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Abstract. The magnetic and transport properties of layered manganese oxides La$_{1.2}$Sr$_{1.8}$Mn$_{2-x}$T$_x$O$_7$ (T = Fe, Co, Cr) are reported. The undoped oxide La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ is ferromagnetic (FM) below 125 K where an insulating–metallic (I–M) transition occurs. Fe and Co doping have similar effects on the properties of La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$, resulting in quick weakening of FM ordering, occurrence of a cluster-glass or spin-glass state for $x > 0.07$, immediate disappearance of the I–M transition and enhancement of low-temperature magnetoresistance. But a different effect is observed for Cr doping. In La$_{1.2}$Sr$_{1.8}$Mn$_{2-x}$Cr$_x$O$_7$, although the I–M transition also disappears quickly, FM ordering is maintained even for $x = 0.5$. These doping effects could be understood by considering the different exchange interactions between Mn and T (Fe, Co, Cr) and the corresponding change of the double-exchange interaction in La$_{1.2}$Sr$_{1.8}$Mn$_{2-x}$T$_x$O$_7$.

(Some figures in this article appear in colour in the electronic version; see www.iop.org)

1. Introduction

The colossal magnetoresistance (CMR) effect has attracted extensive research interest from both scientific and technical fields. The best known CMR material is the mixed valence manganese oxide with ABO$_3$-type perovskite structure, R$_{1-x}$M$_x$MnO$_3$, where R is a trivalent rare-earth element and M is a bivalent alkaline-earth metal. The perovskite oxides show ferromagnetic (FM) and metallic state below the Curie temperature T_C, around which resistivity decreases by several orders under application of a field, resulting in the CMR effect. These properties could be well interpreted in the light of the double-exchange (DE) interaction mechanism [1, 2], according to which the DE interaction between Mn^{3+} and Mn^{4+} gives rise to the simultaneous presence of FM and metallic behaviour. One way to monitor the DE interaction is the substitution at (R, M) sites, which leads to the variation of Mn^{4+}/Mn^{3+} ratio x (i.e., the carrier concentration) and the lattice effect (Jahn–Teller effect) due to the change of A-site size. Another way is the transition metal doping at Mn sites, the centre of the DE process, which directly influences the DE interaction and then the properties. Some previous reports [3–6] have shown that replacing Mn by Fe or Co in the perovskite oxides hampers the electron hopping, and suppresses the DE interaction and thus the FM metallic state. In fact, these substitutions result in the changing of the band structure (the band filling and bandwidth) and then the properties of the oxides.

    Besides the ABO$_3$-type perovskite manganese oxides, the manganese oxides with layered perovskite structure also show the CMR effect [7–9]. This layered oxide, R$_{2-2x}$M$_{1+2x}$Mn$_2$O$_7$,

is the $n = 2$ member of the Ruddlesden–Popper (RP) series phase $A_{n+1}B_nO_{3n+1}$ [10], and shows very different properties compared with the ABO_3-type oxide, the $n = \infty$ end member of the RP phase. The structure of the layered oxides can be considered as a stacking of $(R, M)MnO_3$ perovskite bilayers intercalated by insulating $(R, M)O$ rock-salt layers. Due to the intrinsic quasi-two-dimensional layered structure and Mn–O–Mn networks, the exchange interaction between the bilayers is much weaker than that inside the bilayers. The anisotropic exchange interactions are responsible for some interesting magnetic and transport properties observed in the layered oxides. We have studied the Fe doping effect in $La_{1.2}Sr_{1.8}Mn_2O_7$, and found that compared with the ABO_3-type oxides, the FM metallic state is more 'fragile' in the layered oxide [11]. But Cr doping [12] results in some different effect. Here in this paper we compare the difference among the effect of Fe, Co, Cr doping on the magnetic and transport properties in $La_{1.2}Sr_{1.8}Mn_2O_7$. Selecting Fe, Co, Cr as the doping elements could reduce the lattice effect to the smallest extent, due to their similar ion sizes to Mn ions [13].

