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Study of the colossal magnetoresistance properties of the compound $\text{La}_{1-x}\text{Sr}_x\text{A}_y\text{Mn}_{1-y}\text{O}_3$ ($\text{A} = \text{Cr, Re}$)

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Abstract. We report on the variation of the magnetoresistance property of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ whose Mn sites are doped with chromium and rhenium. Two different series of compounds of the formula $\text{La}_{0.7}\text{Sr}_{0.3}\text{Cr}_y\text{Mn}_{1-y}\text{O}_3$ ($y = 0.05, 0.10, 0.15, 0.20, 0.30, 0.40$ and 0.50) and $\text{La}_{1-x}\text{Sr}_x\text{Re}_{0.10}\text{Mn}_{0.90}\text{O}_3$ ($x = 0.12, 0.20$ and 0.30) are prepared. A detailed study has been carried out to determine the structural, magnetic and transport properties of the chromium and rhenium doped compounds using the x-ray diffraction, dc magnetic susceptibility, four probe method for electrical resistance and magnetoresistance measurement techniques. X-ray diffraction shows the formation of a homogeneous compound with the rhombohedral ($R-3c$ space group) structure within the Cr concentration of $0.05 < y < 0.15$ for the $\text{La}_{0.7}\text{Sr}_{0.3}\text{Cr}_y\text{Mn}_{1-y}\text{O}_3$ and $0.12 < x < 0.30$ for the $\text{La}_{1-x}\text{Sr}_x\text{Re}_{0.10}\text{Mn}_{0.90}\text{O}_3$ compounds. The magnetization, magnetic transition temperature and the metal–insulator transition temperature decrease due to the Cr (Re) substitution. The magnetization curves broaden and the overall resistivity of the compounds increases with increasing Cr or decreasing Sr content except for the $\text{La}_{0.88}\text{Sr}_{0.12}\text{Re}_{0.10}\text{Mn}_{0.90}\text{O}_3$ compound, whose resistivity decreases and which shows metallic behaviour below the transition temperature. The resistivity and the magnetization show a scaling dependence on each other. It is shown that the variation in the magnetic and transport properties of the substituted compounds can be ascribed to a compositional dependence of the Mn^{3+} – Mn^{4+} ferromagnetic interaction as a result of the antiferromagnetic interaction of Cr^{3+} – O – Cr^{3+} ions and to the distortion of the crystal lattice. The magnetoresistance shows an increasing trend due to the increased resistivity of the compounds and is explained on the basis of percolation of the charge carriers through the ferromagnetic clusters present in the insulating antiferromagnetic compounds and scattering effect at the grain boundaries.

1. Introduction

The manganite perovskites of the form $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ ($\text{R} = \text{rare earth}$, $\text{A} = \text{divalent cation}$) are a subject of extensive study because of the phenomenon of colossal magnetoresistance that can be very helpful for technological applications [1]. The structure of these compounds is based on the structure of the parent compound LaMnO_3 , which is orthorhombic and antiferromagnetic [2, 3]. These compounds are the three dimensional limit of the Ruddlesden–Popper series of layered compounds and are represented by $(\text{La}_{1-x}\text{A}_x)_{n+1}\text{Mn}_n\text{O}_{3n+1}$, where n is the number of connected layers of vertex sharing MnO_6 octahedra [4]. For certain values of the concentration, x , of the divalent cation, the compounds exhibit a paramagnetic to ferromagnetic transition at a Curie temperature, T_C . Also associated with it is an insulator–metal transition at a temperature slightly lower than the T_C . Usually the compounds show metallic behaviour in the ferromagnetic region and insulator-like behaviour in the paramagnetic region. Both these phenomena are traditionally explained on the basis of the double exchange

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interaction mechanism [5]. When the parent compound LaMnO_3 is doped by a divalent cation, a portion of Mn^{3+} changes to Mn^{4+} . In such an $\text{Mn}^{3+}\text{--Mn}^{4+}$ system the coupling takes place indirectly through the oxygen ion and the exchange integral is non-vanishing only if the spins of the two d shells are parallel. This lining up of the spins of Mn ions is accompanied by an increased rate of migration of the holes created by the Mn^{4+} ions, thus the overall conductivity of the system increases. As the temperature is lowered the thermally induced spin fluctuations decrease; the total itinerant and local moments align themselves so that the total energy is lowered and the itinerant carriers gain kinetic energy.

The double exchange interaction gives a very high value of T_C as compared to the experimental value and to account for this discrepancy a Jahn–Teller type distortion is considered. Studies by Millis *et al* [6] suggest that for a large electron–phonon interaction the energy is minimized by a distortion so that the e_g electrons of the Mn^{3+} ion are trapped locally in the form of lattice polarons. The existence of a strong electron–phonon coupling can be seen from other experimental results such as the Debye–Waller factor [7] and isotopic substitution T_C shift [8]. The results of thermal conductivity measurements also suggest the existence of strong electron–phonon coupling [9]. The colossal magnetoresistance (CMR) property also depends on the Mn–O–Mn bond angle and on the average radius (r_A) of the divalent cation [10, 11]. There also exists a critical average size of the interpolated cation below which the CMR property cannot be observed [12].

The magnetic and electronic properties of the CMR compounds depend strongly on the Mn valency states, ratio of Mn^{3+} and Mn^{4+} content, electronic configuration and lattice distortion. In Mn^{4+} the lack of an electron in the e_g shell is manifested in the form of a hole that acts as the charge carrier. The Mn provides the effective spins and the local Jahn–Teller distortion. Replacement of Mn by some other element will result in a change of Mn ion density giving rise to a change in the ferromagnetic interaction between the Mn ions and changing the localization effects. The size difference of the substituted element may give rise to a distortion in the lattice and also to a change in the Mn d and O 2p orbital overlap because of the change in the Mn–O–Mn bond angle. The effects of replacing Mn by Al, Ga and Cr have been reported [13–16] and the results show that the CMR properties do change if the Mn sites are substituted. While [15] explains the change in the CMR property by considering the defects in the structure and change in oxygen stoichiometry, [16] explains the results in terms of orbital ordering of the Mn e_g orbitals that causes change in the electrical transport properties.

