden Braggs are actually largely influenced by the local anisotropic structural effects.

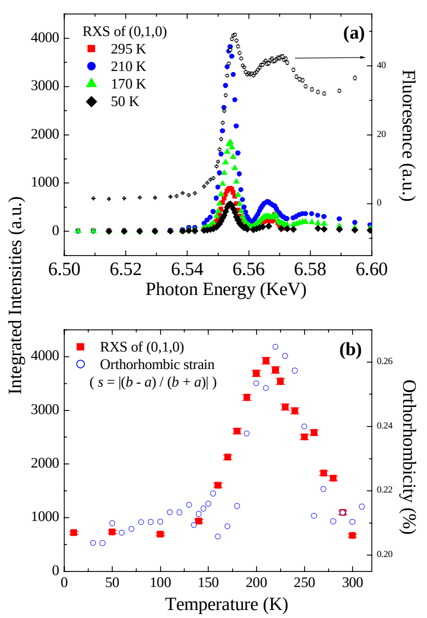

FIG. 2. Energy dependence (a) and temperature dependence (b) of the forbidden (0,1,0).

However, some superstructure reflections were observed to show clear resonant behaviors at the Mn K edge. As shown in Fig. 3, the (1,0,3.5) reflection displays a pure σ-π' resonant component. The temperature-dependence measurements indicate that the resonance at (1,0,3.5) appears only in the FMI regime (below 150K). We argue that this resonant scattering is strongly linked to a novel OO.

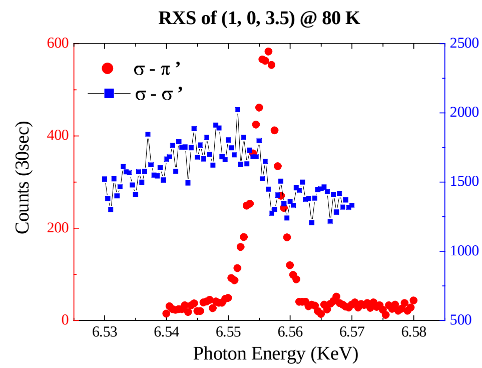

FIG. 3. Energy dependence from the superstructure satellite (1,0,3.5).

Discussion

These latest results indicate that the cooperative JTD, or antiferro-type $(3x^2 - r^2)/(3y^2 - r^2)$ OO, might exist in the whole temperature range, but it reaches the maximum at about 210K. However, the OO is rearranged below 150K, as indicated by the appearance of the resonance scattering from (1,0,3.5). To have a definite model of this novel OO, further experiments are required.

Acknowledgments

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