Vol 17 No 7, July 2008
1674-1056/2008/17(07)/2721-04

Chinese Physics B

© 2008 Chin. Phys. Soc.
and IOP Publishing Ltd

Electron spin resonance study of the Ba-doping manganite $Nd_{0.5}Sr_{0.5}MnO_3$*

Zhao Jian-Jun(赵建军)[a)b)†], Xing Ru(邢 茹)[a)], Lu Yi(鲁 毅)[a)],
Haosibayar(浩斯巴雅尔)[a)], Zhao Ming-Yu(赵明宇)[a)], Jin Xiang(金 香)[a)],
Zheng Lin(郑 琳)[a)], Ning Wei(宁 伟)[b)], Sun Young(孙 阳)[b)], and Cheng Zhao-Hua(成昭华)[b)]

[a)] *Department of Physics, Baotou Normal University, Inner Mongolia Autonomous Regions, Baotou* 014030, *China*
[b)] *State Key Laboratory of Magnetism and Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing* 100190, *China*

(Received 18 January 2008; revised manuscript received 4 March 2008)

We have performed magnetization measurements and electron spin resonance (ESR) on polycrystalline manganites of $Nd_{0.5}Sr_{0.5-x}Ba_xMnO_3$ ($x = 0.1$). Phase separation and phase transitions are observed from the susceptibility and the ESR spectra data. Between 260 K ($\sim T_C$) and 185 K ($\sim T_N$), the system coexists of the paramagnetic phase and the ferromagnetic (FM) phase. Between 185 K and 140 K, the system coexists of the FM phase and the antiferromagnetic (AFM) phase. These results indicate that the system has a very complex magnetic state due to the origin of the instability stemming from manganite $Nd_{0.5}Sr_{0.4}Ba_{0.1}MnO_3$ by partially substituting the larger Ba^{2+} ions for the smaller Sr^{2+} ions.

Keywords: manganite, electron spin resonance, phase separation
PACC: 7530G, 7630, 7530V

1. Introduction

In recent years perovskite-type manganites have aroused considerable interest particularly due to their complex magnetic and transport properties, such as ferromagnetism (FM), antiferromagnetism (AFM), charge/ orbital ordering, phase separation.[1−3] For the hole-doped manganites $Ln_{1-x}AE_xMnO_3$ (Ln = La, Pr, Nd; AE = Ca, Sr, Ba) with a fixed x (constant Mn^{3+}/Mn^{4+} ratio), when the oxygen stoichiometry is controlled, the magnetic and the transport properties are very sensitive to the average ionic radius of the A site cations, $< r_A >$, and the A-site size mismatch, σ^2.[4,5] Generally, substituting the A-site trivalent rare earth by divalent Sr or Ba in $Ln_{1-x}AE_xMnO_3$ changes the filling of the 3d Mn bands, introducing double-exchange interactions and thereby reducing Jahn–Teller-type distortions and orbital order,[6,7] while Nd manganites exhibit an unusual A-site effect compared with other systems like Ln = La, Pr.[8,9] For example, in the undoped $Nd_{0.5}Sr_{0.5}MnO_3$ compounds with $< r_A >= 0.1236$ nm and $\sigma^2 = 5.4\times10^{-5}$ nm^2, the ground state that is of a ferromagnetic metal ($T_C \sim 250$ K) transforms to a charge-ordered (CO) state on cooling to 150 K. After being substituted partially by Ba for Sr, the sample of $Nd_{0.5}Sr_{0.4}Ba_{0.1}MnO_3$ changes its parameters $< r_A >$ and σ^2 into $< r_A >= 0.1252$ nm, and $\sigma^2 = 1 \times 10^{-4}$ nm^2.[10−12] As a result, the simultaneous increases of both $< r_A >$ and σ^2 induce the phase separation phenomena due to the competition between the charge-orbital ordered AFM phase and the double exchange ferromagnetic-metallic phase interaction. At present, there are a few studies about the $Nd_{0.5}Sr_{0.5-x}Ba_xMnO_3$ compounds of the half-doped Nd manganite system, which are related to the complex magnetic transitions states of Ba.[11,13−15] In order to understand the influence of the increase of A-site radius $< r_A >$ when Ba is substituted for Sr, we use the electron spin resonance (ESR) to study the Ba doped $Nd_{0.5}Sr_{0.5}MnO_3$. ESR is a powerful technique that is sensitive to the various properties of magnetic correlations on a microscopic level, and convenient to clarify the complex magnetic state in doped manganese perovskites. The experiment was done at temperatures ranging from 100 to 300 K.[16,17] The ESR results shows that the doped $Nd_{0.5}Sr_{0.5-x}Ba_xMnO_3$ exhibits complex magnetic state due to partially substituting Ba^{2+} ions for Sr^{2+} ions.