In this paper we report the study of the magnetic and CMR properties of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Cr}_y\text{Mn}_{1-y}\text{O}_3$ ($y = 0.05\text{--}0.50$) and $\text{La}_{1-x}\text{Sr}_x\text{Re}_{0.10}\text{Mn}_{0.95}\text{O}_3$ ($x = 0\text{--}0.30$). The aim of the study is to ascertain the regularities in the variation in CMR and magnetic characteristic as function of the Cr and Re concentration. We have chosen the parent compound to be $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ in the Cr substitution case as it is reported that the CMR is most pronounced at 30% strontium concentration [3]. The $\text{Mn}^{3+}\text{--O--Mn}^{3+}$ interaction as well as the $\text{Mn}^{4+}\text{--O--Mn}^{4+}$ interaction is antiferromagnetic but the $\text{Mn}^{3+}\text{--O--Mn}^{4+}$ interaction is ferromagnetic. Also the $\text{Mn}^{3+}\text{--O--Cr}^{3+}$ interaction is ferromagnetic but the $\text{Cr}^{3+}\text{--O--Cr}^{3+}$ interaction is antiferromagnetic [17]. For lower concentrations of Cr doping we can reasonably assume that Cr^{3+} goes into the Mn^{3+} sites thereby changing the Mn^{3+} density without large distortion of the crystal cell. Also Cr has the same t_{2g} electronic configuration as Mn^{4+} . We may therefore expect that electronically Cr behave similarly to Mn^{4+} . This means that in the $\text{Cr}^{3+}\text{--O--Mn}^{4+}$ interaction Cr^{3+} plays the role of Mn^{3+} but with the electronic configuration of Mn^{4+} . We therefore expect to see a change in the magnetic and transport properties of the $\text{La}_{0.7}\text{Sr}_{0.3}\text{Cr}_y\text{Mn}_{1-y}\text{O}_3$ system caused by variation of the d–d exchange interaction. Rhenium, on the other hand, is in the same group as manganese, but has no magnetic moment and a much larger atomic radius. Even a small amount of rhenium is expected to result in a large lattice

distortion. Thus we want to study the change in the CMR property by destabilizing the Mn sub-lattice.

2. Experimental procedure

Ceramic polycrystalline samples of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Cr}_y\text{Mn}_{1-y}\text{O}_3$ ($y = 0.05, 0.10, 0.15, 0.20, 0.3, 0.4$ and 0.5) were prepared using the conventional solid-state reaction method. Stoichiometric amounts of La_2O_3 , SrCO_3 , Cr_2O_3 , and MnO_2 powder were thoroughly mixed and then heated to 1000°C for 12 hours in air for decarbonation. The samples were then reground, pressed into pellets and sintered in air at 1400°C for 36 hours with intermediate grindings. A similar procedure was followed to prepare the $\text{La}_{1-x}\text{Sr}_x\text{Re}_{0.10}\text{Mn}_{0.95}\text{O}_3$ ($x = 0.12, 0.20$ and 0.30) compounds using La_2O_3 , SrCO_3 , ReO_2 , and MnO_2 powders. The samples were then cut into suitable pieces for magnetization measurements and resistivity measurements with a low speed diamond wheel. X-ray diffraction (XRD) of the samples was carried out at room temperature in a Rigaku diffractometer in the 2θ range of 20 – 85 degrees. The data so obtained were analysed using the Rietveld method of analysis. The magnetization measurements were carried out with a Quantum Design SQUID magnetometer in the temperature region of 5 – 400 K. All the measurements were performed at 0.1 T. The samples were zero field cooled from room temperature to 5 K and the data were taken with an increasing temperature. The transition temperatures are taken as the maxima of dM/dT versus temperature curves. The electrical resistivity and the magnetoresistance were measured using the standard four probe method and employing the SQUID in the temperature range of 5 – 400 K and in the field interval of -5.5 to 5.5 T. The magnetoresistance measurements were performed 20 K below T_C and the magnetic field was applied parallel to the length of the sample.

3. Results and discussion

The x-ray diffraction measurements for the compounds show that the compounds are in single phase. The crystal structure for the compound $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ was found to be rhombohedral in the space group $R-3c$. Lattice parameters were found to be $a = 5.480 \text{ \AA}$ and $c = 13.530 \text{ \AA}$ and are close to the reported values [18]. Although we have not explicitly determined the oxygen stoichiometry but on account of the close agreements of our result with [18] we consider our composition to be reasonably correct. The pristine compound LaMnO_3 is orthorhombic while $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ is rhombohedral in structure. This structural transition is due to the introduced divalent cation that causes the Mn–O–Mn bond angle to deviate from 180° . Such deviation is also the reason for the structure not being ideal cubic. The x-ray diffraction results of the compounds $\text{La}_{0.7}\text{Sr}_{0.3}\text{Cr}_{0.5}\text{Mn}_{0.95}\text{O}_3$ and $\text{La}_{1-x}\text{Sr}_x\text{Re}_{0.10}\text{Mn}_{0.95}\text{O}_3$ are shown in figures 1(a) and (b). For both the compounds the structure was indexed as rhombohedral in the space group $R-3c$. The lattice parameters are $a = 5.505 \text{ \AA}$ and $c = 13.359 \text{ \AA}$ for the Cr doped compound and $a = 5.511 \text{ \AA}$ and $c = 13.362 \text{ \AA}$ for the Re doped compound respectively. Analysis of the data for the compound $\text{La}_{0.7}\text{Sr}_{0.3}\text{Cr}_y\text{Mn}_{1-y}\text{O}_3$ reveals that as Cr concentration increases the indexing of the structure in the $R-3c$ space group become more difficult. We have found that at an intermediate Cr content (≈ 10 – 30%) the fit of the XRD data is much better if we consider the phase to be orthorhombic rather than rhombohedral. Since LaCrO_3 is antiferromagnetic and orthorhombic, we believe that as the Cr content is increased there is a gradual shift of the structure from the rhombohedral to orthorhombic phase. At an intermediate concentration the structure becomes complicated with contribution from both $R-3c$ and $Pbnm$ space groups. In the case of the Re doped compound there is a volume expansion in the lattice