2. Experiment

Bulk samples of $La_{1.2}Sr_{1.8}Mn_{2-x}T_xO_7$ ($x = 0$–0.2 for T = Fe, Co; $x = 0$–0.5 for T = Cr) were prepared by a standard ceramic process. Stoichiometric amounts of La_2O_3, $SrCO_3$, $MnCO_3$, and Fe_2O_3 or Co_2O_3 or Cr_2O_3 were mixed, ground and calcined at $1000\,^\circ C$ for 24 h in air. The powders were well ground again, then pelletized and sintered at $1250\,^\circ C$ for 48 h with an intermediate grinding. The samples were characterized by x-ray diffraction on a Rigaku diffractometer using Cu Kα radiation, and the XRD profiles were refined by a Rietveld program. Magnetization measurements were carried out using a SQUID magnetometer (Quantum Design) and an extracting sample magnetometer, and resistivities ρ were measured by a standard four-probe method.

3. Results and discussion

The XRD measurements and the structure refinements show that all the prepared samples of $La_{1.2}Sr_{1.8}Mn_{2-x}T_xO_7$ (T = Fe, Co and Cr) are of single phase with $Sr_3Ti_2O_7$-type tetragonal structure ($I4/mmm$). The calculated lattice parameters are plotted in figure 1 for the three series of samples. For the case of Cr and Co doping, with x increasing, a decreases slightly but c increases apparently. For the Fe-doped samples, with x increasing, a almost remains stable and c increases slightly, which is consistent with the fact that Fe^{3+} and Mn^{3+} ions have almost identical sizes [13].

The temperature dependence of magnetization measured at 0.1 T for $La_{1.2}Sr_{1.8}Mn_{2-x}T_xO_7$ (T = Co, Cr) are shown in figure 2. A detailed description of the properties of the Fe-doped samples has been reported in [11]. Fe doping results in the quick weakening of FM ordering and the appearance of a low-temperature spin-glass state. Co doping has a similar effect, but the weakening speed of the FM ordering is much slower than that in the case of Fe doping. The FM transition temperature T_C of the Co-doped samples decreases with x increasing (also shown in figure 3(a)) in the low doping range. As $x > 0.07$, the discrepancy of the zero-field cooling (ZFC) magnetization and field cooling (FC) magnetization below a certain temperature (which is defined here as the freezing point) is observed, indicating that the spin-glass state probably occurs. In spite of the presence of the low-temperature spin-glass state, there is still an apparent FM transition above the freezing point, just as observed in the case of Fe doping [11] with $x = 0.07$ and 0.10. T_C as function of the doping concentration x is shown in figure 3(a) for the Fe- and Co-doped samples. At a low doping level of $x \leqslant 0.03$, with x
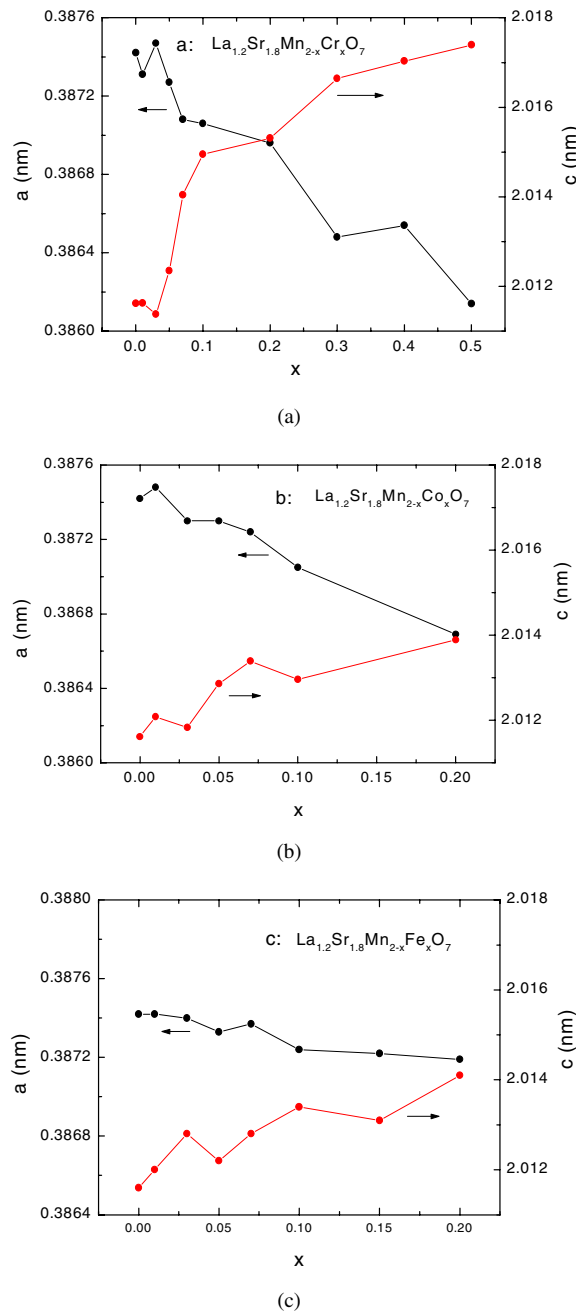
(a)

