Ferromagntic correlation and metallic behavior in slightly electron-doped antiferromagnetic $CaMnO_3$

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Abstract

Eelectron-doped Mn^{4+}-rich compounds $Ca_{1-x}Nd_xMnO_3$ ($0 \leq x \leq 0.12$) were investigated by means of magnetic and transport properties. Unusually strong ferromagnetic behaviors have been observed in $x = 0.05$ and 0.1 compounds. Correspondingly, these two samples show typically metallic features at relatively low temperature, and their resistivities are 8 orders of magnitude smaller than that of $CaMnO_3$.

Key words: CMR; Phase separation; manganite.

1. Introduction

Recent intensive study of ferromagnetism in (RE,AE)MnO_3 (RE = rare earth element, AE = alkaline earth metal) exhibits very interesting pheonomena, such as insulator-metal transition and extraordinarily large magnetoresistance effects around T_c in hole-doped region. In these systems, starting from the electronic configuration of Mn^{3+}, $(t_{2g})^3(e_g)^1$, mobile holes are created in the e_g band of manganite, by partly replacing the trivalent RE with a divalent cation AE. The magnetoresistive behavior has been interpreted on the basis of the double-exchange theory, associated with dynamic Jahn-Teller distortions and electron-phonon coupling. On the other hand, carriers can be created by substituting divalent cation with trivalent ion in AE-rich, i.e. Mn^{4+}-rich manganites. Detailed investigations on Ca-rich (La,Ca)MnO_3[1] seggests the existence of local ferromagnetic regions within the antiferromagnetic host. Lightly electron doping of $CaMnO_3$ was also studied by the Raman scattering and electron paramagnetic resonance. They revealed that doping enhances the ferromagnetic coupling between Mn ions. Ferromagnetism and large magnetoresistance were also reported in $Ca_{1-x}Bi_xMnO_3$ for $x \leq 0.125$[2] and $Ca_{1-x}Sm_xMnO_3$ for $x \leq 0.12$.[3] As reviewed above, electron doped systems exhibit large difference on the electronic and magnetic properties, compared with those of Mn^{3+}-rich hole-doped manganites. In order to understand the unexpected behaviors and the relationship between ferromagnetic interactions and doping level in electron-doped manganites, we have undertaken detailed magnetic and transport studies of the system $Ca_{1-x}Nd_xMnO_3$ for $x \leq 0.12$.

2. Experiments and results

All $Ca_{1-x}Nd_xMnO_3$ specimens were prepared using standard solid state reaction. Powder x-ray diffraction showed clean single-phase pattern in all samples. Magnetizations were registered using a superconducting quantum interference device (SQUID) magnetometer. Transport properties were performed with the four-probe method by Quantum Design PPMS.

Fig. 1(a) shows magnetization curves for $Ca_{1-x}Nd_x$ MnO_3 ($0 \leq x \leq 0.12$) series. The magnetization below

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130 K is strongly enhanced by doping up to $x = 0.1$, but it is abruptly decreased at $x = 0.12$. The magnetic susceptibility is presented as $1/\chi$ vs T in the inset of Fig. 1(a). Notably, $1/\chi$ as a function of x shows the similar behavior as M. Namely, increase of x up to 0.1 considerably suppresses $1/\chi$ at high temperature. Fitting of Curie-Weiss relation $\chi = C/(T - \Theta)$ to the $1/\chi$ data yields the Curie-Weiss temperature Θ values as -150 K, 39 K, 93 K, and -92 K for $x = 0.02, 0.05, 0.1$ and 0.12, respectively. Interestingly, the Θ value changes its sign once from negative to positive, and then from positive to negative again, with respect to x. These observations strongly suggest that in $0.05 \leq x \leq 0.1$ region, ferromagnetic correlations are induced, and therefore, a mixed magnetic phase composed of ferromagnetism and antiferromagnetism is developed. In the $x = 0.02$ and 0.12 specimens with low M (T) and negative Θ, it seems that antiferromagnetic interaction dominates the magnetic response. In addition, we notice that the $M(T)$ curves show an anomalous broad peak around $\sim$ 25 K for $0.05 \leq x \leq 0.1$. The antiferromagneitic ordering of Nd ions are thought to be responsible for this anomaly, because such a phenomenon has not be encountered in other rare earth doped systems.

