Vol 12 No 11, November 2003
1009-1963/2003/12(11)/1301-04

Chinese Physics

© 2003 Chin. Phys. Soc.
and IOP Publishing Ltd

Evidence of phase separation in $Nd_{1-x}Sr_xMnO_3$ (x=0.50, 0.51, 0.52, 0.53, 0.54, 0.55)*

Lu Yi(鲁 毅), Li Qing-An(李庆安), Di Nai-Li(邸乃力),
Li Run-Wei(李润伟), Ma Xiao(马 骁),
Kou Zhi-Qi(寇志起), and Cheng Zhao-Hua(成昭华)

State Key Laboratory of Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, *China*

(Received 24 December 2002; revised manuscript received 18 August 2003)

The temperature dependence of Mn ion magnetization and the conductivity difference versus temperature provide phase separation evidence in $Nd_{1-x}Sr_xMnO_3$ (x=0.50, 0.51, 0.52, 0.53, 0.54, 0.55). This is different from other reports and may suggest that a fully charge-ordered state exists in quite a narrow range; the sample preparation procedure affects the charge ordering. The polaron effect also plays an important role in explaining the conductivity.

Keywords: phase separation, $Nd_{1-x}Sr_xMnO_3$, magnetization, conductivity
PACC: 7530V, 7530E

1. Introduction

The manganites are attracting considerable theoretical and experimental interest because of their unusual magnetic and electronic properties. These properties of the materials challenge our understanding of the physics in them. The compounds are doped systems with a general formula $Ln_{1-x}M_xMnO_3$ (Ln=La, Pr, Nd; M=Ca, Sr, Ba) and their unusual properties define a basic problem that involves the strong coupling between the charge, spin, lattice and orbital degrees of freedom. At lower doping, magnetic and transport properties are explained by double-exchange, super-exchange and polarons.[1−3] Studies on layered manganites confirm the double-exchange selection rule for c-axis conduction[4] and the nature of conductivity is diffusive[5−7] when the materials are in metallic state. When the hole doping is close to 0.5, the charge/orbital ordering plays an important role. For $La_{0.5}Ca_{0.5}MnO_3$, the charge-ordered state includes not only ordinary commensurate but also incommensurate or nearly commensurate charge-ordered states.[8,9] Recently, Sun [10−12] studied the Mn-site doping effects in $La_{0.7}Ca_{0.3}$ (Mn, A)O_3 (A=Fe, Ge, Ti, Sn, etc). Furthermore, both electron and x-ray diffraction experiments have shown the coexistence of ferromagnetism and incommensurate charge-ordered state.[13] Early reports have shown that $Nd_{0.5}Sr_{0.5}MnO_3$ first undergoes a ferromagnetic (FM) transition at 250K and then followed by a first-order transition to an antiferromagnetic (AF) charge-ordered state at 150K.[14−19] For $Nd_{0.45}Sr_{0.55}MnO_3$, it is layered AF with two-dimensional conductivity.[20,21]

In the present paper, we provide the evidence of phase separation of $Nd_{1-x}Sr_xMnO_3$ (x=0.50, 0.51, 0.52, 0.53, 0.54, 0.55) by temperature dependence of magnetization and resistance (or conductivity) data.

2. Sample preparation, characterization and measurements

The samples $Nd_{1-x}Sr_xMnO_3$ (x=0.50, 0.51, 0.52, 0.53, 0.54, 0.55) were prepared by solid-state reaction method. The oxides Nd_2O_3, $SrCO_3$ and $MnCO_3$ (with purities higher than 99.9%) were weighed in stoichiometric amount then mixed and prefired at 800°C for 12h. The ball-milled powder was pressed under a pressure up to 10 MPa and sintered at 1250°C for 24h with O_2 (30%) +Ar flowing. This procedure was repeated for three times to ensure the chemical homogeneity and full reaction. Powder x-ray diffraction (XRD)

*Project supported by the program of the "Hundred Talents Programs" of Chinese Academy of Sciences, the National Natural Sciences Foundation of China (Grant No 2001CB610605) and the State Key Project of Fundamental Research, China (Grant Nos 50272082 and 10274014).

was used to check the crystal quality and determine the lattice parameters at room temperature. Rietveld refinement of XRD patterns indicated that the peaks of all samples could be indexed as single phase of an orthorhombic structure with Pbnm space group.