(b)

(c)

Figure 1. Lattice parameters as a function of x in $La_{1.2}Sr_{1.8}Mn_{2-x}T_xO_7$, (a) T = Cr; (b) T = Co; (c) T = Fe.

increasing T_C decreases almost synchronously for both Fe and Co doping, but as $x > 0.03$, Fe doping reduces T_C more quickly. However, the Cr doping has such a weak influence on the FM ordering that the Cr-doped sample with $x = 0.5$ still shows strong ferromagnetism (as shown in figure 2). Figure 3(b) plots the x dependence of T_C for the Cr-doped samples, as well as another magnetic transition temperature T^*, which is attributed to the two-dimensional
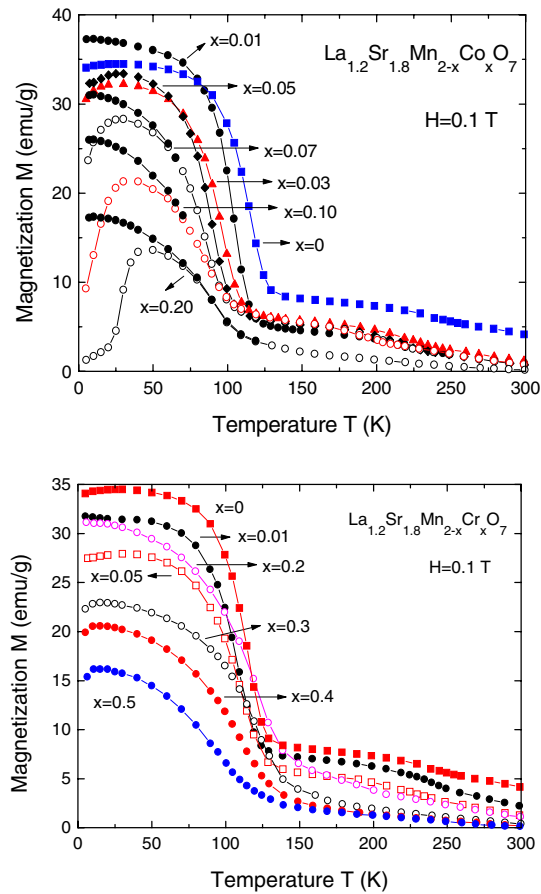
Figure 2. Temperature dependence of magnetization for $La_{1.2}Sr_{1.8}Mn_{2-x}T_xO_7$ measured at 0.1 T. From top to bottom, T = Co and Cr.

magnetic transition above T_C [11, 14] and observed only as $x \leqslant 0.10$. With Mn being replaced by Cr, T_C initially decreases from 125 K ($x = 0$) to 109 K ($x = 0.01$–0.05), then increases to 119 K ($x = 0.1$–0.3), and finally decreases again to 100 K ($x = 0.5$). T^* decreases from 245 K to 219 K as x increases from 0 to 0.10, with almost no change as $x = 0.03$–0.07.

