Ferromagnetic insulating phase in $Pr_{1-x}Ca_xMnO_3$

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Abstract

A ferromagnetic insulating (FM-I) manganite $Pr_{0.75}Ca_{0.25}MnO_3$ has been studied by neutron scattering technique. In contrast to a conventional double exchange picture, $Pr_{0.75}Ca_{0.25}MnO_3$ exhibits a FM-I state, and it has been demonstrated to be ascribed to an orbital ordering rather than charge ordering. The orbital ordering consists of the antiferromagnetic-type orbital ordering like $LaMnO_3$ hybridized with orbitals along the z direction.

Key words: perovskite manganite; orbital ordering; charge ordering

It is well known that by hole doping a number of perovskite manganites show a ferromagnetic metallic (FM-M) state accompanied with a drastic increase of the conductivity. Although the FM-M state has been qualitatively understood by the double exchange (DE) interaction mediated by doped holes, recent intensive studies have revealed that a checkerboard-type (CE-type) charge ordering (CO) is exceedingly robust against hole doping and should be one of the key issues for the insulator-metal transition.

A lightly doped manganite often exhibits a ferromagnetic insulating (FM-I) state [1]. Such a FM-I state is clearly incompatible with a simple DE picture, but might be caused by the existence of the CE-type charge ordered insulating phase [2]. $Pr_{1-x}Ca_xMnO_3$ is a typical example that has a FM-I phase for a relatively wide hole concentration region $0.05 \lesssim x < 0.3$ [3]. The coexistence of the FM-M phase and the charge ordered insulating phase seems to be plausible in this system because the FM-I phase locates adjacent to the CE-type charge ordered phase ($x \geq 0.3$) in the phase diagram. On the other hand, a recent resonant x-ray scattering (RXS) study suggested that the $LaMnO_3$-type orbital ordering (OO), where $d(3x^2 - r^2)$ and $d(3y^2 - r^2)$ orbitals are alternately aligned on all Mn sites, develops below above 500 K in $Pr_{0.75}Ca_{0.25}MnO_3$ [4]. Opposed to the FM spin ordering in $Pr_{0.75}Ca_{0.25}MnO_3$, however, $LaMnO_3$-type OO is generally accompanied with the layered-type (A-type) antiferromagnetic (AFM) spin ordering.

To reveal the true origin of the FM-I state in $Pr_{1-x}Ca_xMnO_3$, we have performed a neutron scattering study on a single crystal of $Pr_{0.75}Ca_{0.25}MnO_3$. We have found that the FM-I state should be ascribed to an OO rather than any COs. The OO established in $Pr_{0.75}Ca_{0.25}MnO_3$ is similar to the $LaMnO_3$-type OO, but has substantial e_g electron density along the z direction.

A single crystal sample studied in the present study was grown by the floating zone method. The crystal structure is orthorhombic $Pbnm$ with pseudo cubic lattice constants $a \sim b \sim c/\sqrt{2}$, and our crystal is fully twined. T_C was determined by the present neutron study as 130 K. The neutron scattering experiments were performed using triple axis spectrometers GPTAS and HQR installed at the JRR-3M research reactor in JAERI, Tokai, Japan with neutron wave lengths $k_f = 3.81$ Å^{-1} (GPTAS) and $k_i = 2.57$ Å^{-1} (HQR).

First, we surveyed (hhl) and $(h0l)$ scattering planes to find signals from CO. We found the nuclear superlattice peaks as well as the pseudo CE-type AFM peaks indicating the presence of the CE-type CO. The intensity of the CE-type AFM peaks are, however, very small

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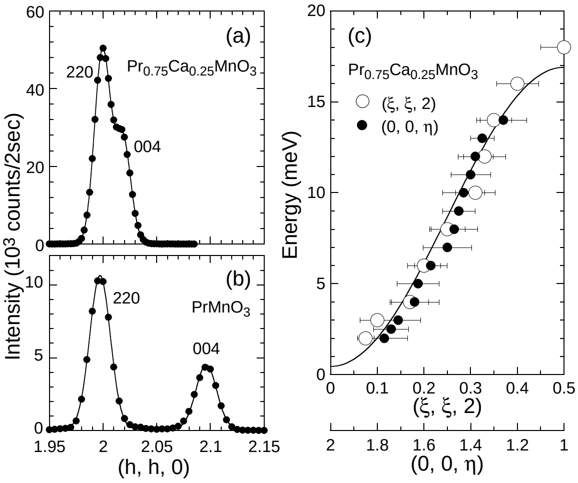

