ARTICLE

Abnormality of Magnetic Behavior and Resistivity of $La_{0.7-x}Dy_xSr_{0.3}MnO_3$ ($0.00 \leq x \leq 0.30$) System at Low Temperature

Ning Liu[a,b*], Guo-qing Yan[a], Su-jun Xu[b], Wei Tong[b]

a. Department of Physics, Suzhou College, Suzhou 234000, China; b. Structure Research Laboratory, University of Science and Technology of China, Hefei 230026, China

(Dated: Received on January 20, 2005; Accepted on May 15, 2005)

By measuring M-T curves, ρ-T curves and MR-T curves of the samples under different temperatures, the influence of Dy doping ($0.00 \leq x \leq 0.30$) on the magnetic and electric properties of $La_{0.7-x}Dy_xSr_{0.3}MnO_3$ has been studied. The experimental results show that, with the increase of the Dy content, the system undergoes a transition from long range ferromagnetic order to the cluster-spin glass state and further to antiferromagnetic order. For the samples with x=0.20 and 0.30, their magnetic behaviors are abnormal at low temperature, and their resistivities at low temperature have a minimum value. These peculiar phenomena not only come from the lattice effect induced by doping, but also from extra magnetic coupling induced by doping.

Key words: Manganite, Abnormality of resistivity at low temperature, Lattice effect, Extra magnetic coupling

I. INTRODUCTION

In recent years, rare-earth manganite with perovskite-like structure has attracted wide attention because the colossal magnetoresistance effect (CMR effect) is found in this kind of compound [1-5]. This kind of compound has the structure of $RE_{1-x}T_xMnO_3$, where RE is trivalent rare-earth ion, and T is divalent alkaline-earth ion. People have put forward many kinds of theoretical models for the origin of CMR effect, in which the most important ones are double-exchange function and Jahn-Teller effect. When the type and content of alkaline-earth element T are changed, the above two effects both change, thus changing the properties and CMR effect of this kind of compound, which is the focal point under investigation in the previous period. On the other hand, if the alkaline-earth element was kept unchanged, and the RE element in the compound is substituted by a second rare-earth ion with a different radius, i.e. $(RE_{1-y}RE_{by})_{1-x}T_xMnO_3$ (RE_b is the second rare-earth ion, the ratio between Mn^{3+} and Mn^{4+} being constant), then only the average radius of the positive ions at A-site is changed, and the properties and CMR effect of the compound are changed by size effect [3,6,7]. In this work, we chose Dy with comparatively small ion radius but with comparatively large magnetic moment to substitute La in $La_{0.7}Sr_{0.3}MnO_3$ compound (the ion radius of La and Dy is 0.122 and 0.108 nm respectively, and the effective magnetic moment of Dy^{3+} is $10.6\mu_B$), and studied the influences of lattice effect and the magnetism of A-site ion on the magnetic and electric properties of the system. The experimental results show that, for the Dy doping system, its magnetic behavior at low temperature is abnormal, and its resistivity at low temperature exhibits a minimum value. These peculiar phenomena come not only from lattice effect induced by doping but also from extra magnetic coupling induced by doping.

II. EXPERIMENTS

Polycrystalline samples $La_{0.7-x}Dy_xSr_{0.3}MnO_3$ (x=0.00, 0.10, 0.20, 0.30) were prepared by the solid-state reaction method, and the preparing procedure is shown briefly as below: The chemical reagents La_2O_3, $SrCO_3$, Dy_2O_3 and MnO_2 of high purity were matched in stoichimetric proportions. They were sufficiently mixed and ground, then pre-fired at 900 °C for 12 h, ground again and then heated at 1000 °C for 12 h and at 1200 °C for 24 h to get good crystal. Finally, it was pressed into pellets, sintered at 1400 °C for 24 h, and cut into thin lump samples with long-strip shape.

Powder X-ray diffraction of the samples was carried out by a Rigaku-D/max-γA diffractometer with highly intense Cu-Kα radiation to test the structure change and phase purity of the samples. The M-T curves were measured by Lake Shore vibrating sample magnetometer (VSM), and the samples were measured in warming condition after being cooled to 5 K in zero field and 0.01T magnetic field respectively. Resistivity in zero field and magnetic field (H=0, 6 T) was measured by the standard four-probe method, and the measuring current was kept at a certain value between 1 and

*Author to whom correspondence should be addressed. E-mail: liuning.szsz@163.com

10 mA to meet the needed sensitivity according to the resistance value of measured samples.