The different effects of these dopings on magnetic properties can also be revealed by their field dependence of magnetization. As reported in [11], the Fe-doped samples with $x > 0.07$ show no spontaneous magnetization, which has also been confirmed by the Arrot plot (not shown). The field dependences of magnetization at 5 K for the Co- and Cr-doped samples are shown in figure 4. For the Co-doped samples, the FM feature persists to $x = 0.10$, suggesting that for $x = 0.07$ and 0.10, the spin-glass state is of cluster-glass type and the low-temperature magnetization derives from the FM clusters. Even for the $x = 0.20$ sample which has no spontaneous magnetization and shows a characteristic S-type M–H curve of the spin-glass state, the high-field magnetization is fairly high and tends to saturation. All of the Cr-doped samples show strong FM ordering, but the saturation magnetization decreases as Cr content increases, which may be attributed to the relatively smaller moment of Cr^{3+} than that of Mn^{3+} and the spin canting of Mn^{3+} or Cr^{3+} moments due to the weakening of FM ordering. It is
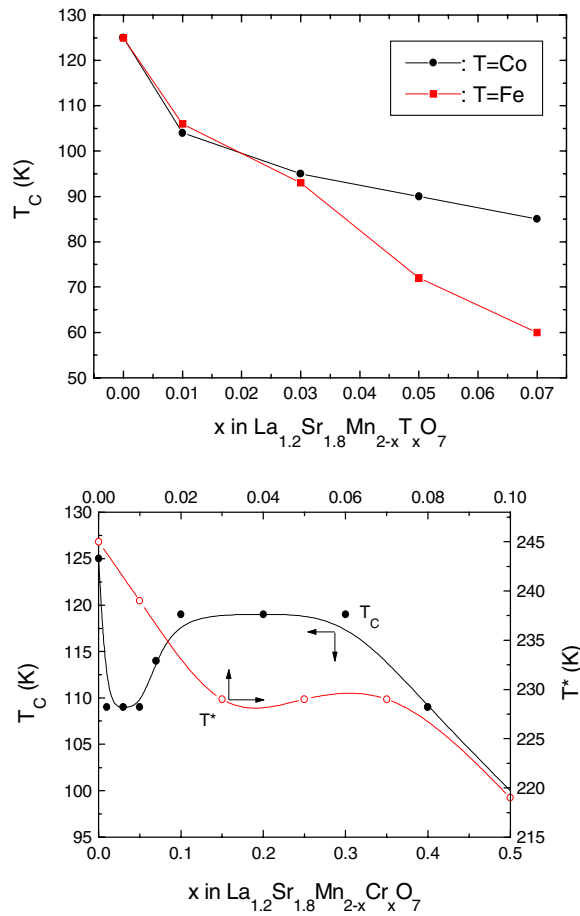
Figure 3. T_C as a function of x in La$_{1.2}$Sr$_{1.8}$Mn$_{2-x}$T$_x$O$_7$. Top, T = Fe and Co; bottom, T = Cr, T^* is also plotted. Magnetic transition temperature T_C and T^* are defined here as the temperatures where $-\mathrm{d}M/\mathrm{d}T$ is maximum.

obvious that among the three transition metals, Cr doping has the smallest effect on the FM ordering of La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$.

