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Cr doping in the $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ system

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Abstract. The effect of doping Cr in the Mn site of the $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ system has been studied. Addition of Cr modifies the transport and magnetic properties of the parent phase. With increasing Cr, the insulator–metal transition observed in the parent phase is suppressed and insulating behaviour is induced. In the range of doping studied (25%), the compositions show ferromagnetic behaviour with the Curie temperature decreasing with increasing Cr. The unit cell volume also shows a decrease. However, the magnetoresistance ratio is not significantly affected. We compare these results with an earlier study of doping Cr in the three-dimensional LaMnO_3 structure, where it was seen that the ferromagnetic and magnetoresistance characteristics are sensitive to Cr doping. The results of the present study suggest that the layered manganates are more accommodative to doping compared to the three-dimensional perovskites.

1. Introduction

Since the observation of colossal magnetoresistance (CMR) in the rare earth manganates, intense research activity has been focused on these materials. The effort is to optimize the properties so that a sufficiently large change in resistance is observed under a low magnetic field, at temperatures close to room temperature. So far, much of the work has been carried out on the system represented by the formula $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ where Ln is a rare earth and A a divalent cation (Ca, Sr, Pb). These compositions undergo a transition to the ferromagnetic state at a critical value of x and exhibit an insulator–metal transition close to the Curie temperature T_C [1]. A large change in electrical resistivity is observed near T_C under the application of a magnetic field [2]. Traditionally, the coupled transport and magnetic properties as well as the CMR in these materials have been explained on the basis of the double exchange (DE) mechanism [3]. However, recent studies have shown that DE cannot alone explain the experimental observations and that a strong electron–phonon interaction arising from the Jahn–Teller splitting of the outer Mn d level must be taken into account [4].

The (Ln, A) MnO_3 system mentioned above is the three-dimensional ($n = \infty$) limit of the Ruddlesden–Popper series which can be represented as $(\text{La}, \text{A})_{n+1}\text{Mn}_n\text{O}_{3n+1}$ [5]. The members of this series may be visualized as consisting of perovskite blocks, n MnO_6 octahedra thick, offset along the c -axis and separated by a layer of (La, A)O ions [6]. The $n = 1$ member has the two-dimensional K_2NiF_4 structure, while the $n = 2$ and $n = 3$ members have the dimensionality between 2 and 3 [5].

The layered members have been the focus of recent attention due to the observation of CMR in the $n = 2$ and $n = 3$ members, similar to the $n = \infty$ member. In an early report, Mohan Ram *et al* [7] had shown that the quasi-two-dimensional oxides of the $\text{La}_{1-x}\text{Sr}_{1+x}\text{MnO}_4$ system show no evidence for ferromagnetic ordering. Mahesh *et al* [5] have reported an investigation of the $n = 1, 2, 3$ and ∞ members of the $(\text{La}, \text{Sr})_{n+1}\text{Mn}_n\text{O}_{3n+1}$ family and have shown that the MR decreases as the dimensionality increases from 2 to 3. Moritomo *et al* [8] have reported that the compound $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ exhibits coupled electronic and magnetic transitions as well as CMR and have attributed these to double exchange. However, Battle *et al* [9] have shown that CMR in the compositions $\text{Sr}_2\text{NdMn}_2\text{O}_7$ and $\text{Sr}_{1.9}\text{Nd}_{1.1}\text{Mn}_2\text{O}_7$ is not readily explained by the DE mechanism. Seshadri *et al* [10] have studied the structural evolution and electronic properties of $\text{La}_{1-x}\text{Sr}_{2-x}\text{Mn}_2\text{O}_7$ and have shown that in the range $0.1 \leq x \leq 0.45$ the phases crystallize in the $I4/mmm$ space group. Battle *et al* [11] have used neutron diffraction and synchrotron x-ray powder diffraction techniques to refine the magnetic and crystal structure of $\text{Sr}_2\text{LaMn}_2\text{O}_7$, showing this composition to be biphasic. Asano *et al* [12] have also reported that the $\text{La}_{2-2x}\text{Ca}_{1+2x}\text{Mn}_2\text{O}_7$ system shows two types of ferromagnetic ordering for $0.22 \leq x \leq 0.5$. Antiferromagnetic short range ordering in $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ has been reported by Perring *et al* [13]. The effect of pressure on the layered materials has been studied by Argyriou *et al* [14], Kimura *et al* [15] and Mahesh *et al* [16]. Recently, Ishikawa *et al* [17] have reported an optical probe of anisotropic and incoherent charge dynamics in $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$. Li *et al* [18] have reported a study of the magnetic properties of the $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ system using neutron diffraction and AC susceptibility measurements.

