Proc. Int. Symposium on Advances in Neutron Scattering Research, Tokai, 2000
J. Phys. Soc. Jpn. **70** (2001) Suppl. A pp. 241-243

Neutron Scattering Study of $La_{1-x}Ca_xMnO_3$ with x=0.15

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Elastic and inelastic neutron scattering measurements have been made on a perovskite hole doped manganite $La_{1-x}Ca_xMnO_3$ with x=0.15 for both powder and single crystal samples to understand the magnetic properties of this compound. Strong diffuse scattering observed in the paramagnetic phase, originates from the ferromagnetic spin fluctuations. New peaks have been observed at 001, 100 and $\frac{1}{2}0\frac{1}{2}$ from 15 K to the ambient indicating the long-range and / or short-range charge and magnetic spin ordering. An anomalous temperature dependent inelastic scatterring intensities were observed by the TOF neutron spectrometer AGNES at 2θ=57-64 ° (close to 101 Bragg peak) at temperatures from 17 to 220 K for powder sample. The peak at about 1.0 meV was only observed at 17 and 98 K being in the ferromagnetic region and smearing in the paramagnetic region, possibly the indication of spin gap formation in the ferromagnetic region. The peak at about 1.0 meV at lower temperatures were also observed for single crystal sample close to $\frac{1}{2}0\frac{1}{2}$ reciprocal point.

KEYWORDS: perovskite manganite, inelastic scattering, ferromagnetic spin fluctuation, charge ordering, orbital ordering

§1. Introduction

Much attention has been given recently to the hole doped perovskite manganite $La_{1-x}Ca_xMnO_3$ since the discovery of colossal magnetoresistance (CMR). Efforts have been focused for the understanding of the sharp resistivity drop near Curie temperature T_c , which are qualitatively explained by the double exchange (DE) mechanism.[1)] It has already been pointed out that the DE model is not sufficient to fully explain the CMR phenomenon in this system, near T_c . The strong electron-lattice coupling arises from Jahn-Teller (J-T) effect of Mn^{3+} (t_{2g}^3 e_g^1) must play an important role in order to perceive the nature of the interaction between the transport properties and magnetism.[2)] The J-T distortion splits the doubly degenerate e_g orbitals into the $3x^2 - r^2$ and $y^2 - z^2$ orbitals, or into the $3y^2 - r^2$ and $z^2 - x^2$ orbitals.[3)] It is found that the charge ordering (CO) and orbital ordering (OO) occur simultaneously at a higher temperature and then spin ordering occurs at a lower temperature.[4)] There are very few spin-excitation studies on doped manganites in the low doping range. Low energy excitations in $La_{1-x}Ca_xMnO_3$ system are still poorly understood. $La_{1-x}Ca_xMnO_3$ system shows strong ferromagnetic (FM) spin fluctuations in the paramagnetic (PM) state with an antiferromagnetic (AFM) ground state.[5-7)] We performed elastic and inelastic neutron scattering experiments on both powder and single crystal samples of $La_{0.85}Ca_{0.15}MnO_3$ to study the magnetic properties of this system. In this report, we present some indication of simultaneous CO and OO, although it was difficult to directly observe an alternating Mn^{3+}/Mn^{4+} pattern, because superlattice peak of CO in our neutron diffraction measurement include the intensity arising from the distortion of crystalline lattice, as a result of oxyzen displacement, *etc.* We also present the indication of spin gap formation at lower temperature in neutron inelastic scattering experiments on both powder and single crystal samples.

