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Phase Transition to Antiferromagnetic State in $La_{1-X}Sr_XMnO_3$ ($X \geq 0.5$)

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Charge carrier doping in antiferromagnetic (AFM) insulators with perovskite-related structures has revealed a variety of attractive phenomena such as the high-T_c superconductivity, metal-insulator transition and so on. Perovskite-type manganites $R_{1-X}A_XMnO_3$, where R is trivalent rare-earth ions such as La^{3+}, Pr^{3+} and Nd^{3+}, and A is the divalent ions such as Sr^{2+}, Ba^{2+} and Ca^{2+}, have attracted renewed interest of many researchers, because these compounds show peculiar "colossal" magnetoresistance (CMR) and applications to the magnetoresistance devices are expected.[1] In the $R_{1-X}A_XMnO_3$ perovskites, the charge ordering (CO) has been confirmed at various A ion concentrations X, *e.g.*, at X~0.66 for $La_{1-X}Ca_XMnO_3$[2] and at X~0.50 for $Pr_{1-X}Sr_XMnO_3$[3] and $Nd_{1-X}Sr_XMnO_3$.[4] The anomalies in the electrical resistivity ρ(T), the magnetization M(T) and the lattice constants were observed at the CO transition temperature T_{CO} and the orbit ordering in Mn ions is also confirmed by neutron scattering study.[5] For $La_{1-X}Sr_XMnO_3$ system Yamada *et al.*[6] recently observed a CO phase in this system centered at $X = 1/8$ by a neutron scattering study and the present authors have found anomalies in the sound velocity v_s(T) related to this CO transition.[7] In this note, we report the magnetic phase transition from the ferromagnetic (FM) to AFM state in $La_{1-X}Sr_XMnO_3$ polycrystals at around $X = 0.50$. The phase transition to the AFM state may be associated with the charge ordering transition. It has been also found that the electron transport changes from metallic to semiconductive in the ferromagnetic region just below $X = 0.48$.

$La_{1-X}Sr_XMnO_3$ ($X = 0.40 \sim 0.55$) samples were prepared from stoichiometric mixtures of La_2O_3, $SrCO_3$ and Mn_3O_4 powders. The mixtures were calcined twice at 1000°C for 24 h in air, pressed into pellets and then sintered at 1500°C for 8 h in air. The sintered crystals were heat-treated at 1500°C for 24 h in flowing O_2. In order to elucidate the effect of oxygen stoichiometry, the samples of $X = 0.50$, 0.52 and 0.55 underwent the heat treatments at 1300°C for 24 h in flowing Ar. The measured densities of each sample were higher than 85% of that of the ideal one. All the samples were confirmed to be in a single phase with X-ray diffraction at room temperature.

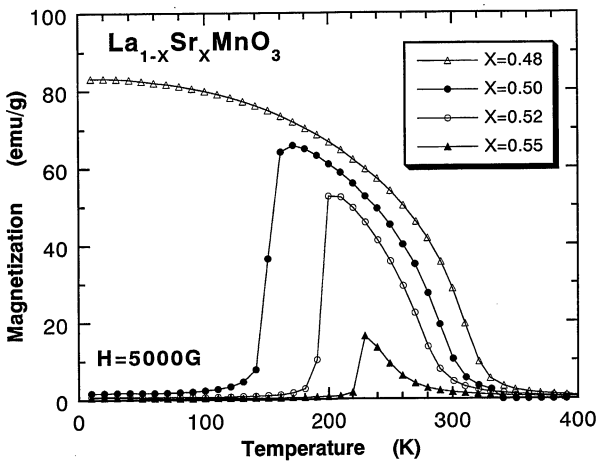

Fig. 1. The magnetization M of $La_{1-X}Sr_XMnO_3$ samples for $X = 0.48$, 0.50, 0.52 and 0.55 as a function of temperature T.

The magnetization M(T) was measured using a commercial SQUID magnetometer from 10 K to 400 K applying a magnetic field of 5000 G. The electrical resistivity was measured by a standard four-terminal method.