*Project supported by the National Natural Science Foundation of China (Grant No 50672126) and the Inner Mongolia Natural Science Foundation of China (Grant No 200607010102).
†E-mail: zhaojianjun197174@163.com

2. Experiment

The polycrystalline sample of $Nd_{0.5}Sr_{0.5-x}Ba_x$ MnO_3 ($x = 0.1$) was prepared by using the conventional solid-state reaction method. The oxides Nd_2O_3, $SrCO_3$, $BaCO_3$, and $MnCO_3$ (with purities higher 99.9%) were used as the starting materials. The mixture was prefired in air at 1000°C for 24 h. The ball-milled powder was pressed under pressures up to 10 MPa, then compressed into pellets and sintered in air at 1350°C for 33 h. The phase purity was tested by x-ray diffraction (XRD). The data for magnetization were collected by using a superconducting quantum interference device (SQUID, Quantum Design, MPMS-7) magnetometer under a 100 Oe (1 Oe $\approx$ 79.577 A/m) magnetic field. The ESR measurements were performed at 9.51 GHz with a JEOL JES-FA200 ESR spectrometer in a temperature range of 100–300 K.

3. Results and discussion

Figure 1 shows the typical powder XRD patterns for the prepared sample. By Rietica refinement for the XRD, it is clearly seen that the diffraction peaks are sharp and asymmetrical, showing that the sample is of a single phase. The XRD patterns can be indexed as an orthorhombic distorted perovskite structure with space group *Pbnm.*

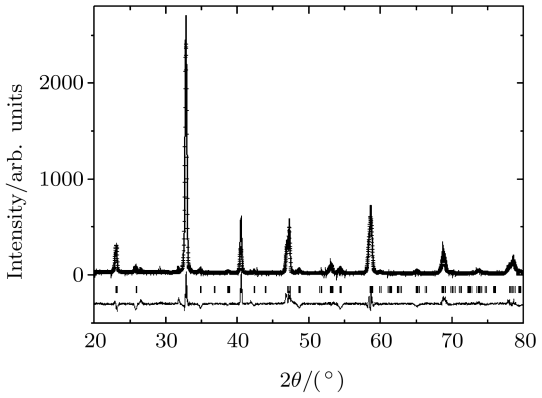


Fig.1. XRD patterns for the sample $Nd_{0.5}Sr_{0.4}Ba_{0.1}$ MnO_3 at room temperature. Upper curve: data and fit, with difference plot below. Bottom ticks indicate nuclear peaks corresponding to the *Pbnm* space group.

The temperature dependence of the magnetization $M(T)$ curve is shown in Fig.2. The magnetization was measured with the zero-field-cooling (ZFC) mode and the field-cooling (FC) mode for the sample in a temperature range from 5 to 350 K. At 260 K, the magnetization starts to increase rapidly with the decrease of temperature. Below 260 K, the FC and the ZFC magnetizations are separate from each other. These results imply the onset of FM ordering within clusters occurring at $T_C = 260$ K. As temperature further decreases, the magnetization shows a peak at $T_N \approx 185$ K and then drops continuously. The decrease of magnetization not only exhibits the presence of a FM–AFM phase transition, but also implies the formation of a charge ordering (CO) state. With the decrease of temperature, the FM phase tends to reduce while the AFM phase becomes dominant, there remains a small fraction of FM states that survive in the AFM environment. Obviously, the doped sample shows a behaviour similar to the undoped compound.[11,18] But the magnetic transition temperatures ($T_C \approx 260$ K, $T_N \approx 185$ K) become higher. This is due to the doping Ba^{2+} ions that contribute to the motion of charge carried.