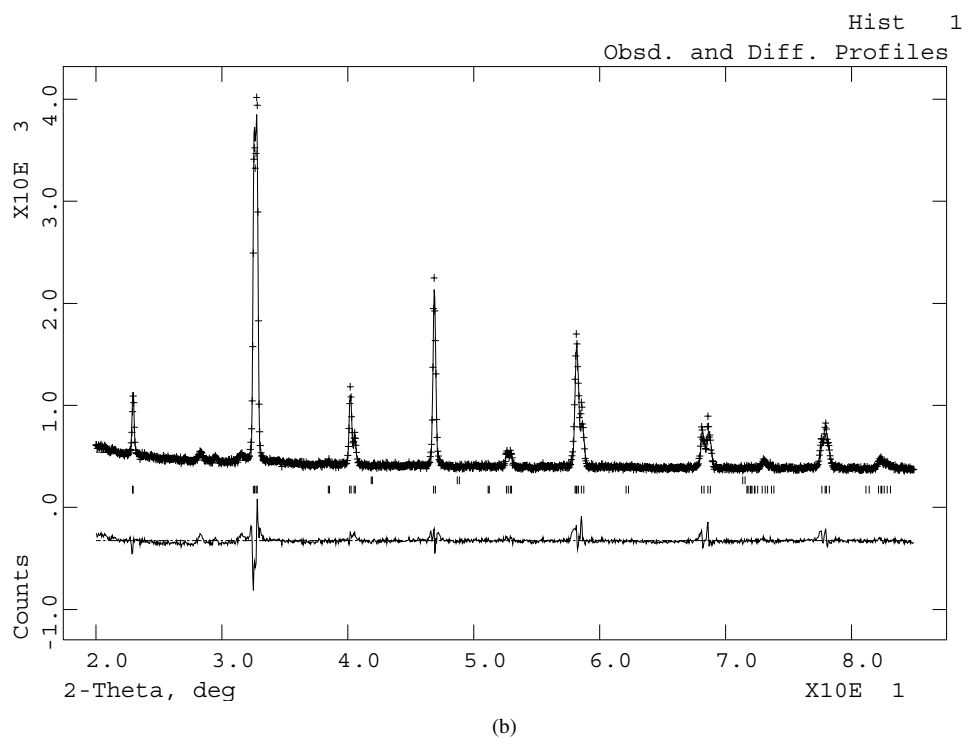
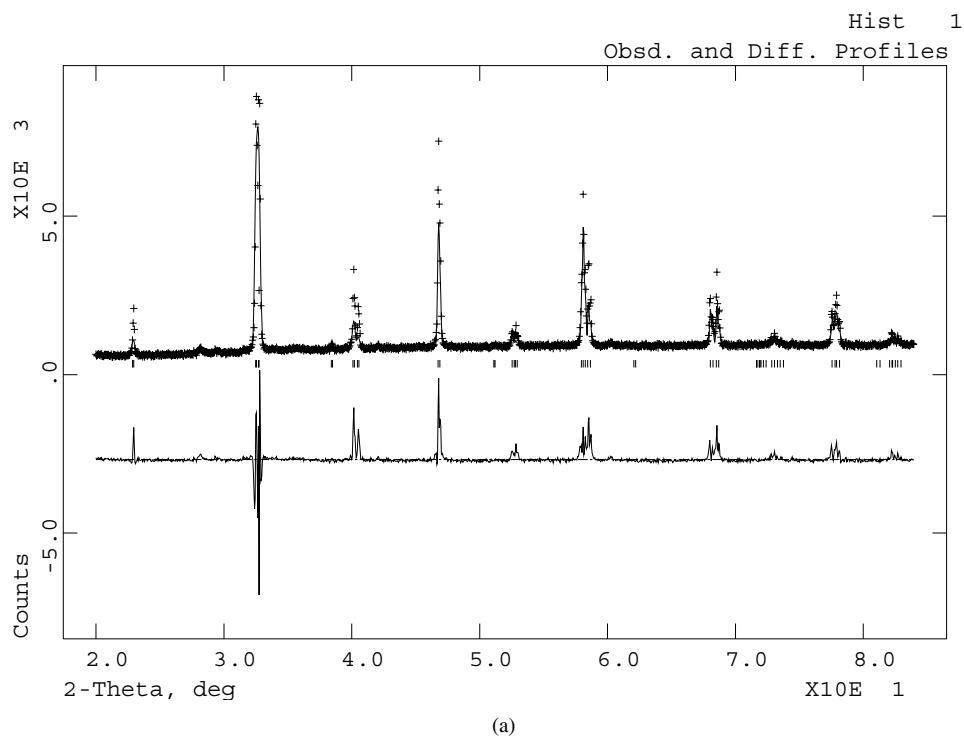


Figure 1. X-ray diffraction of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Cr}_{0.05}\text{Mn}_{0.95}\text{O}_3$ (a) and $\text{La}_{0.7}\text{Sr}_{0.3}\text{Re}_{0.10}\text{Mn}_{0.90}\text{O}_3$ (b). The lower curve in both the figures is the difference profile curve and shows the difference between the experimental and the fitted curve.

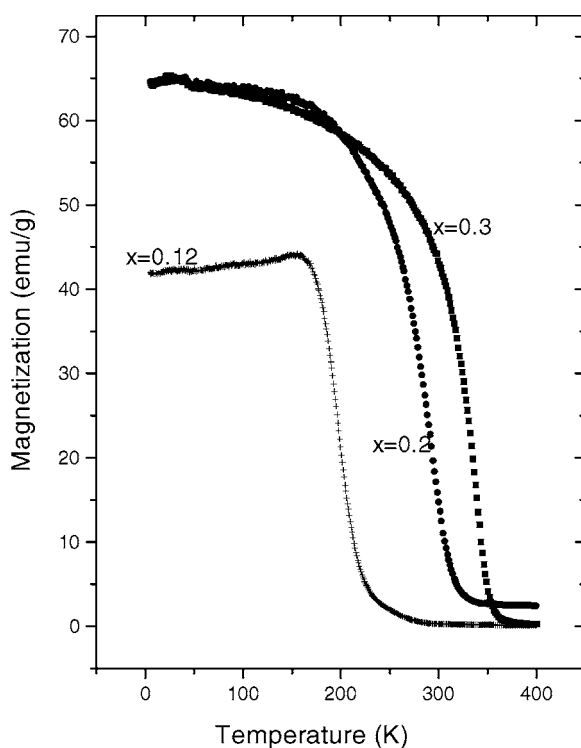


Figure 2. Magnetization versus temperature curves of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, $x = 0.12, 0.20$ and 0.30 at 1000 Gauss.

by 0.2% while the occupation factor for the rhenium site is 0.06. We assume that instead of going into Mn sites the remaining 40% of the Re goes into the interstitial sites of the crystal lattice. We will see later that such an assumption leads to a better explanation of the electrical property of the Re doped compounds.

Figure 2 shows the magnetization versus temperature curves for the compounds $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$. The undoped compounds have a transition temperature of 342.1 K, 293.4 K and 197.4 K for $x = 0.30, 0.20$ and 0.12 respectively, close to the reported value [18]. The ferromagnetic transitions are quite sharp and the sharpness of the transition increases with decreasing strontium concentration. The magnetization of the $x = 0.12$ compound is significantly less at low temperature as compared to the $x = 0.3$ or 0.2 compound. Considering the fact that the ferromagnetic property of the compounds depends on the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio, the smaller magnetization can be attributed to the small amount of strontium present in the compound resulting in a weaker ferromagnetism and increasing antiferromagnetic interaction in these perovskites.

