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Effects of Gd substitution on magnetic and transport properties in $La_{0.6-x}Gd_xSr_{1.4}MnO_4$*

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With the increasing of x, the ZFC (zero-field cooling) $M-T$ curves for the polycrystals $La_{0.6-x}Gd_xSr_{1.4}MnO_4$ (x=0, 0.1, 0.2, 0.4, 0.6) change from spin-glass-like to paramagnetic, and each ZFC $M-T$ curve has an inflection point at 20K. These behaviours can be understood by considering the respective contributions of Mn and Gd to the total magnetism. In addition, for all the samples, thermal activation conducting behaviours are observed from 100 K to room temperature. Due to the strong antiferromagnetic coupling between neighbouring Mn ions, there is no obvious magnetoresistance effect until the magnetic field strength rises to 3.98×10^6A/m.

Keywords: spin glass, magnetism, antiferromagnetic, magnetoresistance
PACC: 7170G, 7550E, 7550L

1. Introduction

Considerable research on the colossal magnetoresistance (CMR) effect has been carried out in the mixed valent manganite perovskites ABO_3,[1,2] the $n=\infty$ member of the series of Ruddlesden–Poper (RP) phases $A_{n+1}B_nO_{3n+1}$.[3] A_2BO_4-type compounds, the n=1 member of the series of RP phases, have also been studied intensively in recent years.[4−7] A detailed study of these materials can bring about a profound understanding of physical properties of layered perovskite family compounds. $La_{1-x}Sr_{1+x}MnO_4$ (x=0) with a tetragonal structure at room temperature, is known as an insulating antiferromagnetic compound.[4] When $x>0$ in the compound, Sr^{2+} replaces La^{3+} partially, and Mn^{4+} ions appear. Then, possibly, the double exchange interaction takes place. The competition between superexchange interaction and double-exchange interaction may induce the spin glass behaviour.[8] In the A_2BO_4-type compound, each MnO_2 layer is separated by an insulating rock-salt-type $(La,Sr)_2O_2$ layer, therefore the carriers are strongly confined in the ab-plane. So the resistivity is very high.[4] Until now, La has been the A-site rare earth element in the studied A_2BO_4-type compound. Compounds containing other magnetic rare earth elements in the A-site are seldom reported. In this paper, we focus our investigation on this aspect. The heavy magnetic rare element Gd is chosen to substitute for La. The effects of substitute on magnetic and transport properties are studied. The Gd substitution gives rise to the enhancement of the low-temperature magnetization, and the disappearance of spin-glass-like behaviour step by step. However, the antiferromagnetic coupling between Mn ions is very strong. None of the samples show any evident magnetoresistance effect.

2. Experiment

The polycrystals $La_{0.6-x}Gd_xSr_{1.4}MnO_4$ (LGSM) were fabricated with the conventional solid-state reaction method. First stoichiometric proportions of La_2O_3 (purity 99.99%), Gd_2O_3 (99.99%), $SrCO_3$ (99.99%) and $MnCO_3$ (99.985%) powder were mixed and ground. Then the mixture was pre-sintered below 1100° for a time. Having been intermediately ground, the resultants were pressed into pellets and sintered repeatedly at 1350°C in flowing 50% O_2 (Ar balance) until the single-phase samples were obtained.

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The magnetization measurements were performed by a superconducting quantum interface device magnetometer. In order to take resistivity measurements by the standard four-probe technique, all the samples were cut into rectangles with a 2mm×2mm×8mm dimension.

3. Results and discussion

The Rietica program[9] was used to obtain the information about the crystal structure. One of the typical x-ray diffraction (XRD) patterns is illustrated in Fig.1. Good agreement between the calculations and the observations in both positions and intensities of the lines implies that the sample with x=0.2 has a single phase of the tetragonal structure, space group $I4/mmm$. In the whole range of x, each sample has the same structure as the sample with x=0.2. At low temperatures, further investigation is needed to confirm whether the structures of LGSM deviate from the tetragonal structure or not.[10] Due to the fact that the radius of Gd^{3+} (0.122nm) is smaller than that of La^{3+} (0.136nm),[11] the substitution of Gd for La leads to the decrease of the lattice parameters as expected. In addition, the Rietveld refinements indicate that with the increasing of the Gd content, the length of the bond Mn-O(1) (along c) elongates, e.g. for x=0, the length of the bond Mn–O(1) is 0.1930(4) nm while for x=0.4, it is 0.2013(4) nm; and the length of the bond Mn–O(2) (in the ab-plane) contracts, e.g. when x=0, the length of the bond Mn–O(2) is 0.1998(9) nm while when x=0.4, it is 0.1918(2)nm.