The temperature dependencies of electrical resistivity are presented in Fig. 1(b). The $\rho(T)$ of pure $CaMnO_3$ shows semiconducting behavior, while the resistivity values of the $x = 0.05, 0.1$ samples are significantly low. Such high conductivity in a wide temperature range could not be found in the hole-doped manganite $L_{1-x}Ca_xMnO_3$, which is insulating for similar x values. This can be explained by the fact that in Mn^{4+}-rich compound, Jahn-Teller distortion is much smaller and carriers are more easily delocalized, contrary to that of Mn^{3+}-rich system with strong electron-phonon interaction. The low resistivity in the paramagnetic state is understandable by the assumption that the doped e_g electrons would fill into the narrow itinerant band and the density of states at the Fermi energy is enhanced. In other words, the characteristic metallic conductivity allows us to infer that the carriers induced by doping are essentially itinerant, and that the chemical potential is positioned in the conducting band. With decreasing temperature, a slight upturn in $\rho(T)$, i.e., $d\rho/dT < 0$, is presented, which might be due to the occurrence of ferromagnetic and antiferromagnetic transitions at the same time. Surprisingly, the resistivity drops by almost 8 orders of magnitude from that of pure $CaMnO_3$ at low temperatures, but is about $1 \sim 2$ orders higher than that of $La_xCa_{1-x}MnO_3$ at the same doping level[1] and that of $Pr_xCa_{1-x}MnO_3$ at $x = 0.025$.[4]

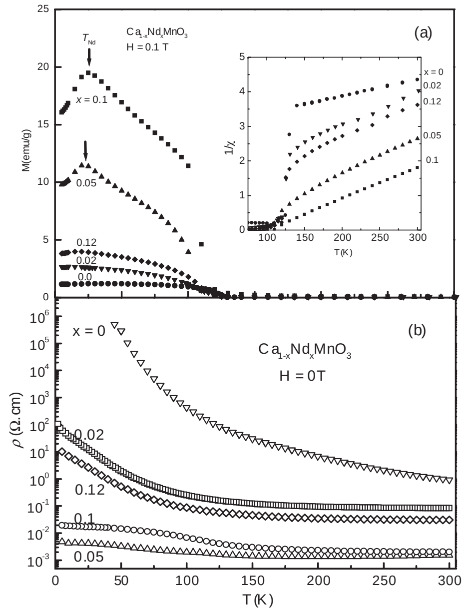

Fig. 1. (a) Temperature dependence of magnetization measured at 0.1 T in the system $Ca_{1-x}Nd_xMnO_3$ for $0 \leq x \leq 0.12$, the inset shows the inverse of susceptibility; (b) Resistivity vs temperature for $Ca_{1-x}Nd_xMnO_3$ $(0 \leq x \leq 0.12)$ in zero field.

3. Summary

We present magnetic and transport properties of slightly Nd^{3+}-doped $CaMnO_3$. A small amount of Nd^{3+} ions induces magnetic phase separation in which ferromagnetic components are embedded in antiferromagnetic environment and the resistivity decreases significantly. In addition, an anomaly of magnetization arising from Nd^{3+} antiparallel alignment is observed at $T \sim 25$ K.

References

[1] J. J. Neumerier, J. L. Cohn, Phys. Rev. B **61** (2000) 14319.

[2] H. Chiba, M. Kikuchi, K. Kusaba, Y. Muraoka, Y. Syono, Solid State Commun. **99** (1996) 499.

[3] A. Maignan, F. Damay, B. Raveau, Chem. Mater. **10** (1998) 950.

[4] M. M. Savosta, P. Novak, M. Marysko, Z. Jirak, J. Hejtmanek, J. Englich, J. Kohout, C. Martin, N. Raveau, Phys. Rev. B **62** (2000) 9532