§2. Experimental

The single crystal (SC) sample was synthesized by the floating-zone method. The systhesis procedure for the $La_{0.85}Ca_{0.15}MnO_3$ (SC) sample is briefly described elsewhere.[8)] The powder sample (PS) of $La_{0.85}Ca_{0.15}MnO_3$ was prepared by a conventional solid state reaction processing from stoichiometric mixture of La_2O_3 (99.9%), Mn_2O_3 (99.9%) and $CaCO_3$ (99.9%). The mixture pressed into pellets were calcined in air at 1000°C for 18 h, then sintered at 1500°C for 8 h in air. X-ray powder diffraction analysis revealed the sample to be single phase. Neutron diffraction measurement of SC was carried out using the double-axis diffractometer, HERMES[9)] implemented with a multi-counter detection system at temperatures 15 and 290 K (λ=1.8196 Å). Cold neutron scattering measurements were carried out on both SC and PS using the TOF-type spectrometer, AGNES with monochromatic pulsed incident neutrons (E_i=4.59 meV, λ=4.22 Å).[10)] The neutron scattering intensities were collected by 120 neutron counters implemented in the scattering angles between 10 and 130 °. The cold neutron scattering measurement was carried out on SC sample in the $h0l$ reciprocal plane at temperatures 50, 80, 175 K and room temperature (RT) and on PS at temperatures 17, 98, 180 and 220 K. Both HERMES and AGNES are installed at JRR-3M reactor in

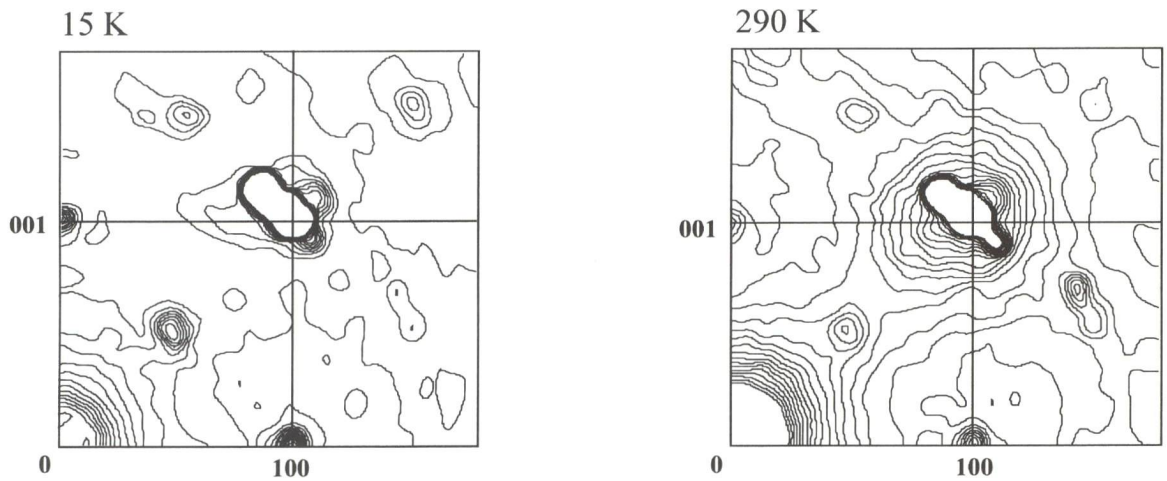

Fig. 1. Contour maps of neutron diffraction intensities at 15 and 290 K of $La_{0.85}Ca_{0.15}MnO_3$ observed in $h0l$ reciprocal plane.

