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# Effect of Cu doping on the magnetic and electrical properties of $n$=2 Ruddlesden–Popper manganates*

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A series of polycrystalline Cu-doped $n$=2 Ruddlesden–Popper manganates $La_{1.2}Sr_{1.8}Cu_xMn_{(2-x)}O_7$ ($x$=0, 0.04, 0.13) were synthesized by the solid state reaction method. The effect of Cu doping on the magnetic and transport properties has been studied. It is found that Cu substitution for Mn greatly affects the magnetic and electrical properties of the parent phase $La_{1.2}Sr_{1.8}Mn_2O_7$. With the increase of Cu content, the system undergoes a transition from long-range ferromagnetic order to the spin glass state and further to an antiferromagnetic order. A little of Cu dopant can lead to the samples showing semiconductor or insulator behaviour in the whole observed temperature range while the parent phase has a metal–insulator transition. These samples show colossal magnetoresistance at low temperatures and the value of it decreases with increasing Cu content.

**Keywords:** layered perovskite, magnetic and electrical properties, spin glass
**PACC:** 7525, 7560

## 1. Introduction

After Jonker and Van Santen[1] found that both metal–insulator and ferromagnetic–paramagnetic phase transitions took place simultaneously in the mixed valence $Mn^{3+}/Mn^{4+}$ $La_{(1-x)}Sr_xMnO_3$ perovskite in the 1950s, a great deal of work has been done to study the effect of valence on magnetic and electrical properties. Kusters *et al*[2] found that when an external field was applied, the resistance of materials could be suppressed extremely, which were called colossal magnetoresistance (CMR). Double exchange (DE) interaction,[3] in which neighbouring spin moments of $Mn^{3+}/Mn^{4+}$ coupled each other through oxygen ion, was used to explain this phenomenon. In addition, the small polaron theory and the Jahn–Teller (JT) effect were proposed because it was hard to explain the CMR effect only using DE for some materials.[4]

Layered perovskite which can be written as $A_{(n+1)}B_nO_{(3n+1)}$ also have CMR effect.[5,6] This type of perovskite whose $Mn^{3+}$ / $Mn^{4+}$ network is interrupted by an $A$-O layer has a two-dimensional structure. The structure consists of perovskite phase in planes and rock salt phase between the planes. Because of this peculiar structure, layered perovskites not only have CMR and magnetocaloric effect[7,8] but also have complex ferro-antiferromagnetic fabric such as ferromagnetic (FM) metal, antiferromagnetic (AFM) insulator, cant antiferromagnetic (CAFM), and charge ordering (CO) etc.[9–11] For layered manganate perovskite, the site of Mn ions also can be substituted by other 3d transition metal such as Cr, Fe and Co.[12–14] Generally speaking, substitution of other elements for Mn will reduce the magnetization greatly because $Mn^{3+}/Mn^{4+}$ bonds are interrupted. In this paper, we study the effect of substitution of Cu for Mn on the magnetic and electrical properties in $n$=2 Ruddlesden–Popper manganates.

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## 2. Experiment

The $n$=2 Ruddlesden–Popper manganates $La_{1.2}Sr_{1.8}Cu_xMn_{(2-x)}O_7$ ($x$=0, 0.04, 0.13) were successfully synthesized by the traditional solid state reaction method. High purity (99.9%) powders of $La_2O_3$, $SrCO_3$, $Mn_3O_4$ and CuO were mixed according to stoichiometric proportion, ground and pressed into pellets, heated in air at 850 and 1100°C for 20h with several intermediate grindings. Finally, the obtained powders were pressed into pellets and sintered at 1350°C for 15h, then cooled to room temperature in the furnace.