The effect of Co doping on transport properties is also similar to the Fe doping effect, as shown in figure 5 as an example, in which the resistivities ρ at zero field and 6 T and the produced MR are plotted for La$_{1.2}$Sr$_{1.8}$Mn$_{2-x}$T$_x$O$_7$ (T = Fe and Co, $x = 0.07$). In the Co-doped samples, the insulating–metallic (I–M) transition observed for the undoped La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ [11, 14] disappears even at such a low doping level as $x = 0.01$ (see figure 6), and so does the MR peak locating around the I–M transition temperature T_{IM}, but the low-temperature MR effect is enhanced. In the ρ–T curve, there is only a change of slope at about 70 K, which is much lower than the corresponding magnetic transition temperature $T_C \sim 105$ K, showing no direct correlation between magnetic and transport behaviour. The low-temperature MR (MR $= (\rho_0 - \rho_{6T})/\rho_0$) increases from $\sim$65% ($x = 0$) [11] to about 85% for $x = 0.01$, then decreases to about 70% for $x > 0.01$. This is different from the Fe doping effect [11] which enhances the low-temperature MR effect strongly and monotonically. The electronic conduction at high temperature above 150 K is dominated by thermally activated behaviour for all Fe- and Co-doped samples, with higher activation energy E for Fe doping than Co
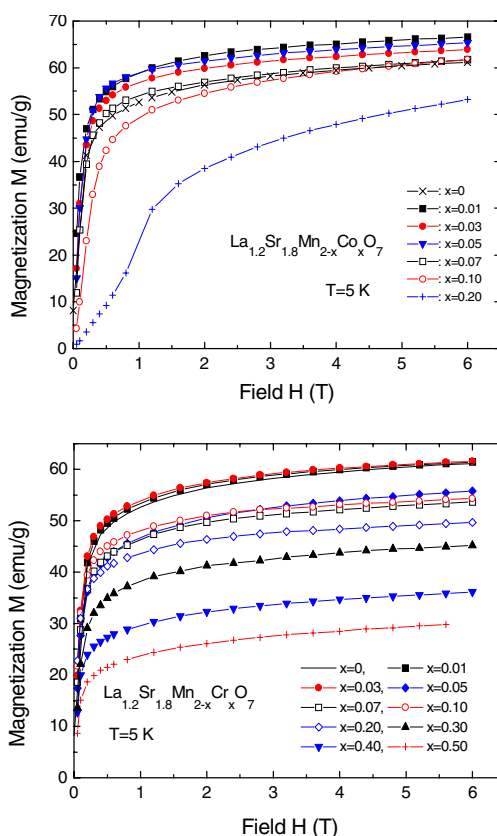
Figure 4. Field dependence of magnetization at 5 K for $La_{1.2}Sr_{1.8}Mn_{2-x}T_xO_7$ (T = Co and Cr).

doping. For example, $E_{0.03}$ ($x = 0.03$) and $E_{0.07}$ ($x = 0.07$) is 114.32 meV and 117.61 meV for Fe-doped samples, and 92.17 meV and 107.34 meV for Co-doped samples, respectively.

For the Cr-doped samples, one may expect that the I–M transition should be observed due to their strong FM ordering. But the transport measurement data shown in figure 7 exhibit anomalous results. The I–M transition is still present for the $x = 0.01$ sample, with $T_{IM} \sim 70$ K lower than its $T_C \sim 109$ K. Following a slight drop below T_{IM}, the resistivity increases again on cooling below 40 K, showing reemergence of insulating-like behaviour. Under 6 T field, T_{IM} shifts to 100 K and the resistivity is reduced, resulting in a large MR ratio (larger than 70%) below 50 K with no MR peak. This low-temperature MR effect is similar to that observed in the Fe- and Co-doped samples. But for the sample with $x = 0.1$, the I–M transition disappears and only a slope change occurs at about 70 K, although the sample is ferromagnetic. As x increases to 0.4, insulating behaviour is observed in the whole measuring temperature range below 300 K. With x increasing, the low-temperature MR ratio almost remains stable and no obvious MR enhancement is observed, which is different from Fe and Co doping. Therefore, it could be concluded that all of the Fe, Co and Cr doping reduce the itinerancy and increase the localization of carriers in $La_{1.2}Sr_{1.8}Mn_{2-x}T_xO_7$, and the doping effect on their transport properties becomes more and more intense in the sequence of T = Cr, Co and Fe, just like that on their magnetic properties.