In the present paper, we report a study of doping Cr at the Mn site in $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ to understand the effect on the coupled electric and magnetic transitions in this system. From the point of view of obtaining the largest value of magnetoresistance, $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ is now believed to be the optimally doped composition in the series $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$, with the $x = 0.3$ and $x = 0.5$ members being under- and over-doped, respectively [18]. Cr has been chosen as Cr^{3+} is isoelectronic with Mn^{4+} and the ionic radius of Cr^{3+} is comparable to that of Mn^{3+} . Also, the effect of doping Cr in LaMnO_3 has been reported in an earlier publication [19]. The present study thus allows a comparison with the earlier work. Our results show that the substitution of Cr modifies the transport and magnetic properties of $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$, similar to the case of LaMnO_3 . However, the MR is not affected in the present system even when 25% of the Mn site is substituted by Cr; indeed, an MR ratio close to 80% has been observed at lower temperatures in a field of 10 T in the composition with $x = 0.5$. This result highlights the need to further study these materials to obtain a better understanding of the mechanisms governing the various properties. The result also suggests that the layered system is more accommodative to Cr doping compared to the three-dimensional manganates.

2. Experiment

Samples of the system $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_{2-x}\text{Cr}_x\text{MnO}_3$ with $x = 0, 0.1, 0.2, 0.3$ and 0.5 were synthesized by the solid state reaction of La_2O_3 , SrCO_3 , MnO_2 and Cr_2O_3 . Well ground mixtures of the starting materials were heated at 1200°C in air for 16 h, followed by two treatments each of 16 h at 1400°C with intermediate grindings. The powders were then pelletized and heat-treated at 1400°C for 16 h. All the treatments were carried out in air. X-ray diffractograms in the 2θ range 20° to 70° were recorded on a SCINTAG (X1) diffractometer using $\text{Cu K}\alpha$ radiation. The lattice parameters were evaluated by the method of least squares. Magnetization measurements at 0.05 T were carried out by means of a SQUID magnetometer (Quantum Design). Magnetoresistance measurements in fields up to 10 T were performed on an Oxford Maglab system.

3. Results and discussion

Figures 1(a) and 1(b) show the variation of the unit cell parameters and the unit cell volume respectively as a function of the Cr concentration. The x-ray diffractogram as well as the lattice parameters for the sample with $x = 0$ match well with earlier reports in the literature [10]. It is known that the synthesis of the $n = 2$ composition is difficult and the 3D perovskite often grows as an impurity. However, no extra reflections of significant intensity were observed from the x-ray diffractograms and, hence, we assume that the amount of the perovskite phase, even if present, is very small compared to the main phase. This permits us to analyse the data from different measurements and draw meaningful conclusions about the effect of doping.

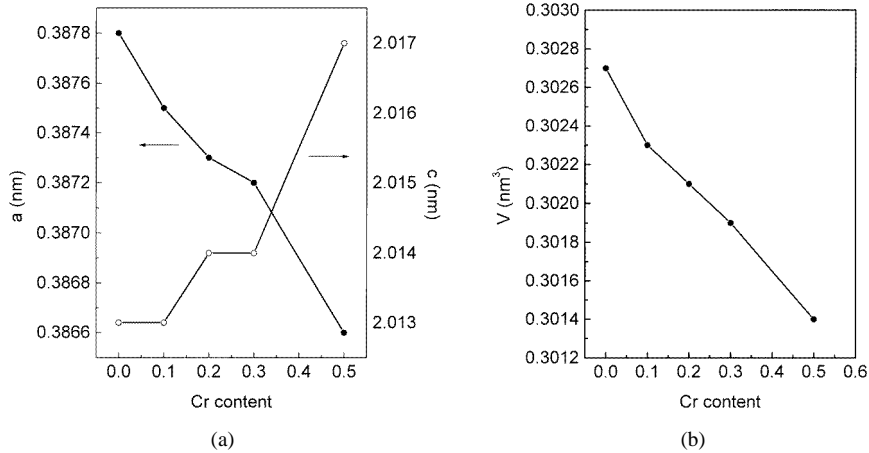


Figure 1. (a) Variation of the a and c parameters as a function of Cr concentration. Lines are guides to the eye. (b) Variation of the unit cell volume as a function of Cr concentration. The line is a guide to the eye.