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§3. Results and Discussion

Figure 1 shows the contour maps of neutron diffraction intensities in $h0l$ plane at 15 and 290 K. It is clearly observed that diffuse scattering intensities exist in the vicinity of FM Bragg point 101 at 290 K, being the PM phase, whereas no diffuse scattering is observed (not shown) at the Bragg point 102 at which the FM structure factor vanishes for Mn ions. The diffuse intensity we observed at 101 is strongest and decreases as Q increases, which is consistent with the magnetic form factor.[5] These results help us to ascertain that the observed diffuse scattering in the PM phase arises from the FM spin fluctuations.[5–7] The development of FM spin fluctuations with increasing temperatures is due to DE induced by the e_g electron hopping.[7] The DE interaction has to compete with the AFM superexchange (SE) interaction, the DE mechanism overcomes the AFM SE interaction and consequently long-range FM order occurs, *i.e.*, FM spin fluctuations exist in the PM state.[5–7] But the peak position at 101 is slighty shifted towards the reciprocal lattice point 002, suggesting that the spin fluctuation contains some modulation.[11] Weak reflections are observed at the reciprocal lattice points 100 and 001, where nuclear reflections are forbidden, an indication of AFM spin ordering. We also observed supperlattice peak at reciprocal lattice point $\frac{1}{2}0\frac{1}{2}$. We have confirmed that contamination due to $\lambda/2$ [since we have used Ge(331) monochromator which does not have higher order contamination from Ge(662)] and multiple scattering are negligible. Similar super-reflection peaks were previously reported for $La_{1-x}Sr_xMnO_3$ with x=0.10 and 0.15 by Yamada *et al.*[12] Their observed peaks at 100, 001 and $\frac{1}{2}0\frac{1}{2}$ are identified as a superlattice reflections due to small distortions at those points originating from CO. Hirota *et al.*[13] proposed the dimensional crossover, due to the AFM-type OO of $d_{3x^2-r^2}/d_{3y^2-r^2}$, in $La_{1-x}Sr_xMnO_3$ with x=0.05.[14] With these in concern, Endoh *et al.*[15] proposed the different orbital state, *e.g.*, the hybridization of $d_{z^2-x^2(y^2-z^2)}$ and $d_{3x^2-r^2(3y^2-r^2)}$. They observed the presence of OO in the low temperature phase where the J-T-type distortion is significantly diminished. Moreover, Murakami *et al.*[4] studied the temperature dependent change of the SOR-X-ray diffraction intensity of the CO superlattice $\frac{1}{2}0\frac{1}{2}$ and concluded that CO and OO occur concomitantly. The same temperature dependent change of the intensity of $LaMnO_3$ was also studied by Murakami *et al.*[16] on the forbidden $h00$ and $0k0$ reflections (h, k odd). They found the forbidden 300 peak, due to the OO, increases with decreasing temperatures. Considering these results, we could argue that the peaks observed in our measurement at 100 and 001 are consistent with those observed by Murakami *et al.*[16] since the peak intensity increase with decreasing temperature, having some inconsistency with the observation of Endoh *et al.*[15] Increasing of the superlattice peaks is not necessarily due to the gradual change of type of OO but the type of AFM ordering at low temperatures. Observed $\frac{1}{2}0\frac{1}{2}$ peak intensity decreases with increasing temperature, being consistent with Murakami *et al.*[4] Therefore, the observed 100 and 001 reflections may be attributed to the long range AFM-type OO of $d_{3x^2-r^2}/d_{3y^2-r^2}$ and $\frac{1}{2}0\frac{1}{2}$ reflections to the CO. It is suggested that long-range AFM-type OO exists in this sample with x=0.15 accompanying with low temperature FM phase. Figure 2 shows the temperature dependent change of the inelastic scattering intensities obtained for powder sample in the counter group situated at 2θ=57-64 ° (very close to FM Bragg point 101) at temperatures from 17 to 220 K. The scattering intensities observed by eight neutron counters were added to obtain better data statistics. An inelastic peak at 1.0 meV (neutron energy-loss side) is only observed in the FM region at 17 and 98 K and disappears in the PM region. The possible origin of this peak could be the formation of spin gap of 1.0 meV. A spin gap is observed in undoped $LaMnO_3$[17] and doped $La_{1-x}Ca_xMnO_3$ with x= 0.05 and 0.08,[18] which was explained by a single ion anisotropy term in the Heisenberg