Figure 1 shows the magnetization M(T) of $La_{1-X}Sr_XMnO_3$ samples for $X = 0.48$, 0.50, 0.52 and $X = 0.55$ as a function of temperature T. For $X = 0.48$ the FM transition occurs at the Curie temperature of about $T_c = 330$ K and the FM state is stable at low temperatures. When X is 0.50, the FM transition occurs at around $T_c = 310$ K, but the FM state changes to the AFM one as indicated by a drastic drop in M(T) at around $T_N = 150$ K. For $X = 0.52$, T_c decreases to ~290 K and T_N increases to ~200 K and for $X = 0.55$ $T_c \sim 260$ K and $T_N \sim 230$ K. These behaviors of M(T) are similar to those of the $La_{1-X}Ca_XMnO_3$ system near $X \sim 0.5$.[8] For $La_{1-X}Ca_XMnO_3$, CO of Mn^{3+}/Mn^{4+} ions at T_N was suggested to suppress the FM state, allowing the system to enter an AFM state. For $X = 0.50$ and 0.52 we observed very large anomalies in the sound velocity $v_s(T)$ at T_N[9] similar to $La_{1-X}Ca_XMnO_3$.[2] It is plausible that the CO transition of the same type as $La_{1-X}Ca_XMnO_3$ takes place also in the $La_{1-X}Sr_XMnO_3$ system.

Figure 2 shows the temperature dependence of the electrical resistivity ρ(T) of the present $La_{1-X}Sr_XMnO_3$ for $0.40 \leq X \leq 0.55$. The ρ(T) curve of $La_{0.60}Sr_{0.40}MnO_3$ shows metallic behavior, while all the remaining samples showed semiconductive temperature dependences. The ρ(T) curves showed no clear change at T_c, but clear increase in ρ(T) with decreasing temperature was observed near T_N for $X = 0.50$ and 0.52. In comparison to the $Nd_{0.5}Sr_{0.5}MnO_3$ system[4] which shows similar M(T) curves as that shown in Fig. 1, however, the change in ρ(T) at T_N is far small. Urushibara *et al.* reported that the electrical resistivity ρ(T) of $La_{1-X}Sr_XMnO_3$ single crystals grown by a floating zone (FZ) method is metallic below T_c for $0.175 \leq X \leq 0.4$ and that the FM metallic state is stable even at around $X \sim 0.5$.[10] The ρ(T) of our sintered polycrystals is also metallic below T_c for $X = 0.40$ but ρ(T) of $X = 0.48$ sample is barely semiconductive, showing intermediate behavior between a metal and semiconductor, which suggests the existence of a

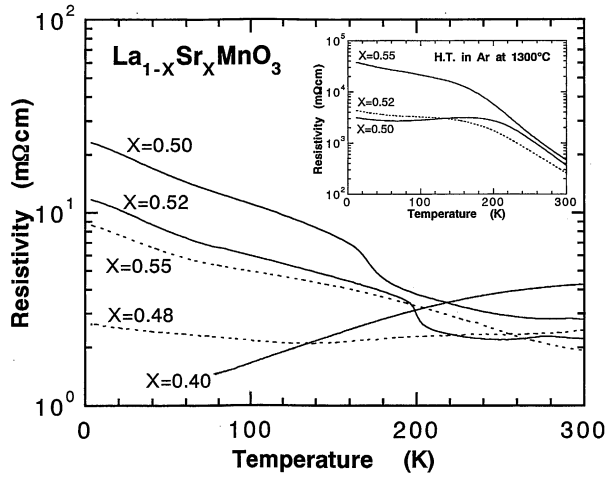

Fig. 2. The temperature dependence of the electrical resistivity ρ(T) of $La_{1-X}Sr_XMnO_3$ samples for $0.40 \leq X \leq 0.55$. The inset shows the the electrical resistivity ρ(T) of $La_{1-X}Sr_XMnO_3$ samples (X = 0.50, 0.52 and 0.55) which were heat-treated at 1300°C in flowing Ar.

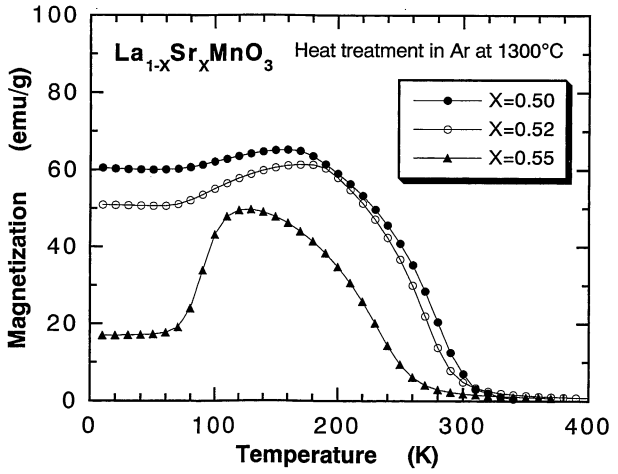

Fig. 3. The temperature dependence of the magnetization M(T) of X = 0.50, 0.52 and 0.55 samples which were heat-treated at 1300°C in flowing Ar.

metal-insulator transition just below $X = 0.48$. Thus there seems to be a discrepancy between the present data and those of ref. 10. The origin of this discrepancy between the present sintered polycrystals and the single crystals prepared by FZ method is not clear at present but must be clarified.