III. RESULTS AND DISCUSSION

Powder X-ray diffraction patterns of the samples are shown in Fig.1. XRD patterns demonstrate that, with the increase of Dy doping concentration, the crystal structure transforms from rhombohedral symmetry to cubic structure, and that all the samples keep in good single phase. At the same time, with the increase of Dy content, the diffraction peaks shift to larger angles, which is reasonable because the ion radius of Dy^{3+} is smaller than that of La^{3+} [8].

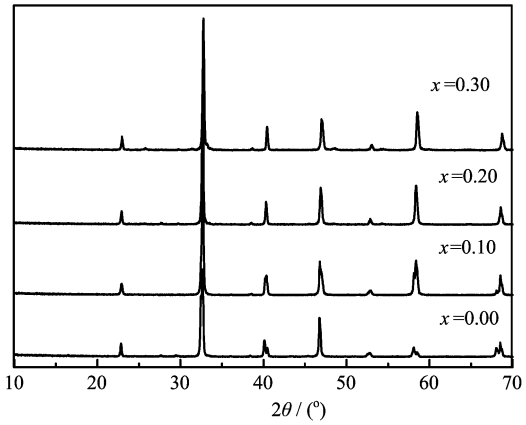

FIG. 1 XRD patterns of $La_{0.7-x}Dy_xSr_{0.3}MnO_3$.

A. Peculiar magnetization peaks

The M-T curves of the samples are shown in Fig.2. With the increase of doping amount, Curie temperature T_c (defined as the temperature where dM/dT is maximum) of the system decreases, the magnetization M becomes weaker gradually, and the magnetic behavior shows three conditions: (i) For the sample of x=0.00 without doping, the M-T curves of zero-field cooling (ZFC) and field cooling (FC) coincide roughly with each other, the paramagnetism-ferromagnetism (PM-FM) transition is very steep, and the system exhibits typical ferromagnetic character and is in long-range ferromagnetic order below T_c; (ii) For the sample of x=0.10, apparent paramagnetic-ferromagnetic (PM-FM) transition occurs near Curie temperature T_c, unreversible behavior appears below this temperature, the disordered freeze of ferromagnetic clusters occurs at low temperature, the ZFC and FC curves form a typical "λ" shape, and the system exhibits the character of cluster glass state; (iii) The M-T curves of samples x=0.20 and 0.30 are similar to that of sample x=0.10, but differing in that anti-ferromagnetic state appears below Néel temperature T_N (defined as the temperature of the transition between ferromagnetism and antiferromagnetism) and a peculiar magnetization peak appears near T_N.

The Dy^{3+} plays an important role in the peculiar changes of magnetic behavior in the samples. On one hand, the effective magnetic moment of Dy^{3+} is comparatively large, which may increase T_c and M; on the other hand, the average radius of Dy^{3+} is comparatively small, which may decrease T_c and M. Figure 2 exhibits that, with the increase of Dy doping amount, the magnetism of the system becomes weaker, and T_c decreases rapidly. But we can not simply attribute this completely to the decrease of the average radius at A-site, which will cause the decrease of the tolerance factor t and the distortion of Mn−O bond length and bond angle and eventually the weakening of the ferromagnetism [6], because lattice effect can not explain the magnetization peak. We should also consider the occupation site of Dy ion in the lattice and the influences of thermal fluctuation and Coulomb potential fluctuation.