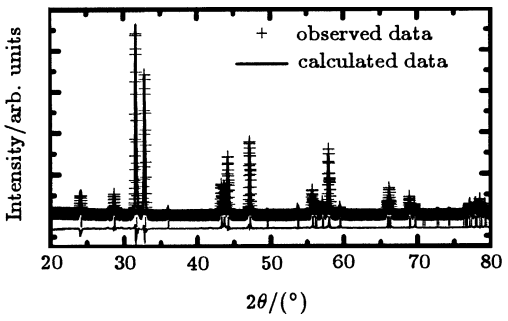


Fig.1. XRD pattern at room temperature and Rietveld refinement for the sample with x=0.2: vertical bars mark the expected positions for tetragonal crystal structure (R_P= 8.4%, R_{WP}= 11.7%, χ^2=5.8).

The temperature dependence of magnetization for x=0 is similar to that reported in Ref.[4]. All the measured magnetizations as a function of temperature for LGSM in a 7.96×10^3A/m field are shown in Fig.2. It is clear that the magnetization at lower temperatures increases with the Gd content. The samples with x=0 and 0.1 show spin-glass-like behaviours: ZFC and FC data split; the ZFC $M-T$ curve has a cusp at a low temperature.[12] Each of them has a cusp at about 20K (T_g). All the ZFC curves of samples with x=0.2, 0.4 and 0.6 have inflection points at about 20K. However, their magnetizations increase with temperature decreasing, unlike the samples with x=0 and 0.1. It seems that the spin-glass-like behaviours disappear. If we take into consideration such a fact that each Gd^{3+} ion has a $\mu = 8\mu_B$ magnetic moment, which makes a contribution to the total magnetism of LGSM, these phenomena could be given a reasonable explanation. The total magnetism for LGSM is determined by the co-contribution of Mn and Gd. The contribution of Mn ions is responsible for the spin-glass-like behaviour, which can be seen from the curve with x=0 in Fig.3. The contribution of Gd^{3+} results in the paramagnetic behaviour, which can be described by a Langevin function as follows:

$$M = \mu\left[\coth\left(\frac{\mu H}{kT}\right) - \frac{kT}{\mu H}\right], \qquad (1)$$

where k is the Boltzmann constant. This conjecture may be further confirmed by the following results. With the magnetic moments for Gd^{3+} subtracted from the measured magnetic moments, as shown in Fig.3, it is found that the modified curves are very similar: the maximums of their magnetizations are almost the same; below 20K, their magnetizations are reduced with temperature decreasing, and form cusps at 20K. Because the magnetization of paramagnetic Gd^{3+} is very strong at low temperatures, with the increasing of the Gd content, the magnetism of Gd blurs the magnetic contribution made by Mn, and the measured $M-T$ curve changes into a paramagnetic one. It is noteworthy that Battle *et al* also observed the similar phenomena in the bilayered manganites.[13] The competition between double exchange interaction and super exchange interaction may be responsible for the spin-glass-like behaviour.[4]

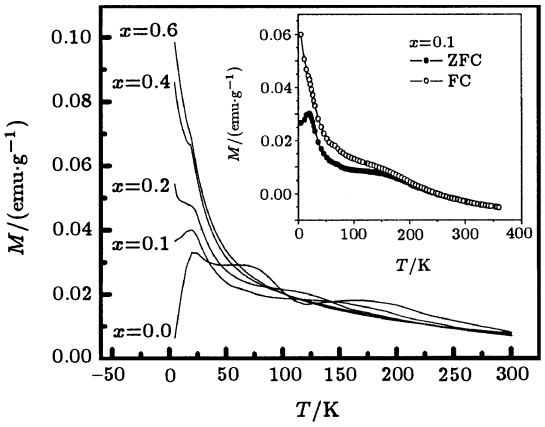


Fig.2. Temperature dependence of ZFC magnetization for LGSM in a 7.96×10^3A/m field. The inset shows the $M-T$ curves in ZFC and field cooling (FC) modes for the sample with x=0.1. The ZFC and FC data exhibit a characteristic splitting at low temperatures, which signifies the occurrence of a spin-glass-like transition.

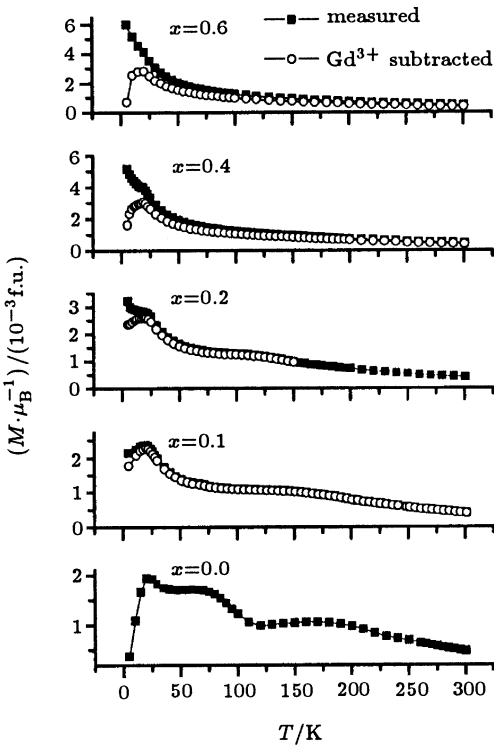


Fig.3. Comparison of the measured ZFC magnetization and the one subtracting the contribution of paramagnetic Gd^{3+}.