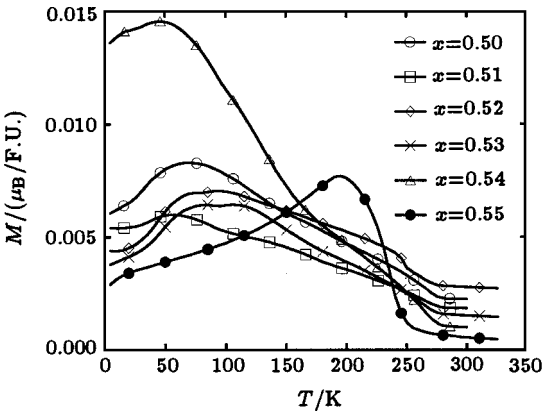


Fig.1. Temperature dependence of magnetization for $Nd_{1-x}Sr_xMnO_3$ (x=0.50, 0.51, 0.52, 0.53, 0.54, 0.55) in a magnetic field of 0.01T.

Temperature dependence of magnetization (shown in Fig.1) was determined by a commercial magnetometer (Quantum Design Co., Ltd). The samples for magnetic measurement were pulverized into fine powder.

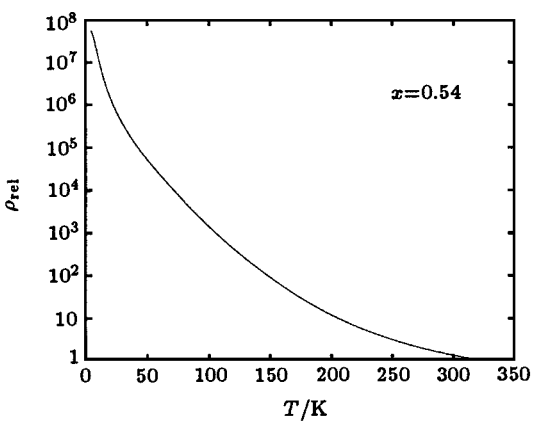


Fig.2. Relative resistivity versus temperature of $Nd_{0.46}Sr_{0.54}MnO_3$, the comparing temperature is 325K.

The resistance measurements were performed by the standard four-probe method. The samples were measured in a standard 4He gas flow cryostat and heating was avoided by using small currents (at which the current-voltage curves are strictly linear). To eliminate the generated error by geometric dimension inaccuracy, we use the relative resistance with respect to the value at 325K. In this way, the relative resistivity or conductivity was determined $\left(R_{\rm rel}\frac{R}{R_{325}} = \frac{\rho}{\rho_{325}} = \rho_{\rm rel} = \frac{1}{\sigma_{\rm rel}}\right)$, and a typical $\rho_{\rm rel}$ versus T curve is shown in Fig.2.

3. Results and discussion

There are some common features in the magnetization versus temperature curves. One feature is the existence of a typical AF peak in the M-T curve. This is consistent with neutron diffraction result on $Nd_{0.5}Sr_{0.5}MnO_3$ and $Nd_{0.45}Sr_{0.55}MnO_3$.[20] If we assume a paramagnetic state for Nd^{3+} ion in $Nd_{1-x}Sr_xMnO_3$ (x=0.50, 0.51, 0.52, 0.53, 0.54, 0.55), we may subtract the contribution of Nd ion from the total magnetization (Nd ion magnetization is described by Brillouin function). The residual magnetization M is from the Mn ions as shown in Fig.3. For all samples, the M-T curve of Mn ions in AF range has a kink. This is an indication of the coexistence of ferromagnetism and antiferromagnetism between kink and AF. The second feature is that the magnetization is decreasing in a step-like way after the AF transition and becomes nearly flat after temperature higher than a certain value indicating paramagnetic (PM) state. According to neutron diffraction result of $Nd_{0.5}Sr_{0.5}MnO_3$, the compound is in FM state between Neel temperature and PM starting temperature. Our results show that the FM state is not homogeneous. We ascribe the step to that some of FM clusters change to PM state, i.e., the FM→PM transition. Therefore, the result suggests that phase separation also occurs in this range.