In the range of doping studied, all the compositions showed tetragonal symmetry. With increasing Cr content, the a -parameter shows a monotonic decrease. As can be seen from figures 1(a) and 1(b), the c -parameter shows a slight increase while the unit cell volume shows an almost linear decrease with increasing Cr. As mentioned earlier, the Cr^{3+} ion is expected to substitute the Mn^{3+} site. As the ionic radius of Cr^{3+} is smaller than that of Mn^{3+} , the unit cell volume is expected to show a decrease with increasing Cr content, which is in line with the present observations.

Table 1 shows the data from the electric and magnetic measurements. It can be seen that all the compositions show ferromagnetic behaviour as the temperature is decreased. The ferromagnetic transition temperature T_C (defined as the minimum in the $dM/dT-T$ curve) increases slightly with increasing Cr content, shows a maximum value of 125 K for $x = 0.2$ and then decreases. For $x = 0.5$, there is a large drop in T_C . Also, the transitions become broader with Cr content. Thus, the effect of doping Cr is to decrease the strength of the ferromagnetic coupling. For $T < 25$ K, the $M(T)$ curves show a decrease for $x = 0.3$ and 0.5 as shown in figure 2. Such a decrease, observed earlier for crystals of $(\text{La}_{1-z}\text{Nd}_z)\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ [20], has been ascribed to a transition from the ferromagnetic state to a spin-glass-like state. This behaviour also manifests itself in the electrical resistivity, as will be discussed later.

Figure 3 shows the temperature variation of the DC electrical resistivity for compositions of the present study. The samples with $x = 0$ and 0.1 show a peak, which is referred to in the literature as an insulator-metal transition. As can be seen from the figure, the value of the

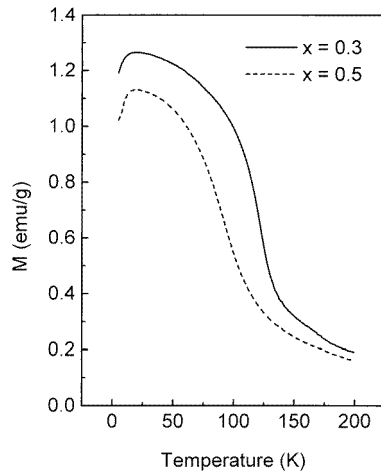


Figure 2. Temperature variation of the magnetization for $x = 0.3$ and $x = 0.5$ showing the decrease of $M(T)$ at low temperature.

Table 1. Data from the transport and magnetic measurements.

x	ρ_{290}^a (Ω cm)	T_p^b (K)	ρ_{peak} (Ω cm)	T_C (K)	T_0^c (K)
0.0	1.08	130	16.31	118	25
0.1	2.02	126	46.10	123	29
0.2	3.12	—	—	125	31
0.3	5.78	—	—	123	33
0.5	6.16	—	—	92	39

^a Resistivity at 290 K.

^b Temperature where $\rho(T)$ shows a maximum.

^c Please see text for definition of T_0 .

resistivity at room temperature is lower than the value at the lowest temperature of our study. A similar observation has been reported in the literature, pertaining to the 3D perovskites [22]. It is indeed intriguing that the value of the resistivity in the ‘metal-like’ region is higher than in the region where the resistivity presumably arises from hopping between localized states. The sample with $x = 0.2$ does not show a well defined peak; only a broad maximum is observed. Compositions with $x = 0.3$ and 0.5 show insulating behaviour. The resistivity at 290 K, ρ_{290} , increases with increasing Cr content (table 1). Thus, the effect of increasing Cr is to suppress charge itinerancy and to induce charge localization.