The sample of x=0.00 without doping, exhibits long-range ferromagnetic order below T_c. Both PM-FM transition and insulator-metal (I-M) transition accord with those reported before. For the sample of x=0.10, La−O−La(Sr) chains in La−O layer are destroyed, in which Dy randomly distributed. And the random magnetic potential and Coulomb potential of Dy ion lead to the formation of Mn−O−Mn clusters (short-range ferromagnetic order). For the samples of x=0.20, 0.30, Dy ions do not randomly distribute in La(Sr)−O layer any more, but form Dy−O−Dy chains, which changes La(Sr, Dy)−O layer into a magnetic layer and, together with Mn−O−Mn, forms two sublattices. We denote the magnetic moments of La(Sr, Dy)−O sublattice and Mn−O−Mn sublattice as $M_{\text{La-Dy}}$ and M_{Mn}, respectively. According to Néel double-lattice model, the inner arrangements of La(Sr, Dy)−O and Mn−O−Mn sublattices are ferromagnetic arrangements, and the arrangement between La(Sr, Dy)−O sublattice and Mn−O−Mn sublattice is anti-ferromagnetic. Thus the net magnetic moment of the system M_s=M_{Mn}−$M_{\text{La-Dy}}$. At extremely low temperature, the coupling between the two sublattices is comparatively strong and the magnetic domain of La(Sr, Dy)−O sublattice can not rotate. Therefore, the samples exhibit apparent antiferromagnetic character. With the temperature increasing, the energy provided by thermal effect makes the magnetic coupling between the two sublattices weeker, and the magnetic domains of some La(Sr, Dy)−O sublattices rotate and tend to be parallel to the applied magnetic field, which causes M to increase. Eventually, La(Sr, Dy)−O sublattice and Mn−O−Mn sublattice are both parallel to the applied magnetic field at T_N, M_s=M_{Mn}+$M_{\text{La-Dy}}$. With the temperature further increasing, the influence of thermal effect on the magnetic moment of La(Sr, Dy)−O sublattice surpasses

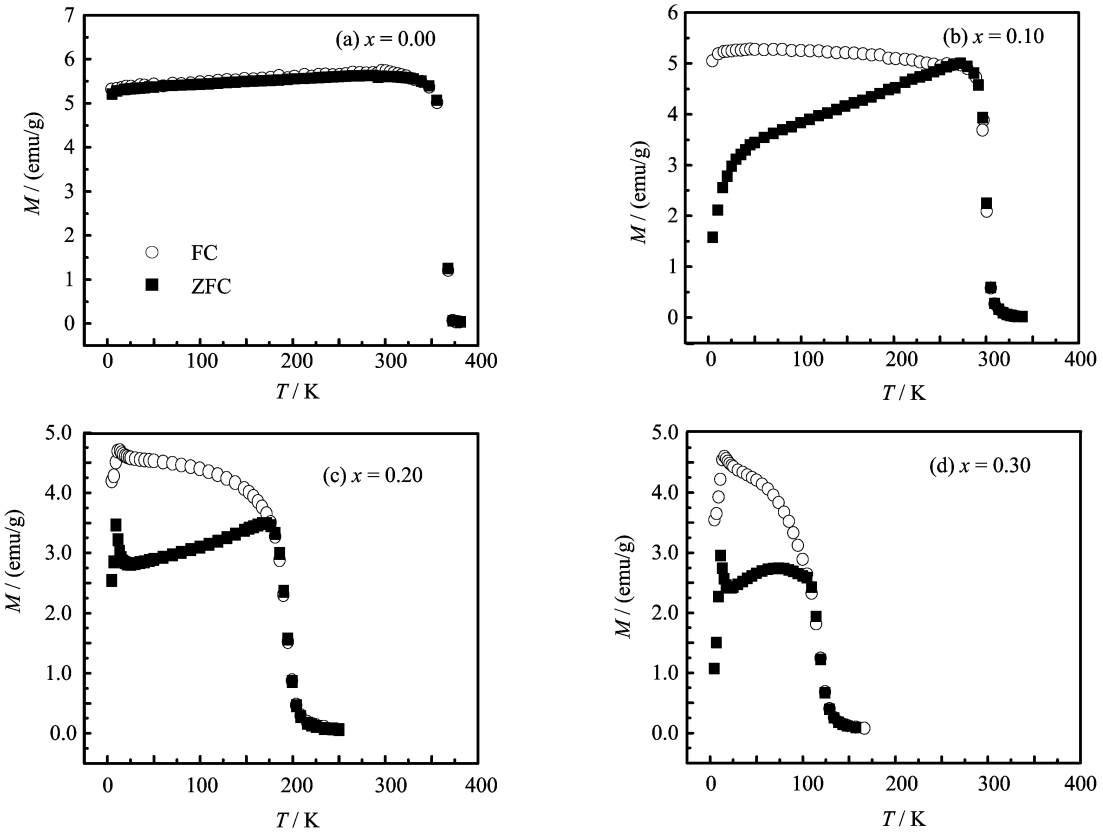

FIG. 2 M-T curves of the samples for $La_{0.7-x}Dy_xSr_{0.3}MnO_3$ ($0.00 \leq x \leq 0.30$).