Fig. 1. (a) Profiles of the (220)/(004) doublets along the [110] direction for $Pr_{0.75}Ca_{0.25}MnO_3$ and (b) for $PrMnO_3$. (c) Spin wave dispersion relations in $Pr_{0.75}Ca_{0.25}MnO_3$ along the [110] and [001] directions. Error bars indicate the FWHMs of the profiles of the constant energy scans. Solid line is a dispersion curve for the simple FM Heisenberg model with nearest neighbor couplings. All the data were measured at 8 K.

compared to the FM Bragg peaks. From their intensities, we estimated the volume fraction of the CE-type charge ordered phase to be in the order of 0.1%. We have also tried to find any other types of CO, but did not detect any clear evidence. Therefore, we conclude that the insulating behavior of $Pr_{0.75}Ca_{0.25}MnO_3$ does not come from the CO but it is intrinsic to the FM state in the $x = 0.25$ sample.

Next, we have tried to check the OO reported by the RXS study [4]. If the $LaMnO_3$-type OO exists, it will produce anisotropies in the crystal structure as well as in spin fluctuations: the lattice constants a and b become longer than $c/\sqrt{2}$ due to the cooperative Jahn-Teller distortions, and the exchange interaction within the ab plane J_{ab} becomes smaller than that along the c axis J_c as observed in $LaMnO_3$ [5].

Figure 1(a) shows a profile of the (220)/(004) doublet along the [110] direction at $T = 8$ K. The profile consists of two peaks, indicative of the $LaMnO_3$-type OO. We observed the peaks begin to split below $T \sim 450$ K, which is consistent to the OO temperature observed by the RXS study [4]. The magnitude of the splitting is, however, quite small compared with $PrMnO_3$ (Fig. 1(b)), the latter is expected to have the $LaMnO_3$-type OO. The smallness of the anisotropy was also observed in the spin fluctuations. Figure 1(c) shows the spin wave dispersion relations along the inplane direction [110] and the out-of-plane direction [001] at $T = 8$ K. Two dispersion curves well coincide, indicating that the spin exchange is isotropic ($J_{ab} \sim J_c$) against the expectation from the possible $LaMnO_3$-type OO.

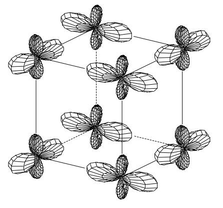

Fig. 2. Schematic view of the orbital ordering of $(|3z^2 - r^2\rangle \pm |x^2 - y^2\rangle)/\sqrt{2}$.

The observed anisotropy in the crystal structure means that there may exist a $LaMnO_3$-like OO, but its smallness and the isotropy in J suggest strongly that there is substantial electron density along the z direction. Such an OO is recently proposed experimentally and theoretically in the insulating phase of $La_{0.88}Sr_{0.12}MnO_3$ [6]. It is expressed by a hybridization of the $d(3z^2-r^2)$ orbital and the $d(x^2-y^2)$ orbital as $\cos(\frac{\theta}{2})|3z^2 - r^2\rangle \pm \sin(\frac{\theta}{2})|x^2 - y^2\rangle$. We show in Fig. 2 a schematic picture of this OO when $\theta = \pi/2$. In this OO, the orbitals are aligned antiferromagnetically in the ab plane like $LaMnO_3$-type OO and also extend along the z direction. The orbitals along the z direction cause small anisotropies in the lattice structure and in spin fluctuations. The AFM-type OO within the ab plane disfavors the electron hopping, while the FM spin couplings are mediated by the super exchange interactions, consequently resulting in the FM-I state. Note that this OO is compatible with the observation by the RXS study [4] because the symmetry of the arrangement of orbitals is same as the $LaMnO_3$-type OO.

The present result suggests that the $(|3z^2 - r^2\rangle \pm |x^2 - y^2\rangle)$-type OO is a ubiquitous phenomenon in the lightly-doped FM-I region in perovskite manganites. This OO becomes more stable as the one electron band width W becomes narrower, because the FM-I region expands in x-T phase diagram when W gets narrow [1].

In conclusion, we have performed a neutron scattering study on a single crystal of $Pr_{0.75}Ca_{0.25}MnO_3$ to reveal the origin of the FM-I state. We have found that the FM-I state should be ascribed to an OO rather than any COs. The OO resembles $LaMnO_3$-type OO with orbitals along the z direction.

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