From table 1, it can be seen that for $x = 0$, the resistivity shows a peak at $T_p = 130$ K, which is somewhat close to the ferromagnetic T_C . For $x = 0.1$, the peak shifts to 126 K. But for $x = 0.2$, there is a marked change and the resistive transition becomes broad. Although the compositions with $x = 0.2$ and 0.3 do not show a peak, there is a change in slope around 125 K and 120 K, respectively, which might be due to the opening of an energy gap. These temperatures are close to the ferromagnetic T_C for these samples. To display this feature, we plot $d(\log \rho)/dT$ against T for the sample with $x = 0.2$ in figure 4. The change in slope is indicated by an arrow in the figure. A similar change is seen for the sample with $x = 0.3$, although the magnitude of the change is less compared to the sample with $x = 0.2$. This shows that similar to the case of the 3D perovskites, the resistive and magnetic transitions

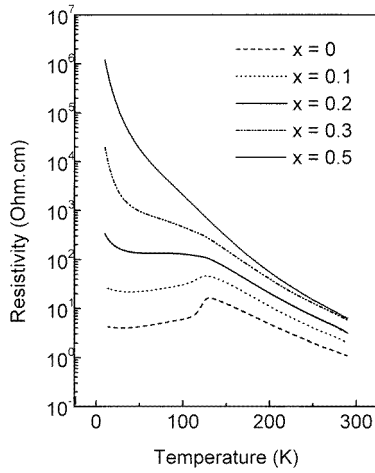


Figure 3. Temperature variation of the DC electrical resistivity for $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_{2-x}\text{Cr}_x\text{O}_7$ compositions.

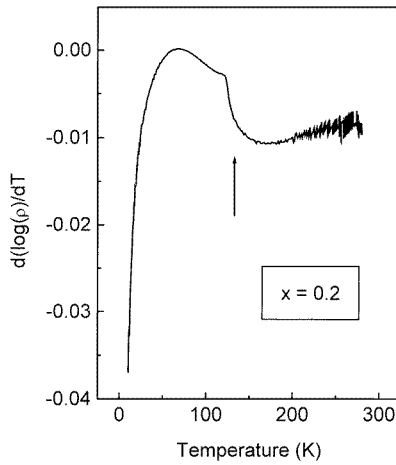


Figure 4. Plot of $d(\log \rho)/dT$ against T for $x = 0.2$. The arrow indicates the change of slope near T_C .

up to $x = 0.3$ are coupled. For $x = 0.5$, no change in slope has been observed. In this composition, the T_C is 92 K (table 1) whereas the resistivity shows a sharp increase only below 25 K. As these two temperatures are well separated, the effect of increasing Cr is to de-couple the resistive and magnetic transitions.

From figure 3, it can be seen that there is an upturn in the $\rho(T)$ curves below 25 K for compositions with $x = 0.3$ and 0.5 . This corresponds to the temperature where the magnetization shows a drop, as mentioned earlier. The upturn is also observed for the composition with $x = 0.2$ and marginally for $x = 0.1$. The transition from the ferromagnetic state to a spin-glass-like state causes the magnetization to drop, which is accompanied by an increase in the resistivity.

It has been observed in the 3D manganates that the functional dependence of the electrical resistivity above T_p is similar for several compositions [21]. From figure 3, it can be observed