that of applied magnetic field, which destroys the orderly arrangement of the spin magnetic moment of La(Sr, Dy)−O sublattice and decreases M. When La(Sr, Dy)−O sublattice is completely in paramagnetic state, M_s=$M_{\rm Mn}$, M reaches a minimum value. This process forms the sharp peak in the M-T curves.

B. Minimum value phenomenon of resistivity at low temperature and CMR effect

The ρ-T curves of the samples in zero field and 6 T magnetic field are shown in Fig.3. Figure 3 demonstrates that, along with the paramagnetism-ferromagnetism (PM-FM) transition of the magnetism in the samples, the transport behavior also transforms from insulator state to metal state, and that all the samples of $x \geq 0.10$ have an apparent transition temperature T_p (defined as the temperature where $d\rho/dT = 0$). With the increase of x, the transition temperature T_p of the samples shifts gradually to low temperature, and the corresponding resistivity peak value ρ_m increases sharply, and change as much as two orders of magnitude. The relationship between the changes of T_p, ρ_m and x is monotonous, and only 30% substitution amount of Dy can increase the resistivity of the sample by about 125 times and decrease the transition temperature by about 200 K, which indicates that the influences of rare-earth doping on transport properties of the samples are very apparent. The changes of T_p and ρ_m with x firstly come from the lattice effect induced by doping: when La in $La_{0.7}Sr_{0.3}MnO_3$ is substituted by Dy with a smaller ion radius, with the increase of Dy content, the average ion radius decreases gradually, the bond angle of Mn−O−Mn also decreases gradually, which causes manganese ions to approach each other and thus changes the hopping process of electrons at Mn lattice points, causing the decrease of T_p and the increase of ρ_m. This kind of structure appears con-

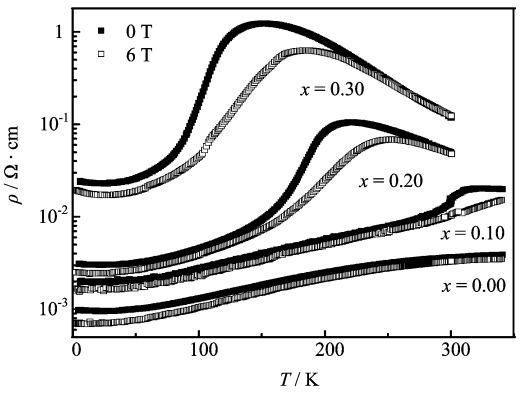

FIG. 3 ρ-T curves of the sample for $La_{0.7-x}Dy_xSr_{0.3}MnO_3$.