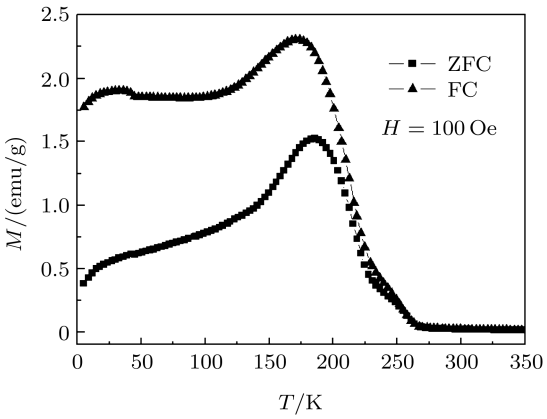


Fig.2. Temperature dependence of the magnetization M in a 100 Oe field for $Nd_{0.5}Sr_{0.4}Ba_{0.1}MnO_3$.

Figure 3 shows the ESR spectra for the $Nd_{0.5}Sr_{0.4}Ba_{0.1}MnO_3$ powder sample in a temperature range from 100 to 300 K. Above 260 K, a single line is observed in the spectra. As temperature decreases below 260 K, an additional line appears on the lower side of the main paramagnetic line (PMR) that is a ferromagnetic resonance line. Upon further decreasing the temperature, the ferromagnetic resonance line grows up and continually moves towards low field regions. But the paramagnetic resonance line becomes weaker and disappears at about 185 K ($\sim T_N$). Below 185 K, a high-field resonance line appears which should correspond to antiferromagnetic

resonance line. Between 185 and 140 K, there occur two signals in the spectra at the same temperature. Below 140 K, the FMR signal disappears and the system enters into an entire AFM state.

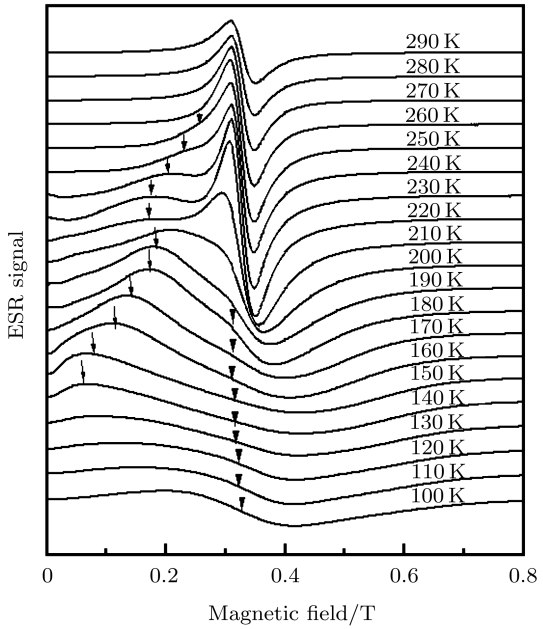


Fig.3. Electron spin resonance spectra of $Nd_{0.5}Sr_{0.4}Ba_{0.1}MnO_3$ compound at different temperatures, where the arrow indicates the peak position.

The ESR spectra are fitted to the Lorentzian line shape function. The line shape parameters, including the resonance field and linewidth, are extracted from the fits.[19−21] The temperature dependence of the g-factor $g_{\rm eff}$ obtained from the resonance field is shown in Fig.4(a). Above $T_{\rm C} = 260$ K, the $g_{\rm eff}$ value is close to 2 and shows weak temperature dependence in contrast with that of the undoped $Nd_{0.5}Sr_{0.5}MnO_3$, in which the g value increases dramatically in the paramagnetic state and it is attributed to the formation of magnetic clusters. This indicates that the doping of Ba^{2+} suppresses the formation of FM correlations in the paramagnetic state. As temperature further decreases, the g value increase significantly, which is an unambiguous signature of the presence of ferromagnetic correlations. When temperature is lower than 150 K, the g value begins to decrease rapidly. This is due to the disappearance of the FM correlation below 140 K, in consistent with the behaviour seen in the ESR spectra. Figure 4(b) shows the linewidth $\Delta H_{\rm pp}$ for the spectra. In a high temperature region, the linewidth shows a weak temperature dependence. However, as temperature decreases from the FM transition close to $T_{\rm N}$, the linewidth becomes broader obviously. Conversely, below 150 K, the abrupt decrease is consistent with the disappearance of FM phase and the appearance of entire AFM state of the system.[22,23]