For the Cr containing samples the nature of the magnetization versus temperature curve is similar to the parent compound but the sharpness in the ferromagnetic to paramagnetic transition decreases (figure 3). The curves become more and more broad as the Cr content increases and the broadening is quite pronounced at or above $y = 0.15$. This broadening is ascribed to the presence of chromium that enters the Mn site randomly and hinders the ferromagnetic interaction between the $\text{Mn}^{3+}-\text{Mn}^{4+}$ ions. As a result of such broadening the transition temperature T_C is not very well defined. The value of the magnetization also decreases with increasing chromium content. This may be due to the formation of

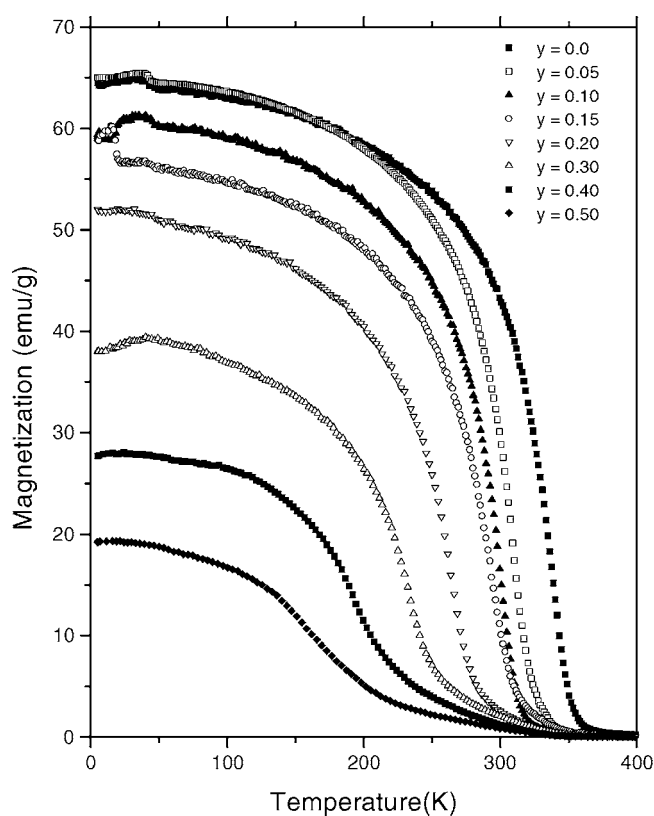


Figure 3. Magnetization versus temperature curves of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Cr}_y\text{Mn}_{1-y}\text{O}_3$, $y = 0.05\text{--}0.50$ at 1000 Gauss.

embedded antiferromagnetic cluster due to the presence of Cr in the ferromagnetic matrix. The magnetization versus temperature curves for $\text{La}_{1-x}\text{Sr}_x\text{Re}_{0.10}\text{Mn}_{0.90}\text{O}_3$ is shown in figure 4. The curves become broad as in the Cr case and T_C decreases with decreasing Sr content in the compound. The T_C for both the series are given in table 1. The kink seen at 43 K is most probably due to unreacted MnO_2 that show a peak in the magnetization versus temperature curve at that temperature. Figure 5 shows a plot of chromium concentration, y , versus the transition temperature T_C . The plot shows that T_C decreases linearly with increasing Cr concentration. This decrease in transition temperature corresponds to an extension of the antiferromagnetic insulating phase of the compounds and is explained by the change in the ferromagnetic Mn–O–Mn interaction due to Cr in the Mn sites. The inset of figure 5 shows a plot of Cr concentration versus the effective paramagnetic moment of the compound. In this case also we find that the effective moment decreases linearly with increasing Cr content. Considering that chromium goes into the manganese sites in the compound, we explain this result by the fact that Mn^{3+} has a larger magnetic moment than chromium. At smaller concentrations, Cr goes into the Mn^{3+} sites and the Mn^{3+} density changes. The fewer Mn^{3+} ions (and an equal increase of chromium ions) result in a decrease in the average effective paramagnetic moment. Since chromium and manganese are the only ions in the compound that have a magnetic moment, we can conclude that the average effective paramagnetic moment is due to the manganese and chromium. Therefore it is likely that Cr carries away the moment

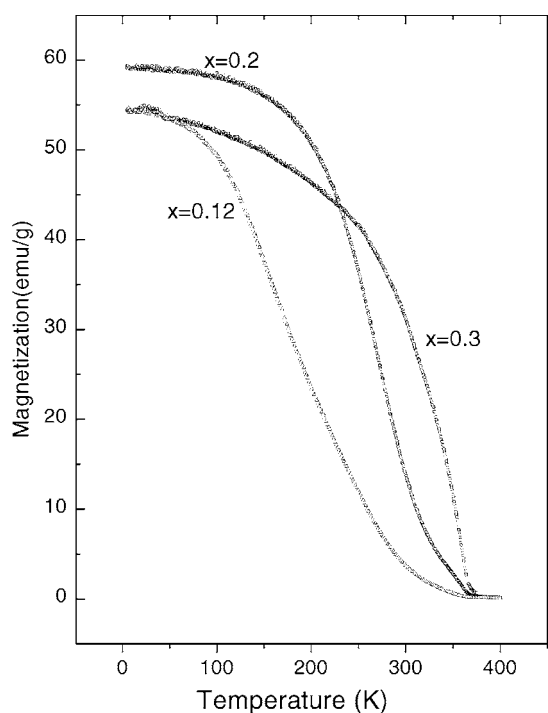


Figure 4. Magnetization versus temperature curves of $\text{La}_{1-x}\text{Sr}_x\text{Re}_{0.10}\text{Mn}_{0.90}\text{O}_3$, $x = 0.12, 0.20$ and 0.30 at 1000 Gauss.

from the Mn ions and drives the compound towards the paramagnetic region. Extrapolating the curve reveals that at $y = 1.0$ the effective paramagnetic moment becomes zero. Such zero effective paramagnetic magnetic moment may be explained if it is considered that the Cr ion becomes an itinerant system so that there is no net localized moment on the atom. The effective magnetic moments for the compounds are given in table 1.

Table 1. Magnetic transition temperature T_C , metal-insulator transition temperature T_{im} and effective magnetic moment μ_{eff} for the $\text{La}_{0.7}\text{Sr}_{0.3}\text{Cr}_y\text{Mn}_{1-y}\text{O}_3$, $y = 0.05-0.50$ compounds. The T_C , T_{im} values for the Re doped $\text{La}_{1-x}\text{Sr}_x\text{Re}_{0.10}\text{Mn}_{0.90}\text{O}_3$ compounds are also given.