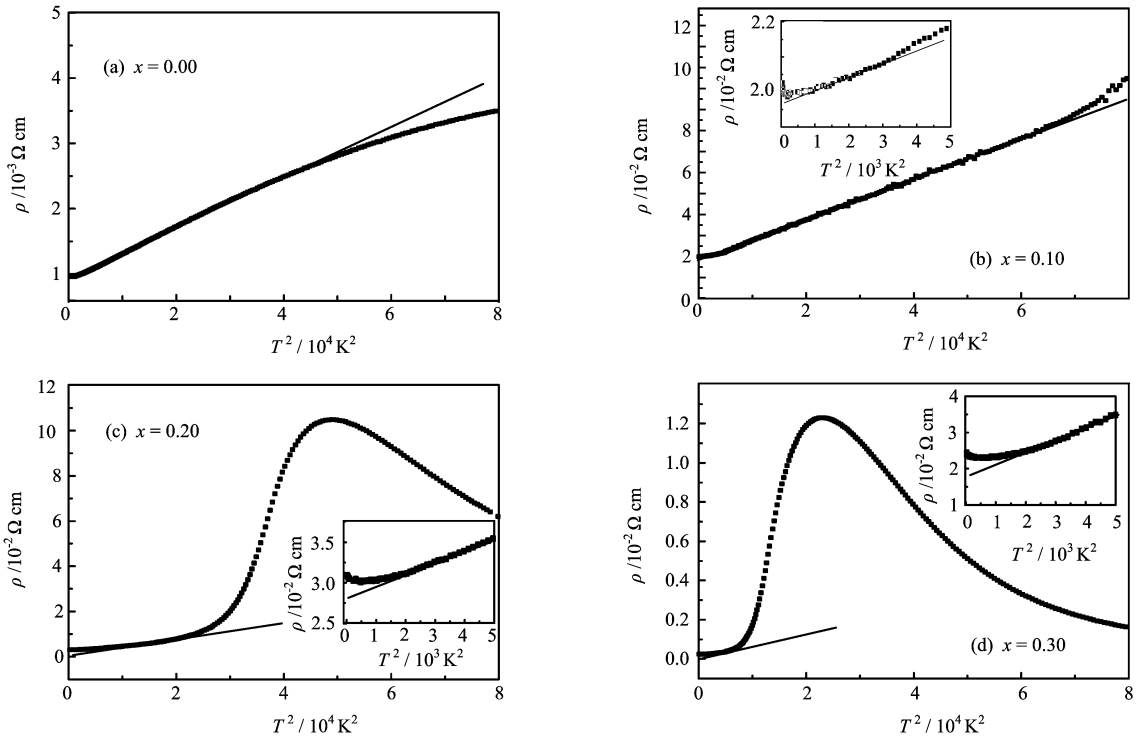

FIG. 4 ρ-T^2 fitted curves of the samples for $La_{0.7-x}Dy_xSr_{0.3}MnO_3$ ($0.00 \leq x \leq 0.30$) at low temperature range.

trary to intuition, and Hwang *et al.* call it as the result of "anti-intuition" [6]. In addition, the increase of Dy doping strengthens the localization degree of e_g electron in Mn^{3+} and thus the random potential and Coulomb potential, thus the movement of carriers is largely hindered by scattering, which also leads to the increase of resistivity with the increase of doping.

The ρ-T^2 fitted curves of the samples at the low temperature range are shown in Fig.4. Figure 4 exhibits that, except for a little deviation on extremely low temperature range, the ρ-T^2 curves increase nearly linearly and coincide very well. For the stuck-up phenomenon of the resistivity at low temperature in the system (shown in the inserts of Fig.4), the temperature corresponding to the minimum value of resistivity accords very well with Néel temperature T_N. This is because that, at T_N, the magnetic moment of La(Sr, Dy)−O sublattice completely rotates to the direction of applied field under the competitive function between applied field and thermal fluctuation, and then forms ferromagnetic parallel arrangement with the magnetic moment of Mn−O−Mn sublattice, thus the decrease of magnetic scattering function leads to the minimum value of resistivity. Below this temperature, partial La(Sr, Dy)−O sublattices form anti-parallel arrangement with Mn−O−Mn, which produces anti-ferromagnetic background for carrier transport and causes resistance to increase, leading to the minimum value of resistivity at low temperature.

Figure 5 gives the relationship between magnetoresistance MR and temperature T in $La_{0.7-x}Dy_xSr_{0.3}MnO_3$ system. MR is defined as:

$$MR = \frac{\rho(\mathrm{O}) - \rho(\mathrm{H})}{\rho(\mathrm{H})} \times 100\% \qquad (1)$$

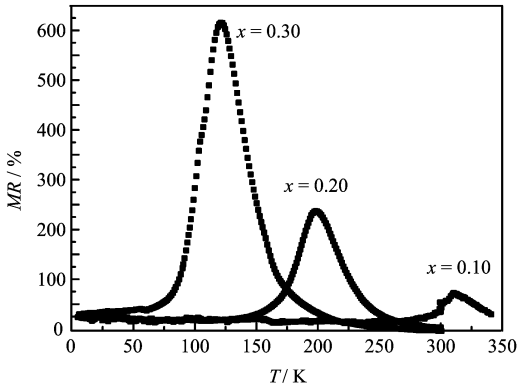

FIG. 5 MR-T curves of $La_{0.7-x}Dy_xSr_{0.3}MnO_3$.