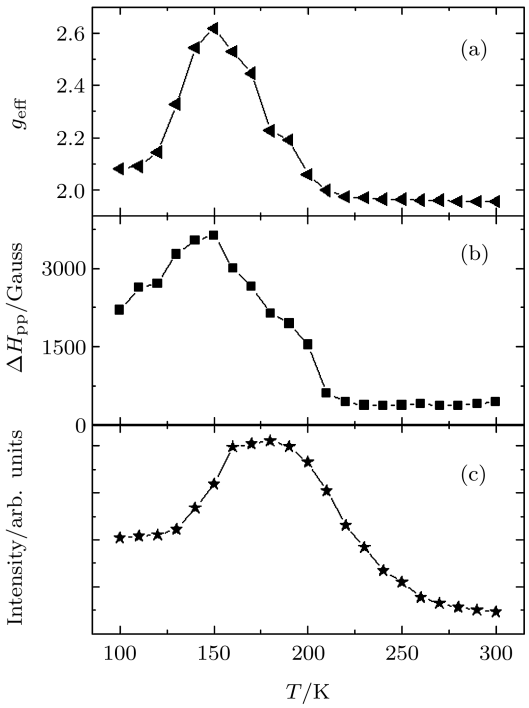


Fig.4. Temperature dependence of ESR spectra parameters: (a) g-factor, (b) linewidth, (c) intensity.

ESR intensity is another important parameter that can be used to identify the nature of the ions contributing to the resonance in the paramagnetic state.[24,25] The intensity of the ESR spectrum, which is proportional to the number of paramagnetic spins, is the area under the absorption curve. Here we use the double integration to calculate the intensity. The temperature dependence of the intensity is shown in Fig.4(c). The intensity increases gradually above $T_{\rm N} \approx 185$ K and then decreases as temperature further decreases to 100 K. The temperature dependence of intensity is very similar to that of the susceptibility shown in Fig.2, giving evidence that all Mn ions contribute to the spin susceptibility. The broad peak near $T_{\rm N}$ should be attributed to the competition between the FM phase and the AFM phase.

The $Nd_{0.5}Sr_{0.5}MnO_3$ compound has an FM metallic state ($T_{\rm C} = 250$ K), which transforms into a CO CE-type AFM state on cooling down to 150 K.[13,20] The study of compound shows that the increases of $< r_A >$ and σ^2 lead to the decrease of crystal structural distortion, a magnetic transition, and

a phase separation at low temperatures. In contrast with $Nd_{0.5}Sr_{0.5}MnO_3$, the $Nd_{0.5}Sr_{0.4}Ba_{0.1}MnO_3$ compound exhibits two magnetic transition temperatures, T_C and T_N, increasing ($T_C = 260\,K$ and $T_N = 185\,K$). When the Ba^{2+} cations are embedded in the pseudocubic perovskite matrix with disordered cations, the change of the Mn–O–Mn bond angle is dominated by Ba^{2+} cations doping on *A*-site, thereby leading to not only the increasing of Mn^{3+}–O–Mn^{4+} bond angle, but also the strengthening of FM coupling and the increasing of the curie temperature from 250 to 260 K. At the same time, Ba+ doping also results in the increasing of Mn^{4+}–O–Mn^{4+} bond angle, and the strengthening of AFM coupling, and the increasing of the Néel temperature from 150 to 185 K.

4. Conclusions

The temperature dependence of ESR spectra of doped $Nd_{0.5}Sr_{0.5-x}Ba_xMnO_3$ ($x = 0.1$) is reported. Above T_C, the compound is paramagnetic and ESR spectra consist of a single Lorentzian line. With $T_N < T < T_C$, in the system there coexist the paramagnetic phase and the ferromagnetic (FM) phase. Phase separation is evidenced for $Nd_{0.5}Sr_{0.4}Ba_{0.1}MnO_3$. Various parameters of the ESR signals like g_{eff} value, linewidth and intensity are sensitive to, typically dependent on temperature and definite signatures. Consequently, our electron spin resonance study of $Nd_{0.5}Sr_{0.4}Ba_{0.1}MnO_3$ polycrystalline shows the complex nature of the paramagnetic phase and the temperature evolution of coexisting ferromagnetic and antiferromagnetic phase.