The ZFC $M-T$ curves for the sample with x=0.0 in different magnetic fields indicate that with the strengthening of the magnetic field, T_g decreases (T_g are 20K, 17K and 9K when the magnetic field strengths are 7.96×10^3A/m, 7.96×10^4A/m and 7.96×10^5A/m, respectively.). In fact, for the sample with x=0.1, a 3.98×10^6A/m magnetic field can suppress the spin-glass-like behaviour throughout: namely, the ZFC magnetization does not decrease as temperature falls to 5K. A plausible explanation is that magnetic field suppresses the spin frustration.

The isothermal magnetization curves for the sample with x=0.1 are shown in Fig.4. At the temperatures shown in the figure, all the curves pass through zero, which indicates that there exists no spontaneous magnetization. According to the calculations, every nominal molecular has a $4.4\mu_B$ magnetic moment if all the magnetic moments are aligned, whereas the measured value is only about $1.2\mu_B$ at 5K in a 3.98×10^6A/m field. The behaviours, difficult to make magnetization saturated at 5K and 20K, are another signature for the spin glass phase.[14] At 75K, 150K and 300K, the $M-H$ curves are all straight-lines passing through zero, suggesting that the sample with x=0.1 is antiferromagnetic or paramagnetic.

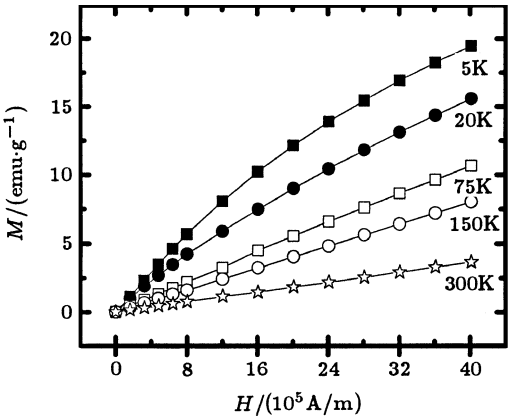


Fig.4. Isothermal magnetization curves for the sample with x=0.1.

Because the LGSM magnetism for every sample is clearly different from each other at low temperatures, possibly, the low-temperature resistivities are also different. However, the resistivities of LGSM (Fig.5) are too high for our measurement equipment to obtain reliable results below 100K due to what was mentioned previously. Exponential fittings indicate that all the samples have thermal activation conduction mechanisms above 100 K (as shown in Eq.(2))

$$\rho(T)=\rho_0\exp\left(\frac{E_a}{kT}\right). \tag{2}$$

Activation energy E_a for each sample is listed in Fig.5. The response of resistivities to the magnetic field within 3.98×10^6A/m is very weak. Above 100K, we did not observe the conspicuous magnetoresistance effect up to a 3.98×10^6A/m field for all the samples. The curves in a zero field nearly overlap the ones in a

nonzero field. The possible reason for that is that the antiferromagnetic coupling between neighboring Mn ions in our sample is too strong.[15]

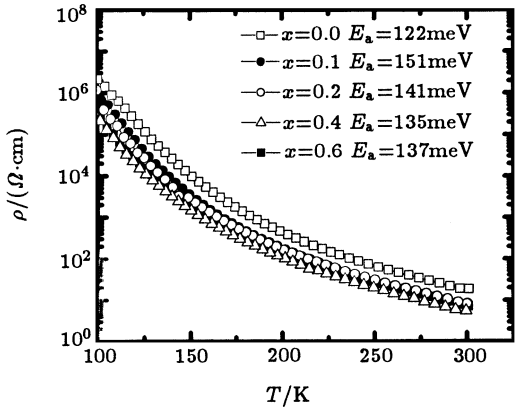


Fig.5. Temperature dependence of resistivity for LGSM in a zero-field.

4. Conclusions

The effects of the Gd substitution for La on the magnetic and transport properties in polycrystalline compounds of $La_{0.6-x}Gd_xSr_{1.4}MnO_4$ (x=0, 0.1, 0.2, 0.4, 0.6) have been studied in detail. The magnetism of LGSM comprises two parts: the magnetism of Mn ion and that of Gd^{3+}. The magnetism of Mn ion leads to the spin-glass-like behaviours; while the magnetism of paramagnetic Gd ion brings on the increase of the low temperature magnetization with temperature lowing. In addition, at low temperatures, magnetization is enhanced with the Gd content due to the great Gd^{3+} magnetic contribution. The conduction mechanisms (above 100K) of all the samples obey thermal activation law. Because the antiferromagnetic coupling between Mn ion spins is very strong, the magnetoresistance effect is very weak until the magnetic field strength rises to 3.98×10^6A/m.

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