Figure 5 exhibits that CMR appears mainly near Curie temperature T_c. In the 6 T magnetic field, MR peak value of sample x=0.30 is 620%, that of x=0.20 is 240%, and that of x=0.10 is also 74%, thus it has comparatively high value of practical application.

The ρ-T curves in Fig.3 demonstrate that the resistivity in magnetic field of all the samples is lower than that in zero field, and that the temperature of IM transition T_p shifts to higher temperature and the resistivity

peak is brought down, which lead to colossal magnetoresistance effect. As we know, applied magnetic field has two functions upon CMR materials: one is that applied magnetic field can suppress the thermal fluctuation and cause the PM-FM transition to occur at higher temperature, i.e. IM transition temperature T_p shifts to higher temperature; the other is that it causes the FM state on the same temperature range to become more orderly, and the scattering function upon carrier to become weaker, which causes the resistivity in magnetic field of the samples to be lower than that in zero field.

Figure 5 also exhibits that *MR* increases with the increase of Dy concentration, which is because although random magnetic potential and Coulomb potential induced by extra magnetism strengthen with the increase of doping, the function of 6 T magnetic field not only suppresses random potential and Coulomb potential of Dy but also causes Dy and Mn to form ferromagnetic arrangement easily, which decreases the scattering for carrier and increases the transport rate of electron hopping. Consequently the resistivity decreases greatly, and the phenomenon appears that the magnetoresistance increases with doping. The CMR effect of the doped system is related not only with extra magnetism induced by doping but also with the average radius of the A-site ion, which is because that $\langle r_A \rangle$ has direct influences on the ratio of Mn^{3+}/Mn^{4+} as well as charge ordering. And larger $\langle r_A \rangle$ is beneficial to double-exchange, so the adjustement of the ion radius at A-site can change CMR. Hwang *et al.* gave a detailed study to the relation between MR and x in $La_{0.7-x}Pr_xCa_{0.3}MnO_3$ system [6], and found that MR increases regularly with the decrease of the average ion radius at A site. Our experiment also confirms the deduction of Hwang *et al.*

IV. CONCLUSIONS

With the increase of Dy doping amount, paramgnetism-ferromagnetism transition temperature of the samples decreases gradually, and the magnetic structure transforms from long-range ferromagnetic order to cluster-spin glass state and further to anti-ferromagnetic state. The corresponding resistance peak value increases gradually, and the magnetoresistance increases rapidly. These phenomena demonstrate that the substitution of a second rare-earth ion with a different radius for RE in the compound has great influence on the properties of the samples.

For the system at low temperature, the magnetic behavior exhibits a magnetization peak and the electric behavior exhibits a minimum value of resistivity, which come from both the lattice effect and the extra magnetic coupling induced by doping.

V. ACKNOWLEDGMENT

This work was supported by the National Nature Science Foundation of China (No. 19934003) and the State Key Project of Fundamental Research of China (No. 001CB610604) and the Item of Nature Science Research of Anhui (No. 2001kj244).

[1] R. V. Helmolt, J. Wecker, B. Holzapfel, *et al.* Phys. Rev. Lett. **71**, 2331 (1993).
[2] S. Jin, T. H. Tiefel, Mccormack, *et al.* Science **264**, 413 (1994).
[3] S. Jin, H. M. Bryan, T. H. Tiefel, *et al.* Appl. Phys. Lett. **66**, 382 (1995).
[4] Y. Moritomo, A. Asamisu, H. Kuwahara, *et al.* Nature **380**, 141 (1996).
[5] J. Y. Fei, W. L. Xin, G. Z. Liang, G. M. Zhu and X. Y. Ma, Chin. J. Chem. Phys. 16, 425 (2003)
[6] H. Y. Hwang, S. W. Cheong, P. G. Radaelli, *et al.* Phys. Rev. Lett. **75**, 914 (1995).
[7] J. Blasco, J. Garcia, J. M. D. Teresa, *et al.* J. Phys.: Condens Matter **8**, 7427 (1996).
[8] J. Wu, Q. Q. Cao, K. M. Gu, *et al.* Acta Phys. Sin. (in Chinese) **48**, 370 (1999).