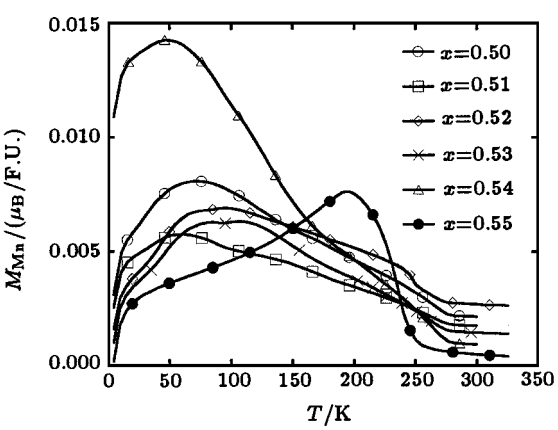


Fig.3. Temperature dependence of the Mn ion magnetization of $Nd_{1-x}Sr_xMnO_3$ in a magnetic field of 0.01T.

In temperature range of paramagnetic state, the conduction proceeds via thermal hopping. When fitting the activated conductivity in this temperature

range, a function of the form $\sigma_{act} = \sigma_{act0}\exp\left(-\frac{E}{k_B T}\right)$ may be used as an approximation. If we subtract this activated conductivity from the measured conductivity in the whole temperature range, the difference, defined as $\Delta\sigma = \sigma_{rel} - \sigma_{act}$, can give us some useful information.

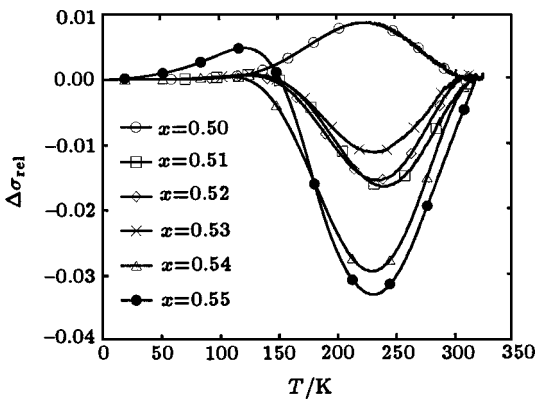


Fig.4. $\Delta\sigma$-T curves of $Nd_{1-x}Sr_xMnO_3$. $\Delta\sigma$ is the difference between relative conductivity and relative thermal activated conductivity.

Figure 4 shows the $\Delta\sigma$-T curves obtained by using the above-mentioned procedure. Clearly, the curves are smooth without first-order transition at Neel temperature. This behaviour is different from other reports[14,16,20,21] and suggests phase separation. There is a broad negative valley for each hole doping within 0.51, 0.52, 0.53, 0.54, 0.55 but a peak at 0.50. The valleys or peak are in the temperature region where materials are partially in the ferromagnetic state discussed above. Thus they are due to the competition between charge ordering/polaron effect and ferromagnetic ordering induced DE contribution to the conductivity.

Figure 5 shows the M-T and $\Delta\sigma_{rel}$-T curves for x=0.54. The valley temperature does not correlate with Neel temperature and the starting temperature of deviation from semiconductor behaviour is higher than the temperature at which ferromagnetic step appears. This is a common feature for all x=0.51, 0.52, 0.53, 0.54, 0.55 samples and indicates that polaron effect also plays an important role to trap the conduction electrons. At lower temperature, there is a positive peak for each hole doping within 0.51, 0.52, 0.53, 0.54, 0.55. The peak, either in the AF range (such as x=0.55) or in step region (such as x=0.51, 0.52, 0.53, 0.54), indicates the existence of ferromagnetic composition which is consistent with the magnetization data. If we consider the AF charge-ordered resistivity is higher than paramagnetic one, the positive $\Delta\sigma$ of x=0.50 manganite in AF range indicates some ferromagnetic DE contribution. So it is also consistent with the coexistence of AF and FM at temperature lower than AF peak even for x=0.50.