Compound Cr content	T_C (K)	T_{im} (K)	μ_{eff} (μ_B)
$y = 0.0$	342.1	329.3	4.805
$y = 0.05$	325.8	320.0	4.649
$y = 0.10$	298.2	293.2	
$y = 0.15$	291.8	298.3	3.929
$y = 0.20$	265.0	No M-I transition	3.686
$y = 0.30$	230.0	No M-I transition	3.361
$y = 0.40$	195.1	No M-I transition	3.104
$y = 0.50$	159.2	No M-I transition	2.683
Re doped compounds			
$x = 0.30$	344.2	329.3	
$x = 0.20$	267.9	244.8	
$x = 0.12$	157.6	120.0	

Figure 6 shows the resistivity versus temperature curve for the $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ compounds. The measurements are made at zero applied fields. The parent compound $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ has a distinct metallic phase below a temperature of 329.3 K and above this temperature it becomes an insulator. The curve for $x = 0.12$ has been plotted on a logarithmic scale. It can be seen that the resistivity increases with decreasing strontium concentration. The first arrow in the $x = 0.20$ compound at a temperature of 127 K indicates a structural phase change from rhombohedral to orthorhombic as the temperature is lowered below 127 K [19]. For the Cr doped compounds the resistivity versus temperature curves show that with an increase of Cr content there is an overall increase of the resistivity along with an increase of the residual resistivity of the compounds (figure 7). The metal–insulator transition for the compounds takes place at a temperature T_{im} that is lower than T_{C} and is given in table 1. There are some kinks seen at higher temperatures (~ 375 K) but we do not know their origin. Below T_{im} the compounds with Cr concentrations of 0.05, 0.10 and 0.15 show metallic character and above it the resistivity decreases with increasing temperature thereby indicating the insulating nature of the compounds. For $y = 0.10$ a distinct hump can be seen at a temperature of 261.8 K and for 15% chromium concentration this hump becomes very prominent (figure 8). The presence of Cr^{3+} on the Mn^{3+} sites give rise to a ferromagnetic interaction through $\text{Mn}^{3+}\text{--O--Cr}^{3+}$ and also a strong antiferromagnetic interaction through $\text{Cr}^{3+}\text{--O--Cr}^{3+}$. This antiferromagnetic interaction increases with increase in Cr content and for the compounds above 20% Cr content it has a substantial contribution to the overall resistivity. The majority of the spins get unfavourably aligned and the number of scattering sites increases. The occurrence of the hump is due to the charge ordering and antiferromagnetic nature of the chromium. The resistivity therefore increases and the sample shows an insulating nature. At 20% or more Cr concentration in $\text{La}_{0.7}\text{Sr}_{0.3}\text{Cr}_y\text{Mn}_{1-y}\text{O}_3$ the charge ordering antiferromagnetic ground state takes over from the ferromagnetic ground state. The compound becomes an insulator over the whole temperature region and shows no metal–insulator transition. Considering that the Cr^{3+} takes the place of Mn^{3+} we can conclude that Cr^{3+} reduces the double exchange interaction so that the magnetic transition temperature, T_{C} , and metal–insulator transition temperature, T_{im} , decrease. We also conclude that the $\text{Mn}^{3+}\text{--Mn}^{4+}$ ratio must have a maximum value in order that the CMR effect can be seen. The existence of such a maximum value for the occurrence of CMR has already been reported [18].

Figure 9 shows the resistivity versus temperature curves for $\text{La}_{1-x}\text{Sr}_x\text{Re}_{0.10}\text{Mn}_{0.90}\text{O}_3$ at zero field. The behaviour of the resistivity with temperature remains the same as that of the $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ compound. Except for the $x = 0.12$ compound all other compounds show an increase in the resistivity and an increasing residual resistivity. The $\text{La}_{0.88}\text{Sr}_{0.12}\text{MnO}_3$ compound, which is an insulator, shows metallic character in the temperature region 50–120 K after rhenium doping. One possible way to explain this result is by assuming the presence of the Re in the interstitial sites. In a metallic system the size of the insulating clusters is small and there is enough space for the charge carrier to move. The presence of Re in the interstitial sites acts as a potential scattering sites for the dynamic charge carriers so that the overall resistivity increases. However when the system is an insulator ($\text{La}_{0.88}\text{Sr}_{0.12}\text{MnO}_3$) the clusters become big enough that there is very little or almost no space for the carriers to move through. Because of the big size of Re its presence in the lattice results in redistribution of the clusters in such a way the charge carriers have enough space to percolate through it and consequently the overall resistivity decreases. The resistivity curves broaden for the compounds $\text{La}_{0.8}\text{Sr}_{0.2}\text{Re}_{0.10}\text{Mn}_{0.90}\text{O}_3$ and $\text{La}_{0.7}\text{Sr}_{0.3}\text{Re}_{0.10}\text{Mn}_{0.90}\text{O}_3$ and the T_{im} decreases (table 1). Such broadening is explained as due to the magnetic inhomogeneity caused by the presence of rhenium.

The resistivity versus applied magnetic field for some selected Cr doped samples and

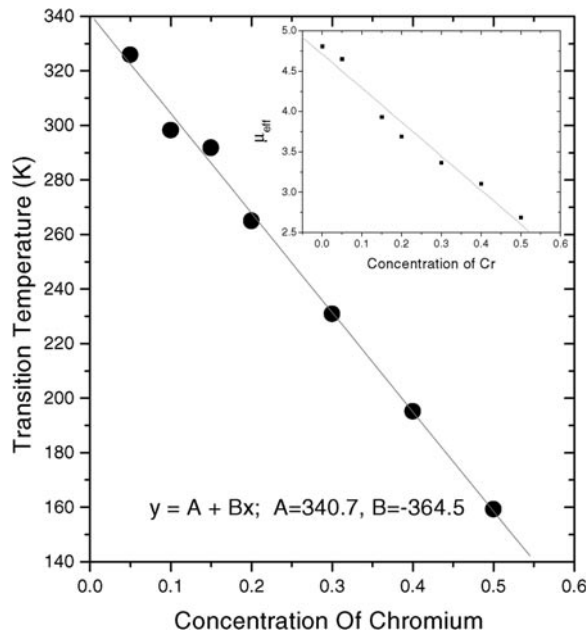


Figure 5. Plot of transition temperature as a function of concentration of chromium. The inset shows the plot of effective magnetic moment as a function of chromium concentration.