The structure of the samples was determined by x-ray powder diffraction (XRD) using Cu $K\alpha$ radiation, and the measurements were carried out at room temperature. Magnetization was measured in the warming after zero-field-cooling (ZFC) and field-cooling (FC) using vibrating samples magnetometer (VSM). The electron spin resonance (ESR) measurements were performed at 9.48 GHz using a BRUKER EMX -10/12. Resistivity was measured under magnetic fields up to 5T by the standard four probes technique on the Physics Property Measurement System (PPMS) facility from Quantum Design. The magnetoresistance is defined as $MR=\Delta\rho/\rho_0=(\rho_H-\rho_0)/\rho_0$, where $\rho_0$ and $\rho_H$ is the resistivity at zero field and applied field, respectively. The external field was applied vertically to the direction of the current.

## 3. Results and discussion

### 3.1. Structure

The XRD patterns of samples $La_{1.2}$ $Sr_{1.8}$ $Cu_x$ $Mn_{(2-x)}O_7$ ($x$=0, 0.04, 0.13) are shown in Fig.1. XRD analysis indicates that all samples are single-phase with layered-perovskite $Sr_3Ti_2O_7$ structure without impurity phase. The ratio of lattice parameters $c/a$ and the volume of unit cell augment monotonously with increasing concentration of Cu as shown in Table 1. This may be due to the fact that the radius of $Cu^{2+}$ ion is larger than that of $Mn^{3+}$ and $Mn^{4+}$. As a result, the structure shows a large distortion, and the volume of unit cell becomes larger with doping more Cu ions.

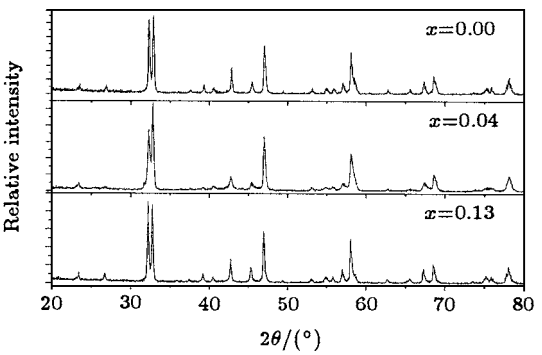



**Fig.1.** XRD patterns of $La_{1.2}Sr_{1.8}Cu_xMn_{(2-x)}O_7$ ($x$=0, 0.04, 0.13).

**Table 1.** Space group, crystal lattice parameters and volume of unit cell of $La_{1.2}Sr_{1.8}Cu_xMn_{(2-x)}O_7$.

| $x$ | space group | $a$/nm | $c$/nm | $c/a$ | $V$/nm$^3$ |
|---|---|---|---|---|---|
| 0.00 | $I_{4/mmm}$ | 0.3864 | 1.9880 | 5.145 | 296.8 |
| 0.04 | $I_{4/mmm}$ | 0.3866 | 1.9913 | 5.151 | 297.6 |
| 0.13 | $I_{4/mmm}$ | 0.3868 | 1.9976 | 5.164 | 298.9 |

### 3.2. Magnetic properties

Magnetization measurements indicate that the ground state of the sample with $x$=0 is ferromagnetic (the result is not shown here), which agrees well with the previous study.[13] With increasing Cu content, the ground state is changed to spin glass or antiferromagnetism as shown in Fig.2. From Fig.2(a), we see that the ZFC magnetization of the sample with $x$=0.04 increases to a cusp with decreasing temperature. Below the cusp, the magnetization decreases with further cooling down to 78K. But FC magnetization increases with the decrease of temperature. Namely, there is a large and clear irreversibility between ZFC and FC magnetizations. The cusp and irreversibility in the magnetization are reminiscence of a spin glass behaviour.[15,16] However, Fig.2 (b) shows that the FC and ZFC magnetizations of the sample with $x$=0.13 almost overlap and have one cusp, indicating that the sample is likely AFM at low temperatures. But further experiments prove that FM and AFM phases coexist in this sample.