The doped transition metals Cr, Fe and Co are the neighbours of Mn in the periodic table of the elements. It is generally believed that in the manganese oxides with perovskite or layered
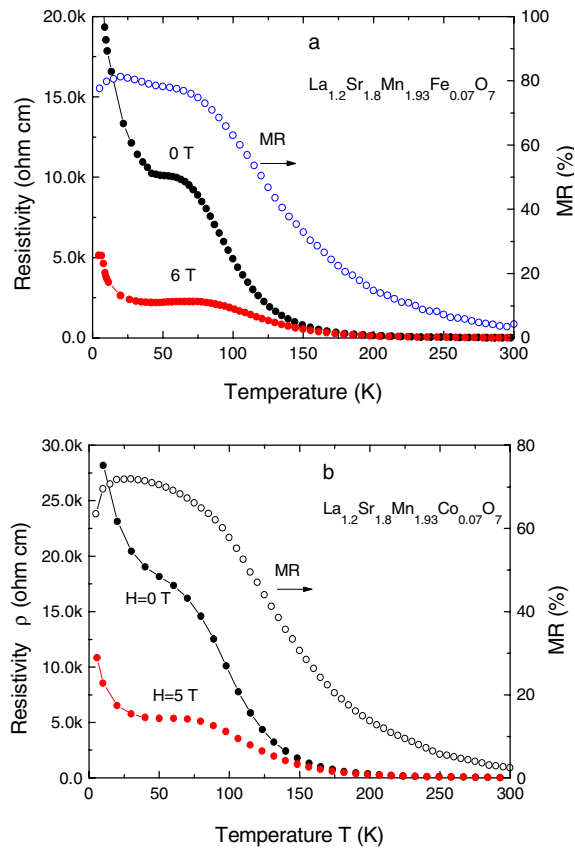
Figure 5. Resistivities ρ at zero field and 6 T and the produced MR for La$_{1.2}$Sr$_{1.8}$Mn$_{2-x}$T$_x$O$_7$ with $x = 0.07$. (a) T = Fe; (b) T = Co.
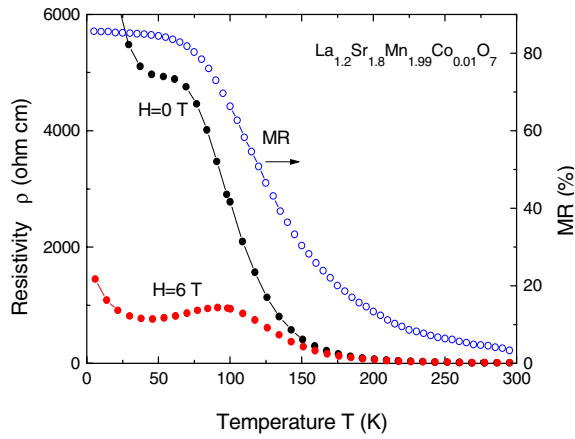
Figure 6. Resistivities ρ at zero field and 6 T and the produced MR for La$_{1.2}$Sr$_{1.8}$Mn$_{1.99}$Co$_{0.01}$O$_7$ ($x = 0.01$).