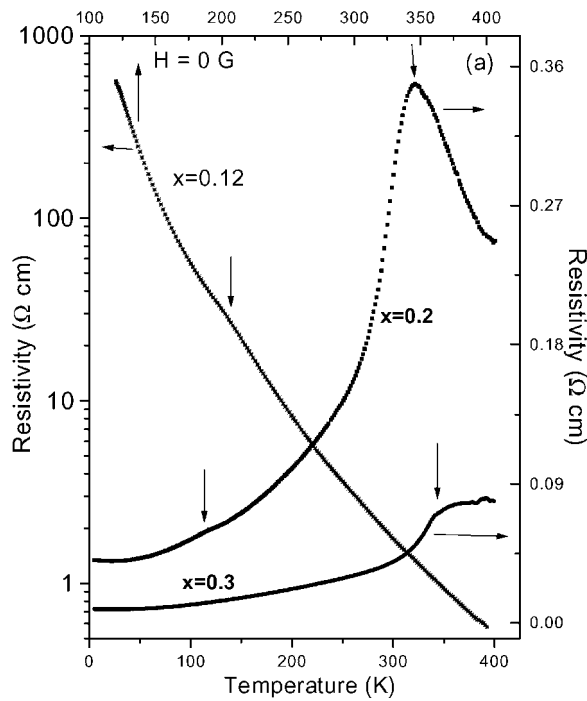


Figure 6. Resistivity versus temperature curves of $La_{1-x}Sr_xMnO_3$, $x = 0.12, 0.20$ and 0.30 at zero field.

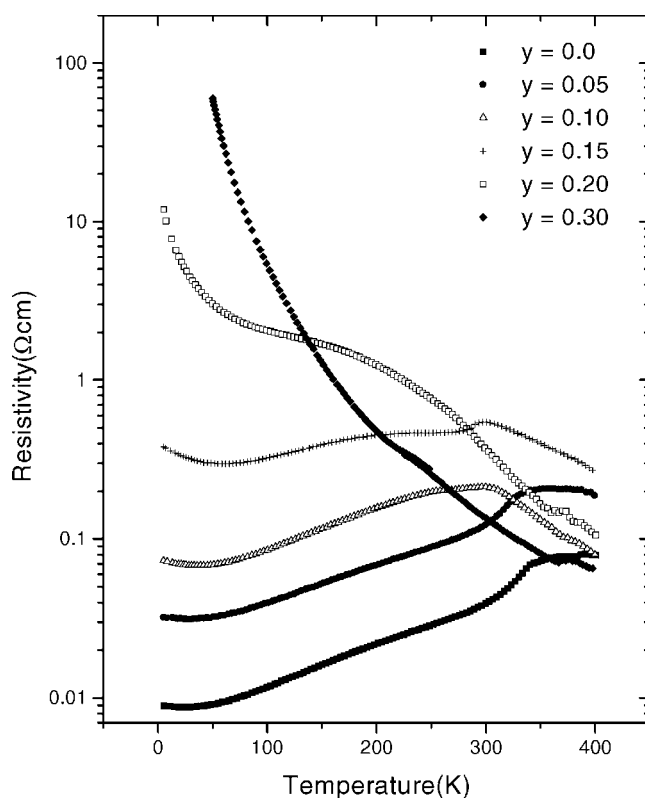


Figure 7. Resistivity versus temperature curves of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Cr}_y\text{Mn}_{1-y}\text{O}_3$, $y = 0.05\text{--}0.30$ at zero field.

Re doped samples is shown in figures 10 and 11. The measurements were performed at a temperature 20 K below the magnetic transition temperature since the magnetoresistance is a maximum at a temperature near the transition temperature. We see that with increasing Cr content there is an increasing trend in the magnetoresistance of the compounds, but we believe it is mainly due to an increase in the insulating nature of the compounds. An increase in the insulating nature results in an increase in antiferromagnetic clusters in the compounds. This explains the large residual resistivity of the compounds. When a large field is applied the ferromagnetic moments are aligned and by percolation the charge carriers are able to conduct, thereby causing a decrease in the resistivity. This is manifested in the form of increased magnetoresistance. Magnetization versus applied magnetic field for Re doped compounds at 20 K below T_C is shown in figure 11. At very low temperatures there exist two distinct regions. At low magnetic field the magnetization field increases very rapidly and then it assumes an almost constant value even if the field is increased. The low field increase of the magnetization is due to the motion of the domain walls whereas at high fields the change in magnetization takes place due to the spontaneous magnetization on application of the magnetic field. As the temperature increases the magnetization decreases. This is because an increase in temperature causes an increase in thermal motion and so there is less alignment of the moments. We have used the M – H and ρ – H curves to determine the change in the resistivity as a function of the magnetization at a particular temperature. Figure 12 shows the plot of resistivity as a function of the magnetization. We found that the resistivity decreases as

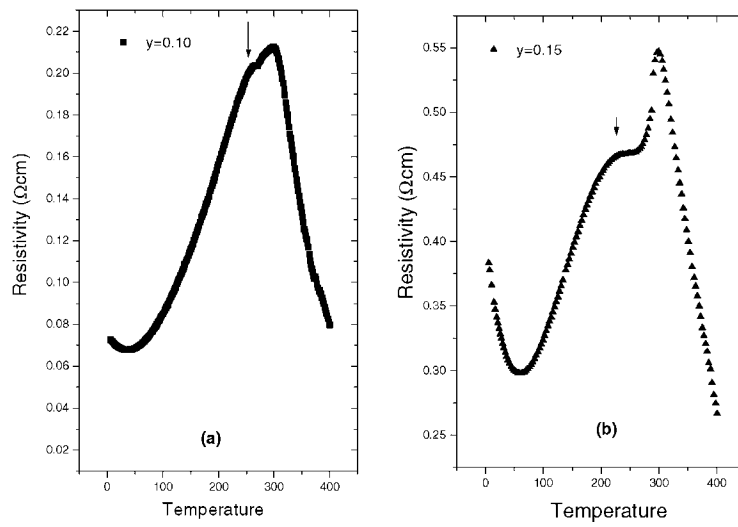


Figure 8. Resistivity versus temperature curves of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Cr}_y\text{Mn}_{1-y}\text{O}_3$, (a) $y = 0.10$ and (b) 0.15 showing the appearance of the hump due to the antiferromagnetic interaction of the Cr ions.