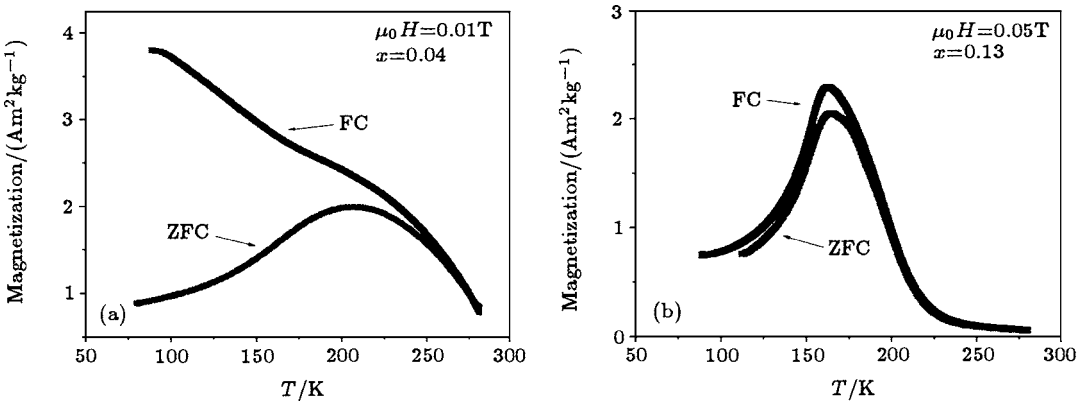



**Fig.2.** Temperature dependence of magnetization of the samples: (a) $x$=0.04 and (b) $x$=0.13 under ZFC and FC (indicated by arrows).

The $M$–$H$ curves of the samples with $x$=0.00, 0.04 and 0.13 are shown in Fig.3. It can be seen that there is an obvious hysteresis loop, and the magnetization tends to saturate at high fields for the sample with $x$=0. This is the typical character of FM. We know that the external field will make the moments arrange parallel to the direction of field though there is spin cluster.[17] So we also observe an evident loop for the sample with $x$=0.04. From the inset in Fig.3, we notice that a visible hysteresis loop is also observed in the sample with $x$=0.13. But the magnetization does not saturate even under high fields, which is the character of AFM.[18] We think that FM and AFM phases may coexist in this sample.

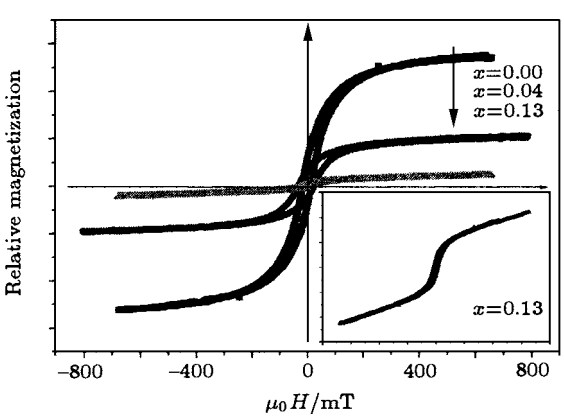



**Fig.3.** Magnetization versus field curves of the samples with $x$=0, 0.04, 0.13 measured at the temperature of liquid nitrogen; the inset is the amplified $M$-$H$ curve of the sample with $x$=0.13.

In order to understand whether AFM and FM phases do coexist in the sample with $x$=0.13, election spin resonance (ESR) spectra of the samples with $x$=0.04 and $x$=0.13 are measured, as shown in Fig.4. From Fig.4(a), we see that the spectra have two cusps in the temperature range from 300 to 220K. When temperature decreases, the left cusp is enhanced and widened, the right one is reduced. It is obvious that the right one corresponds to the paramagnetic line (PL) while the left one corresponds to the ferromagnetic line (FL).[19] And the FL separates from the PL with decreasing temperature. In other words, this sample undergoes a phase separation.[19,20] For the sample with $x$=0.13, the sharp cusp transits gradually from PL to FL at about 200K and the FL cusps retain from 200 to 110K, as shown in Fig.4 (b). Namely, the sample shows FM in this temperature range. But we know that this sample is AFM below 165K from Fig.2(b). It is noticed that a weak cusp appears at low fields below 165K and is enhanced with decreasing temperature. According to the result of magnetic measurement (see Fig.2(b)) and the comparison between Figs.4(a) and 4(b), these weak cusps may be related to the AFM signal. That is to say, this sample owns both FM and AFM phases at low temperatures. We interpret this phenomenon as: when temperature is below 165K, AFM exchange interaction appears and is enhanced with further cooling in the FM background. So ESR spectra show FM phase (see Fig.4(b)) while magnetization of the bulk is reduced, just like that shown in Fig.2(b).