perovskite structure, these elements exist in the form of Cr^{3+}, Mn^{3+}, Mn^{4+}, Fe^{3+}, Co^{3+} and Co^{4+}. Their electronic configurations are Cr^{3+}: t$_{2g}^3$ ($S = 3/2$), Mn^{3+}: t$_{2g}^3$e$_g^1$ ($S = 2$), Mn^{4+}: t$_{2g}^3$
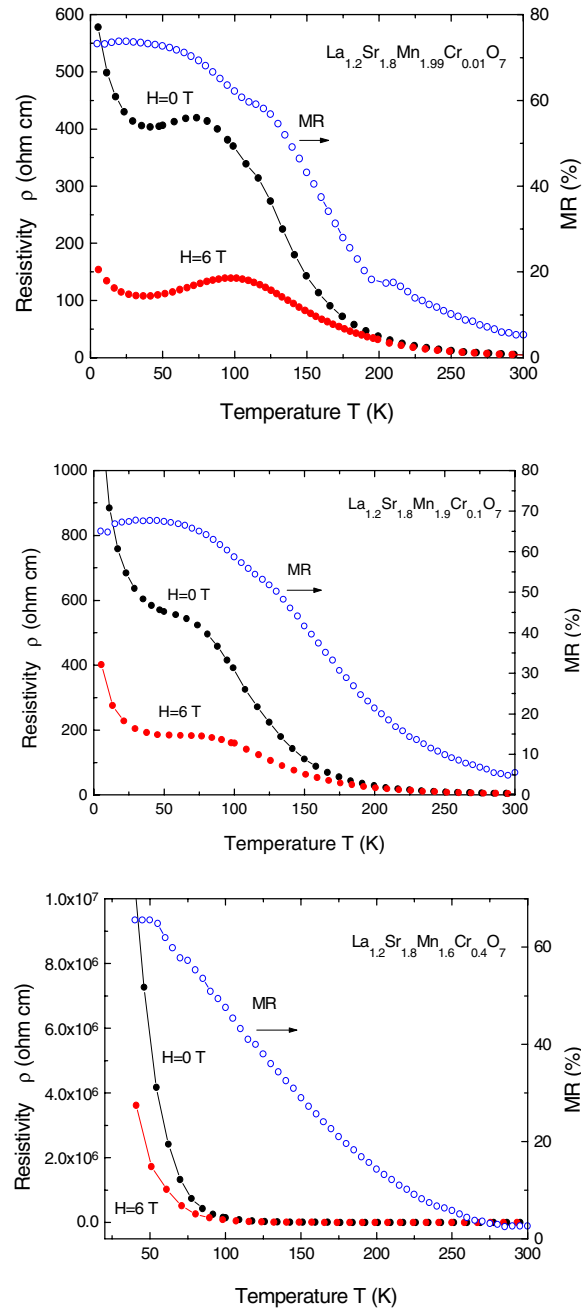
Figure 7. Resistivities ρ at zero field and 6 T and the produced MR for $La_{1.2}Sr_{1.8}Mn_{2-x}Cr_xO_7$. From top to bottom: $x = 0.01, 0.1, 0.4$.

$(S = 3/2)$, Fe^{3+}: $t_{2g}^3 e_g^2$ $(S = 5/2)$, Co^{III}: t_{2g}^6 $(S = 0$, low spin$)$, Co^{3+}: $t_{2g}^4 e_g^2$ $(S = 2$, high spin$)$, Co^{IV}: t_{2g}^5 $(S = 1/2$, low spin$)$, and Co^{4+}: $t_{2g}^3 e_g^2$ $(S = 5/2$, high spin$)$, respectively. The doped Fe^{3+} ions directly replace Mn^{3+}, so Fe doping reduces Mn^{3+} amount and the concentration of carriers. In addition, the doped Fe^{3+} ions do not join the DE process, hampering the

DE interaction and reducing the available sites for electron hopping. These effects result in quick weakening of FM ordering and carrier localization. The quasi-two-dimensional Mn–O–Mn network of the layered oxides is more sensitive to Fe doping than the three-dimensional network in ABO$_3$-type oxides. So Fe doping easily destroys the FM metallic state; especially the I–M transition is removed by a very low Fe doping. With the weakening of the FM DE interaction, the antiferromagnetic (AFM) super-exchange interaction becomes stronger, and the competition between the two interactions results in the spin-glass state and spin canting [11].