References

[1] Huber D L 1998 *J. Appl. Phys.* **83** 6949

[2] Li R W, Sun J R, Wang Z H, Chen X and Shen B G 1999 *Acta Phys. Sin.* **48** S105 (in Chinese)

[3] Radaelli P G, Cox D E, Marezio M, Cheong S W, Schiffer P E and Ramirez A P 1995 *Phys. Rev. Lett.* **75** 4488

[4] Rodriguez-Martinez L M and Attfield J P 1996 *Phys. Rev.* B **54** R15628

[5] Damay F, Martin C, Maignan A and Raveau B 1997 *J. Appl. Phys.* **82** 6181

[6] Simon F, Atsarkin A, Demidov V V, Gaal R, Moritomo Y, Miljak M, Janossy A and Forro L 2003 *Phys. Rev.* B **67** 224433

[7] Angappane S, Pattabiraman M, Rangarajan G and Sethupathi K 2005 *J. Appl. Phys.* **97** 10H705

[8] Autret C, Gervais M, Gervais F, Raimboux N and Simon P 2004 *Solid State Science* **6** 815

[9] Angappane S, Pattabiraman M, Rangarajan G, Sethupathi K and Sastry V S 2004 *Phys. Rev.* B **69** 094437

[10] Lambert C A, Gervais M, Gervais F, Simon P and Raimboux N 2005 *Solid State Science* **7** 1035

[11] Fan J Y, Ying Y, Pi L and Zhang Y H 2007 *Solid State Commun.* **141** 141

[12] Millange F, de Brion S and Chouteau G 2000 *Phys. Rev.* B **62** 5619

[13] Lu Y, Li Q A, Di N L and Cheng Z H 2003 *Acta Phys. Sin.* **52** 1520 (in Chinese)

[14] Millis A J, Littlewood P B and Shraiman B I 1995 *Phys. Rev. Lett.* **74** 5144

[15] Lu Y, Li Q A, Di N L, Li R W, Ma X, Kou Z Q and Cheng Z H 2003 *Chin. Phys.* **12** 1301

[16] Shengelaya A, Zhao G M, Keller H, Muller K A and Kochelaev B I 2000 *Phys. Rev.* B **61** 5888

[17] Tian H W, Zheng W T, Zhao Z D, Ding T, Yu S S, Zheng B, Li X T, Meng F L and Jiang Q 2005 *Chem. Phys. Lett.* **401** 585

[18] Kimura T, Tomioka Y, Kumai R, Okimoto Y and Tokura Y 1999 *Phys. Rev. Lett.* **83** 3940

[19] Huber D L, Alejandro G, Caneiro A, Causa M T, Prado F, Tovar M and Oseroff S B 1999 *Phys. Rev.* B **60** 12155

[20] Deisenhofer J, Eremin M V, Zakharov D V, Ivanshin V A, Eremina R M, Krug von Nidda H A, Mukhin A A, Balbashov A M and Loidl A 2002 *Phys. Rev.* B **65** 104440

[21] Moreno N O, Pagliuso P G, Rettori C, Gardner J S, Sarrao J L, Thompson J D, Huber D L, Mitchell J F, Martinez J J and Oseroff S B 2001 *Phys. Rev.* B **63** 174413

[22] Yang R F, Sun Y, He W, Li Q A and Cheng Zh H 2007 *Appl. Phys. Lett.* **90** 032502

[23] Joshi J P, Gupta R, Sood A K, Bhat S V, Raju A R and Rao N R 2001 *Phys. Rev.* B **65** 024410

[24] Lu Y, Li Q A, Di N L, Ma X, Kou Z Q, Luo Z and Cheng Z H 2003 *Chin. Phys.* **12** 0789

[25] Ivanshin V A, Deisenhofer J, Krug von Nidda H A, Loidl A, Mukhin A A, Balbashov A M and Eremin M V 2000 *Phys. Rev.* B **61** 6213