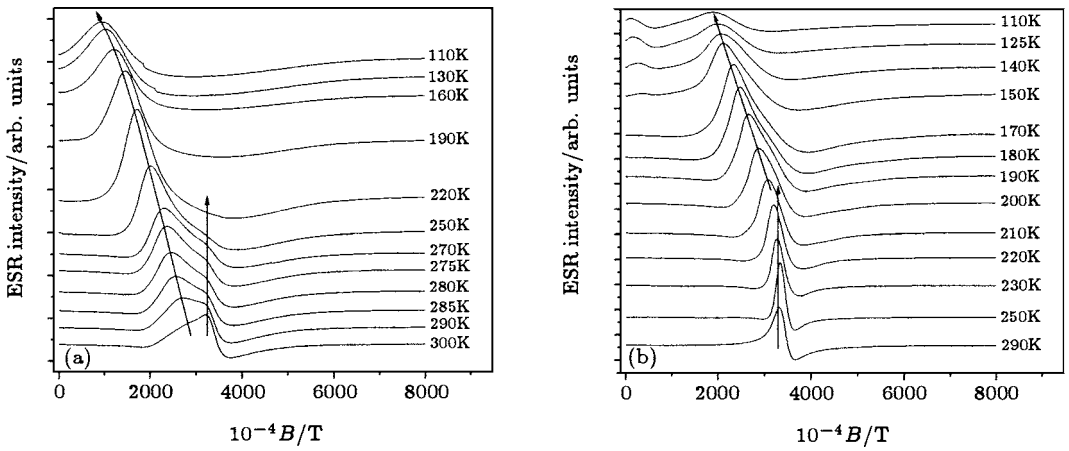



**Fig.4.** ESR spectra of the samples: (a) $x$=0.04 and (b) $x$= 0.13; the arrows are to guide the eyes.

We know that $Mn^{3+}$ and $Mn^{4+}$ co-exist in $Ln_{1-x}A_xMnO_3$ perovskite. Neighbouring $Mn^{3+}$ and $Mn^{4+}$ ions couple each other through O ion by double-exchange or superexchange interaction. The double-exchange always leads to FM while the superexchange induces AFM. The magnetic properties of these samples are controlled by the competition between the two kinds of exchange interactions. If the double-exchange interaction predominates, the sample will exhibit FM. Otherwise, the sample will show AFM. For the undoped parent phase $La_{1.2}Sr_{1.8}Mn_2O_7$, the double-exchange interaction is overwhelming so it shows FM. When Cu ions are introduced into $La_{1.2}Sr_{1.8}Mn_2O_7$, the structure shows a large distortion and part of Mn-O-Mn bonds of intralayer will be interrupted. So the double-exchange interaction is weakened. On the other hand, it will lead to the increasing ratio of $Mn^{4+}/Mn^{3+}$, which also can decrease the double-exchange interaction.[11] As a result, the double-exchange interaction is reduced but the superexchange interaction is enhanced. When the intensity of the two kinds of exchange interactions is equal, spin-glass is formed with increasing content of Cu. With further Cu-doping, the sample will become AFM when the intensity of the superexchange is larger than that of the double-exchange.