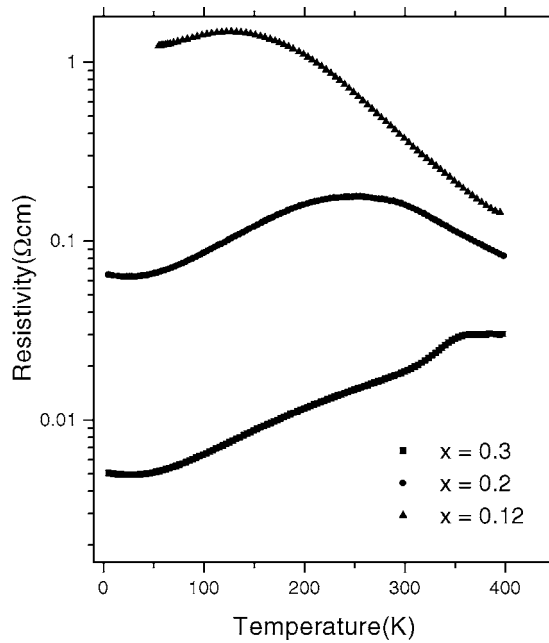


Figure 9. Resistivity versus temperature curves of $\text{La}_{1-x}\text{Sr}_x\text{Re}_{0.10}\text{Mn}_{0.90}\text{O}_3$, $x = 0.12, 0.20$ and 0.30 at zero field.

the magnetization increases. The curves can be fitted to a second order polynomial thereby confirming the existence of a relation between the magnetization and resistivity as reported by Furukawa [20]. The nature of the curves is similar to the curve obtained using the relation given by Furukawa. It can be seen from figure 12 that magnetoresistance also correlates with

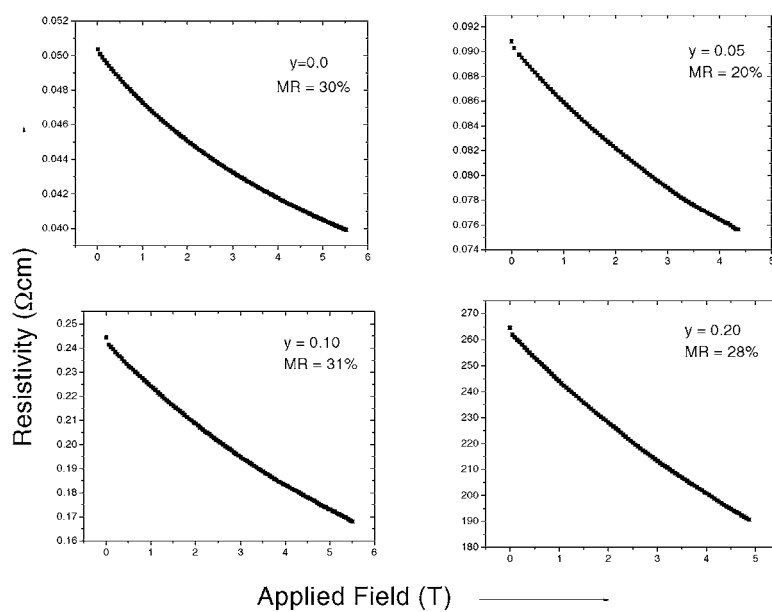


Figure 10. Resistivity versus applied magnetic field for $\text{La}_{0.7}\text{Sr}_{0.3}\text{Cr}_y\text{Mn}_{1-y}\text{O}_3$, $y = 0.05, 0.10, 0.20$.

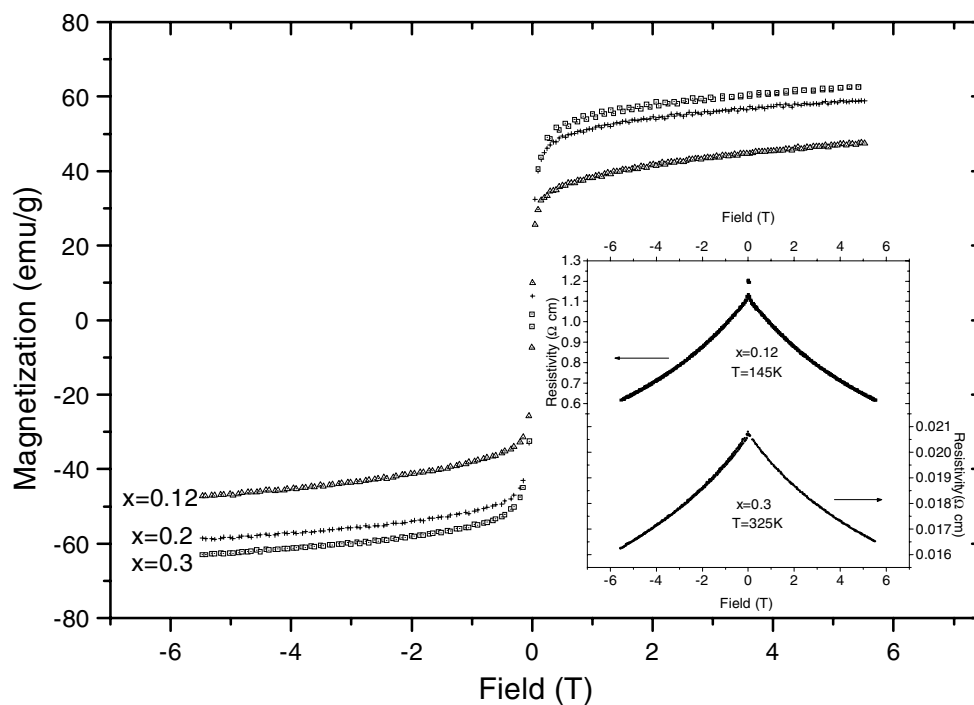


Figure 11. Magnetization versus applied field curves for $\text{La}_{1-x}\text{Sr}_x\text{Re}_{0.10}\text{Mn}_{0.90}\text{O}_3$, $x = 0.12, 0.20$ and 0.30 compounds. The inset shows the resistivity curves for $x = 0.12$ and 0.30 compounds.

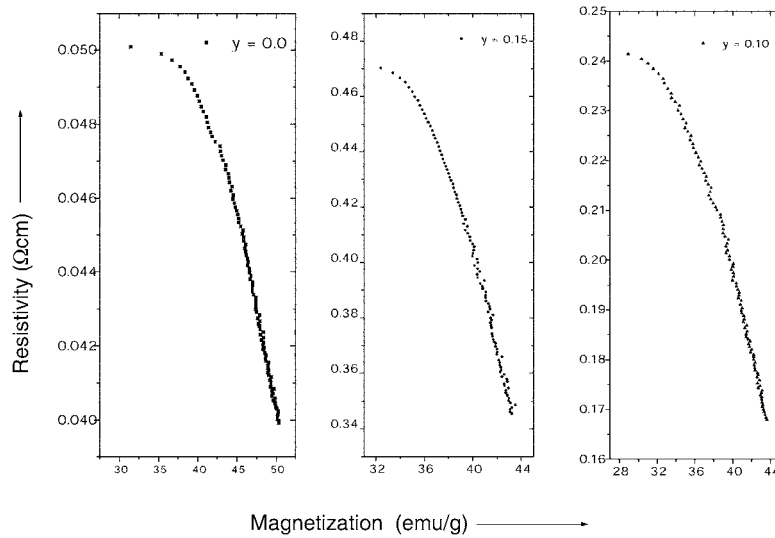


Figure 12. Resistivity versus magnetization curve of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Cr}_{0.15}\text{Mn}_{0.85}\text{O}_3$, $y = 0.0, 0.10$ and 0.15 .