Similar to the Fe-doping case, the doped Co ions destroy the Mn–O–Mn network and the DE interaction between Mn ions. So Co doping has similar effect on the magnetic and transport properties to Fe doping. But there is still some difference between the two cases. The influence of Co ions on exchange interaction must be more complicated. Although some researchers argue that Co^{2+} is present in the perovskite oxides, it is more generally agreed that Co ions are in the form of Co^{3+} and Co^{4+}. In manganese oxides, since the Hund coupling energy is higher than the crystal-field splitting energy, the stable state of Mn ions is the high-spin state. But in cobalt oxides the two kinds of energy are comparable, resulting in the coexistence of high-spin and low-spin states and the transition between the two states [6, 15]. This transition will have a complex influence on the properties of the oxides. Some previous studies on perovskite cobalt oxides [15–17] showed that there are AFM exchange interactions between the Co ions with the same valence, and FM exchange interactions between the Co ions with different valence (between Co^{4+} and Co^{3+}, or Co^{IV} and Co^{3+}). In some cobalt oxides such as La$_{1-x}$Sr$_x$CoO$_3$, the FM metallic state is considered to result from the mix-valence of Co ions, just as in the well known ABO$_3$-type manganese oxides. But there are still controversies about whether the exchange interaction between Co^{4+} and Co^{3+} or Co^{IV} and Co^{3+} is controlled by the DE mechanism. The absence of a half-filled t$_{2g}$ orbital in Co ions weakens the coupling interaction between carriers and local spins due to the Hund rule, and arouses doubt about the presence of DE interaction between Co ions. It is suggested that in cobalt oxides the FM ordering is of short range and results from FM clusters, and the common ground states are the spin-glass state and the cluster-glass state, indicating that the FM interaction between Co ions is weak. These behaviours mentioned above must also be present in the Co-doped layered oxides. So, besides the doping effect similar to Fe doping, the FM interaction between Co ions will slow down the weakening of FM ordering of La$_{1.2}$Sr$_{1.8}$Mn$_{2-x}$Co$_x$O$_7$, although the FM interaction is of short range. But the short-range interaction does not contribute to electronic conduction, resulting in almost the same transport behaviour in the Co- and Fe-doped samples.

However, Cr doping is very different from Fe and Co doping. The doped Cr ions replace Mn^{3+} in the form of Cr^{3+}. Cr^{3+} has the same electronic configuration (t$_{2g}^3$) as Mn^{4+}, so that there should be FM DE interaction between Cr^{3+} and Mn^{3+} just as between Mn^{4+} and Mn^{3+}. This proposal has been proved by some experimental results [18, 19], and is consistent with our observation of magnetization behaviour in La$_{1.2}$Sr$_{1.8}$Mn$_{2-x}$Cr$_x$O$_7$, i.e., the FM ordering in the high Cr-doped sample ($x = 0.5$) suggests that doped Cr ions have FM interaction with Mn ions. With Cr^{3+} doping, Mn^{3+}/Mn^{4+} decreases (Cr^{3+} acts as Mn^{4+}), and FM interaction becomes weaker, resulting in the decrease of T_C and magnetization. But the complex doping (x) dependence of T_C is not easy to understand. It was suggested by Gundakaram *et al* [12] that with increasing Cr, there is an increase in the interaction across the bilayers, i.e., an increase in three-dimensional interaction, which will lead us to consider the possible anisotropic doping effect on the exchange interactions inside or outside the bilayers. Another interesting observation is the quick disappearance of metallic conduction in an FM samples, giving rise to FM insulating state below T_C. This phenomenon is also present in the Fe- and Co-doped samples, and reflects that the transport behaviours are more sensitive to Mn-site substitution than magnetic properties in the layered oxides.

4. Conclusions

We have investigated and compared the Mn-site doping effect by Fe, Co and Cr on the magnetic and transport properties in $La_{1.2}Sr_{1.8}Mn_2O_7$. Fe and Co doping have similar effects, which hamper the FM DE interaction between Mn^{3+} and Mn^{4+}, and increase the localization of carriers, resulting in quick disappearance of FM ordering and immediate disappearance of the I–M transition. But the magnetic property is more sensitive to Fe doping. However, Cr doping shows different effects. Although the metallic conducting state is also fragile to Cr doping, the FM ordering survives up to a high doping level ($x = 0.5$) in $La_{1.2}Sr_{1.8}Mn_{2-x}Cr_xO_7$, with complicated variation of T_C. The difference among Fe, Co and Cr doping effects is considered to be related to the electronic configurations of these doped ions and the exchange interaction between these ions and Mn ions.

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