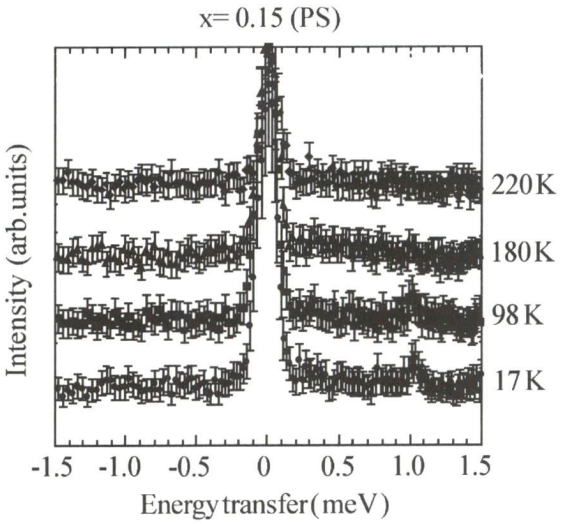

Fig. 2. Temperature dependence of the neutron scattering intensities of $La_{0.85}Ca_{0.15}MnO_3$ (PS) observed at the counter group situated at 2θ=57-64 ° (very close to FM Bragg point 101).

Hamiltonian: $-D\Sigma S_i^{z^2}$ (z axis being along $\boldsymbol{c}$), which is responsible for the gap observed in the spin wave spectra. The spin gap energy are somewhat lower in our observations, being consistent with the previous reports[17,18] as it was suggested that the spin gap energy decreases with increasing x.[17,18] Moreover, Kajimoto *et al.*[5] observed the spin wave peak at 0.9 meV in the FM region in $Pr_{0.65}Ca_{0.35}MnO_3$, which is also the evidence of decreasing the value of spin gap energy with increasing the value of x. Cold neutron spectra observed around the reciprocal lattice points $\frac{1}{2}0\frac{1}{2}$ or its adjacent area for SC sample are shown in Fig. 3 (see inset). Inelastic peak at about

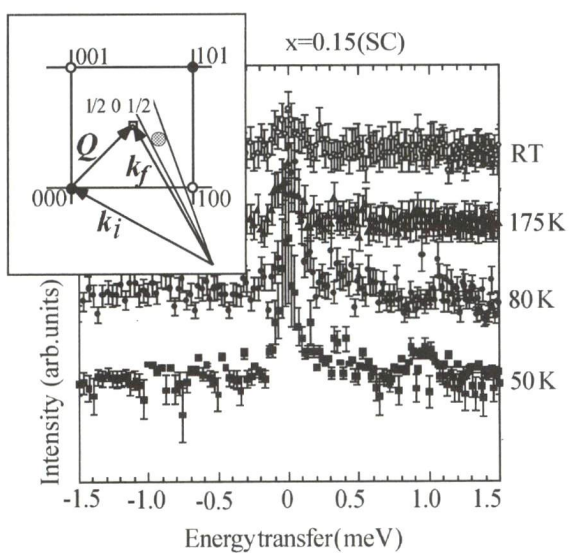

Fig. 3. Temperature dependence of the neutron scattering intensities of $La_{0.85}Ca_{0.15}MnO_3$ (SC) observed at the counter group situated at 2θ=35-42 ° (at an adjacent area of $\frac{1}{2}0\frac{1}{2}$, see inset).

1.0 meV is shown in the FM region, *i.e.*, 50 and 80 K, the origin of which are also the same as that of PS. The gap-like excitations slightly shifted to the higher energy with temperature and disappear above T_c . Further experiments are necessary to observe full branch of magnon dispersion and its Ca concentration dependency.

§4. Summary

The present neutron diffraction measurement of $La_{0.85}Ca_{0.15}MnO_3$ (SC) suggests the existence of FM spin fluctuations in the PM phase. We could also observe the evidence of CO and OO occur simultaneously, the OO ordering do not disappear until T=290 K, indication of orbital degree of freedom accompanying with a structural phase transition. The neutron inelastic scattering measurements on both powder and single crystal samples of $La_{0.85}Ca_{0.15}MnO_3$ might have evidenced the presence of a spin gap at about 1.0 meV in the FM region. We have outlined that, within our experimental accuracy, the gap-like peak at lower energy could be due to the spin gap formation, as the energy is close enough to the estimated value.[17,18]

Acknowledgements

This work was partly supported by a Grant-in-Aid for Scientific research from the Ministry of Education, Science and Culture of Japan.

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