the magnetization. At low fields the change in resistivity is at a slower rate than at higher fields. Thus the domain motion does not have much effect on the resistivity. But at higher fields the resistivity changes fast. So we can conclude that the resistivity is affected mainly by the spins so that when the spins become oriented towards the applied field the resistivity decreases. However we find that at high enough field, even though the change in magnetization ΔM is very small, the magnetoresistance still persists. This points towards the fact that apart from the spins other processes like scattering at the grain boundary also play an important role and contribute towards the resistivity. Considering that the magnetoresistance is due to ordering of local spin fluctuation, the grain boundaries can act as a source of such local spin fluctuation [21]. The grain boundaries can have antiferromagnetic interaction and therefore can act as scattering sites. At high enough field the grain boundary spin gets aligned and there is an increase in spin polarized tunnelling resulting in decrease of resistivity. But however even at high enough field complete alignment of the intergrain spin is not attained even though the bulk magnetization shows saturation. Due to this fact the resistivity persists even though the magnetization saturates.

Finally in order to see the role of vacancies we have prepared a 5% Mn vacant $\text{La}_{0.80}\text{Sr}_{0.20}\text{Mn}_{0.95}\text{O}_3$ (LSMO) compound and measured the magnetization versus temperature (figure 13, inset). We found that the T_C increases as opposite to the Re doped compound. So we can conclude that Re does has an effect on the LSMO compound. To ascertain whether Re has a magnetic moment in the manganite compounds we have measured the magnetization versus field at 5 K (figure 13). We found that there is no substantial change in the magnetization data. So we can conclude that Re does not seem to have any moment by itself in the compound. But since the electrical transport properties change due to Re doping it seems that the change in the transport properties is because of a change in the band structure of the material due to Re doping. However this point needs to be investigated in more detail.

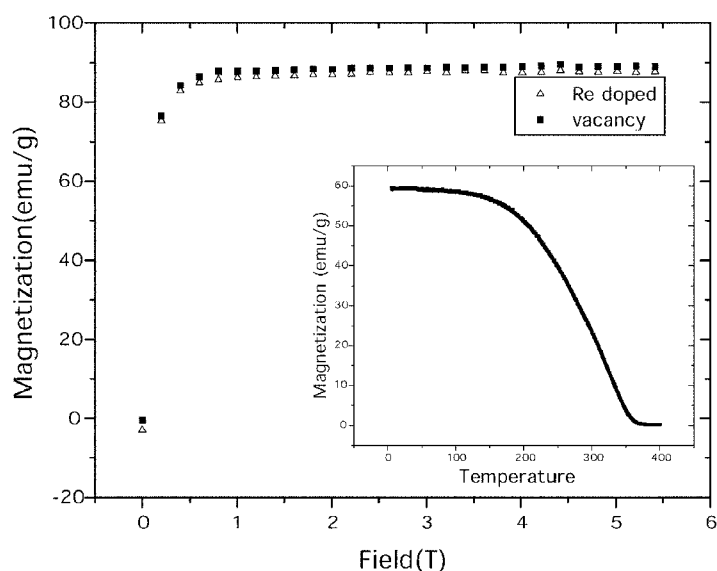


Figure 13. Magnetization versus applied field curve for a 5% vacant $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.95}\text{O}_3$ sample at 5 K. The inset shows the magnetization versus temperature curve for the same compound.

4. Conclusions

We have studied the effect of Cr and Re doping on the magnetic and transport properties of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$. We found that the structure of the Cr doped compound is rhombohedral at low Cr concentration but tends to deviate from this at higher Cr concentration. In the case of Re doping the structure of the compounds remains rhombohedral for whole Re concentration and there is an expansion of the lattice. The magnetic and transport properties of Cr doped compounds can be interpreted by suggesting that $\text{Cr}^{3+}\text{-O-Mn}^{4+}$ negative interaction or antiferromagnetic $\text{Cr}^{3+}\text{-O-Cr}^{3+}$ interaction is dominant in the system. Thus, increase of Cr concentration in $\text{La}_{0.7}\text{Sr}_{0.3}(\text{Cr}, \text{Mn})\text{O}_3$ compounds results in an increase of negative $\text{Cr}^{3+}\text{-O-Mn}^{4+}$ and $\text{Cr}^{3+}\text{-O-Cr}^{3+}$ interactions. As a result, magnetization and metal-insulator transition temperature decrease and for 20% or more Cr doping, the compound shows an insulating nature. Considering the fact that Cr^{3+} replaces the Mn^{3+} it can be concluded that Cr causes a change in the density of Mn^{3+} ions and could form insulating antiferromagnet clusters. So there is a change in the double exchange interaction along with an increase in the number of scattering sites for the charge carriers. This affects the magnetization and the resistivity of the compounds. The increase in resistivity is mainly due to antiferromagnetic interaction through $\text{Cr}^{3+}\text{-O-Cr}^{3+}$ and also may be due to a charge ordering effect. The strong antiferromagnetic interaction between the Cr ions is manifested in the form of a hump in the resistivity curve. This hump becomes very broad at higher Cr concentrations due to the increased amount of insulator antiferromagnet clusters.

In the case of $\text{La}_{1-x}\text{Sr}_x\text{Re}_{0.10}\text{Mn}_{0.95}\text{O}_3$ compounds, Re doping, the $x = 0.12$ compound shows drastic changes of transport properties from insulator (without Re) to metallic-like behaviour below the magnetic transition temperature. Taking into account that about 40% of Re goes into the interstitial space of the crystal cell such behaviour could be caused by the presence of Re that causes redistribution of the antiferromagnet cluster thereby creating space for the charge carrier to percolate through. For other rhenium based compounds there

is an overall increase in resistivity from the metallic state due to defects of the crystal cell caused by Re doping. Increased magnetoresistance values for compounds with high Cr and Re containing compounds is due to the higher resistivity of the compounds. The Mn–O–Cr interaction does lead to decreased ferromagnetic ordering and an increased insulating nature. The plot of resistivity versus magnetization shows that in CMR manganites the resistivity can be scaled with magnetization.

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