Figure 3 shows the temperature dependence of the magnetization M(T) of $X = 0.50$, 0.52 and 0.55 samples which were heat-treated at 1300°C for 24 h in Ar. The phase transition from the FM to AFM state almost disappeared in Ar-annealed $X = 0.50$ and $X = 0.52$ samples. For $X = 0.55$, a broad transition to the AFM state survived at around 100 K in spite of Ar-annealing. The transition to the AFM state was not complete and a pretty large FM component remained as seen in Fig. 3. The introduction of oxygen vacancies by the Ar-annealing may result in the decrease of Mn^{4+} ions and the effect is equivalent to the decrease in the Sr concentration X. The disappearance of the AFM state in the Ar-annealed samples seems to be consistent with the absence of the AFM state in $La_{1-X}Sr_XMnO_3$ crystals for $X \leq 0.48$. On the other hand, ρ(T) of Ar annealed samples increased more than two orders of magnitude as shown in the inset of Fig. 2. This increase of ρ(T) after Ar heat-treatment may be understood as due to the increase of the electron scattering by oxygen vacancies. However, the FM state associated with very large semiconductive resistivity in Ar-annealed samples for $0.48 \leq X \leq 0.52$ is again contradictory with the results of ref. 10. The present results of the heat-treatment in Ar may suggest that the oxygen deficiency is a key factor to explain the different behavior between the present sintered $La_{1-X}Sr_XMnO_3$ and melted $La_{1-X}Sr_XMnO_3$.

In summary, we confirmed the magnetic phase transition from a ferromagnetic insulator to an antiferromagnetic insulator in $La_{1-X}Sr_XMnO_3$ polycrystals at around $X = 0.50$. The heat-treatment in Ar for the $X = 0.50$, 0.52 and 0.55 samples was found to heavily influence the magnetic transition. This phase transition may result from the charge ordering in Mn^{3+}/Mn^{4+} ions similar to the $La_{1-X}Ca_XMnO_3$ system. For the identification of the origin of the phase transition, however, detailed studies of neutron scattering and/or electron diffraction are highly desirable.

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1) B. Raveau, A. Maignan and B. Caignaert: J. Solid State Chem. **117** (1995) 424.
2) A. P. Ramirez, P. Schiffer, S-W. Cheong, C. H. Chen, W. Bao, T. T. M. Palstra, P. L. Gammel, D. J. Bishop and B. Zegarski: Phys. Rev. Lett. **76** (1996) 3188.
3) Y. Tomioka, A. Asamitsu, Y. Moritomo, H. Kuwahara and Y. Tokura: Phys. Rev. Lett. **74** (1995) 5108.
4) H. Kuwahara, Y. Moritomo, Y. Tomioka, A. Asamitsu, M. Kasai, R. Kumai and Y. Tokura: Phys. Rev. B **56** (1997) 9386.
5) H. Kawano, R. Kajimoto, H. Yoshizawa, Y. Tomioka, H. Kuwahara and Y. Tokura: Phys. Rev. Lett. **78** (1997) 4253.
6) Y. Yamada, O. Hino, S. Nohdo, R. Kanao, T. Inami and S. Katano: Phys. Rev. Lett. **77** (1996) 904.
7) H. Fujishiro, M. Ikebe, Y. Konno and T. Fukase: J. Phys. Soc. Jpn. **66** (1997) 3703.
8) P. Schiffer, A. P. Ramirez, W. Bao and S.-W. Cheong: Phys. Rev. Lett. **75** (1995) 3336.
9) H. Fujishiro, T. Fukase and M. Ikebe: unpublished.
10) A. Urushibara, Y. Moritomo, T. Arima, A. Asamitsu, G. Kido and Y. Tokura: Phys. Rev. B **51** (1995) 14103.