### 3.3. Electrical properties

Temperature dependence of resistivity for $La_{1.2}Sr_{1.8}Cu_xMn_{(2-x)}O_7$ at 0 and 5T are shown in Fig.5. We find that the resistivity of the sample with $x$=0 shows a peak with decreasing temperature. It indicates that there is a metal-insulator transition in this sample. And the applied field greatly suppresses the resistivity at low temperatures. For these samples containing Cu, the resistivity rises monotonously with decreasing temperature. The metal-insulator transition disappears, and the value of resistivity augments with increasing content of Cu. All theses samples are insulator or semiconductive at the whole temperature range of the study. Although the resistivity reduces largely when a 5T field is applied, the metal-insulator transition still does not reappear. Data analysis indicates that these samples show CMR effect at low temperatures and the MR increases with decreasing temperature. The maximum of MR reaches 45%. Additionally, the MR is also reduced with increasing content of Cu.

We note that only 2% Cu doping can lead to the large change of electrical properties. The disappearance of the metal-insulator transition and the increase of resistivity result from the Cu doping. In these samples containing Cu, parts of Mn–O–Mn bonds are interrupted and Cu ions cannot effectively participate in the DE process. As a result, DE interaction is weakened and the itineration of $e_g$ electrons decreases. So the resistivity augments and shows semiconductor behaviour in the sample with $x$=0.04. With more Cu doping, DE interaction is further weakened and superexchange interaction appears. Consequently, the sample with $x$=0.13 is insulator in the whole temperature range of observation. On the other hand, the effect of magnetic field on the spin ordering is smaller and smaller, so the MR also decreases.

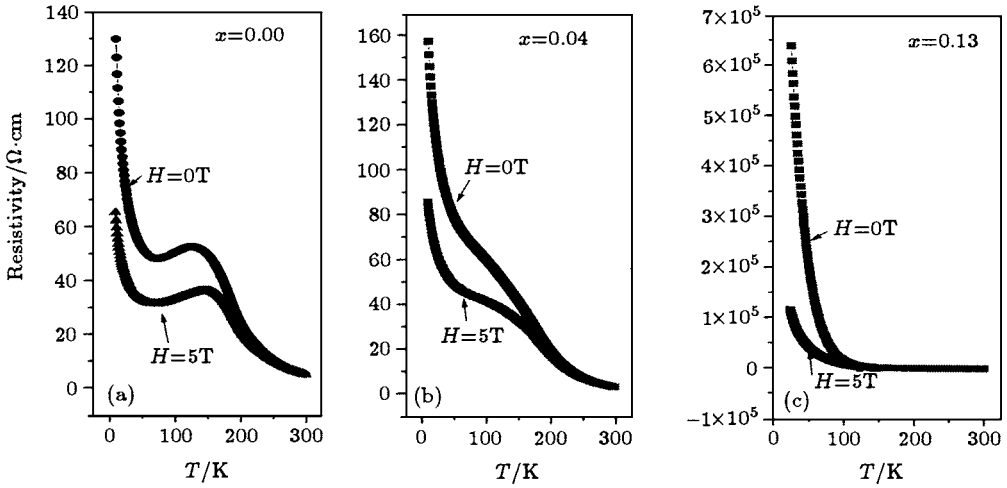



**Fig.5.** Resistivity as a function of temperature under 0 and 5T fields for the samples with (a) $x$=0, (b)$x$=0.04 and (c)$x$=0.13.

# 4. Conclusion

Single-phase polycrystalline samples $La_{1.2}Sr_{1.8}Cu_x Mn_{(2-x)}O_7$ ($x$=0, 0.04, 0.13) have been synthesized by the traditional solid state reaction method. We find that the effect of Cu on the magnetic and electrical properties is remarkable. Magnetic measurements show that with increasing content of Cu, the system undergoes a transition from long- range ferromagnetic order to spin-glass state and further to antiferromagnetic order. Meanwhile, the metal–insulator transition disappears for these samples containing Cu. The behaviour is semiconducting or insulative in the whole observation temperature range. We believe that it is due to the weakening of double-exchange interaction caused by Cu doping. In addition, the system shows CMR at low temperatures and the MR decreases with increasing content of Cu.

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