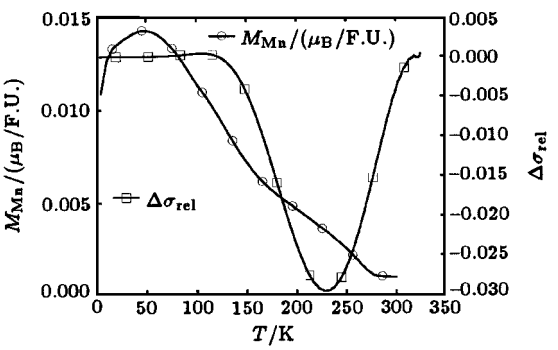


Fig.5. M-T and $\Delta\sigma_{rel}$-T curves of $Nd_{0.46}Sr_{0.54}MnO_3$. M_{Mn} is the Mn ion magnetization and $\Delta\sigma_{rel}$ is the difference of relative conductivity and relative thermal activated conductivity.

4. Conclusion

In summary, both magnetic and electrical results show the phase separation evidence in $Nd_{1-x}Sr_xMnO_3$ (x=0.50, 0.51, 0.52, 0.53, 0.54, 0.55). This is different from other reports and may suggest that fully charge-ordered state exists in a quite narrow range and sample preparation procedure affects the charge ordering. Polaron effect also plays an important role to explain the conduction.

Acknowledgements

Thanks to T. S. Ning and S. Y. Fan for their help in measurements.

References

[1] Zener C 1951 *Phys. Rev.* **82** 403
[2] Anderson P W and Hasegawa 1955 *Phys. Rev.* **100** 675
[3] Millis A J, Littlewood P B and Shraiman B I 1995 *Phys. Rev. Lett.* **74** 5144
[4] Li Q A, Gray K E, Mitchell J F Berger A and Osgood R 2000 *Phys. Rev.* B **61** 9542
[5] Li Q A, Gray K E and Mitchell J F 1999 *Phys. Rev.* B **59** 9357
[6] Li Q A, Gray K E and Mitchell J F 2001 *Phys. Rev.* B **63**

24417
[7] Li Q A and Gray K E 2001 *Phys. Rev.* B **63** 52413
[8] Radaelli P G, Cox D E, Marezio M and Cheong S W 1997 *Phys. Rev.* B **55** 3015
[9] Chen X *et al* 2001 *Chin. Phys.* **10** 751
[10] Sun J R, Rao G H and Shen B G 1998 *Appl. Phys. Lett.* **73** 2998
[11] Li R W, Sun J R, Wang Z H and Shen B G 2000 *J. Appl. Phys.* **88** 5924
[12] Li R W, Wang Z H, Chen X and Shen B G 1999 *Acta Phys. Sin.* **48** S105 (in Chinese)
[13] Chen C H and Cheong S W 1996 *Phys. Rev. Lett.* **76** 4042
[14] Kuwahara H, Tomioka Y, Asamitsu A, Moritomo Y and Tokura Y 1995 *Science* **270** 961
[15] Khazeni K, Jia Y X, Lu L, Crespi V H, Cohen M L and Zettl A 1996 *Phys. Rev. Lett.* **76** 295
[16] Caignaert A, Millange F, Hervieu M, Suard E and Reveau B 1996 *Solid Stat. Commun.* **99** 173
[17] Moritomo Y, Kuwahara H, Tomioka Y and Tokura Y 1997 *Phys. Rev.* B **55** 7549
[18] Kuwahara H, Moritomo Y, Tomioka Y, Asamitsu A, Kasai M, Kumai R and Tokura Y 1997 *Phys. Rev.* B **56** 9386
[19] Akimoto T, Maruyama Y, Moritomo Y, Nakamura A, Hirota K, Ohoyama K and Ohashi M 1998 *Phys. Rev.* B **57** R5594
[20] Kawano H, Kajimoto R, Yoshizawa H, Tomioka Y, Kuwahara H and Tokura Y 1997 *Phys. Rev. Lett.* **78** 4253
[21] Kuwahara H, Okuda T, Tomioka Y, Asamitsu A and Tokura Y 1999 *Phys. Rev. Lett.* **82** 4316