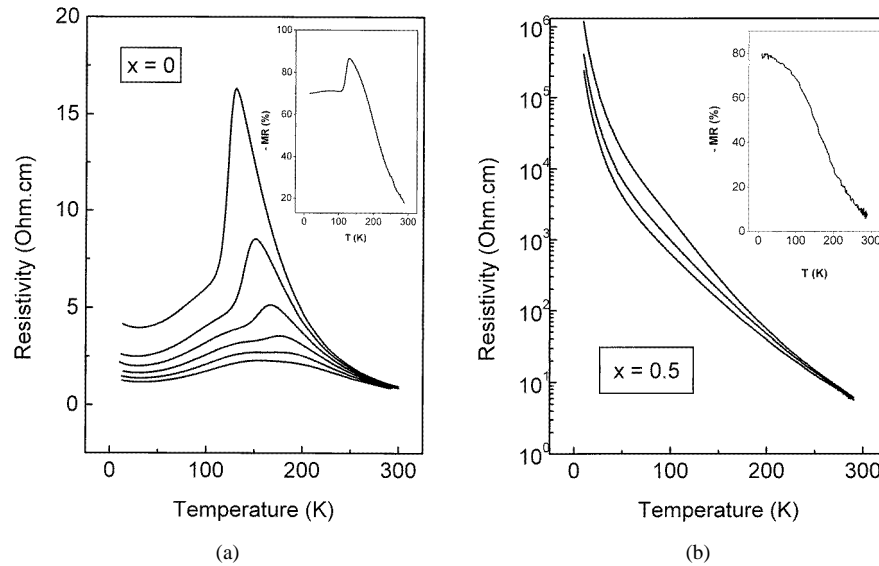


Figure 5. (a) $\rho(T)$ plots for $x = 0$ at different fields. Top to bottom in the figure: $H = 0, 2, 4, 6, 8$ and 10 T respectively. The inset shows the temperature variation of MR at $H = 10$ T. (b) $\rho(T)$ plots for $x = 0.5$ at different fields. Top to bottom in the figure: $H = 0, 5$ and 10 T respectively. The inset shows the temperature variation of MR at $H = 10$ T.

that at $T > T_p$ for compositions with $x = 0$ and 0.1 , and, in general, above 150 K for all the five compositions, the resistivity curves show a similar temperature dependence. The data in the regime $150 \text{ K} < T < 290 \text{ K}$ fit well to the relation $\rho(T) = \rho_0 \exp(T_0/T)^{1/4}$, which represents conduction by hopping between localized states. Here, the parameter T_0 is related to the spatial extension (l) of the localized states and the density of states $g(E_F)$ [21]. With increasing Cr content, the parameter T_0 increases (table 1), which manifests itself as an increase in the resistivity.

We now discuss the behaviour of magnetoresistance. Figures 5(a) and 5(b) show the temperature variation of resistivity for compositions with $x = 0$ and $x = 0.5$, respectively. The insets in these figures show the temperature variation of the magnetoresistance at an applied field of 10 T. (The magnetoresistance is defined as $\text{MR} = (\rho(H) - \rho(0))/\rho(0)$ where $\rho(H)$ is the resistivity in the applied field and $\rho(0)$ is the resistivity in zero field.) The peak in the resistivity displayed by samples with $x = 0$ and $x = 0.1$ shifts to higher temperatures with increasing field. For $H \geq 6$ T, the peak is suppressed altogether and the transition becomes broad.

The notable feature in compositions of the present study is the observation of a large MR at low temperatures although the Cr content is increased. Particularly interesting is the case of $x = 0.5$, where an MR ratio close to 80% is observed under a field of 10 T. This is in marked contrast to the case of doping Cr in LaMnO_3 , where 0.3 of Cr in the Mn site reduces the maximum observed MR to about 20% [19]. It thus appears that the two-layer system is more accommodative to dopants than the 3D perovskites. Here, we would like to point out an essential difference between the earlier work on Cr doping in LaMnO_3 and the present one. Care was taken earlier to see that there was no Mn^{4+} in the samples, thus avoiding the possibility of double exchange. The samples of the present study are expected to have both the Mn^{3+} and Mn^{4+} ions. It would be interesting to study Cr doping in the present system where Mn^{4+} (and hence DE) is prevented by suitable synthesis conditions.

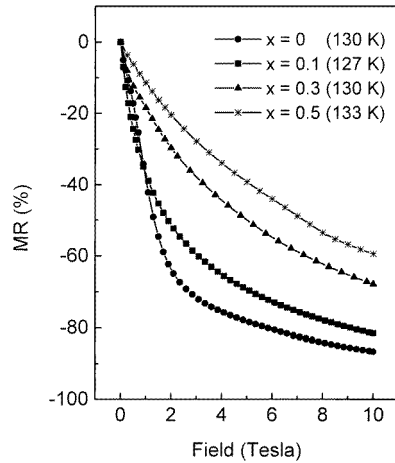


Figure 6. Field variation of MR for $x = 0, 0.1, 0.3$ and 0.5 . The temperature at which each measurement has been performed is indicated in the figure.

To study the field variation of MR, we have carried out MR measurements at a constant temperature using fields up to 10 T. Figure 6 shows the field variation of MR for compositions with $x = 0, 0.1, 0.3$ and 0.5 at temperatures close to the IM transition (or a change in slope in the resistivity).

The field variation of MR for the composition with $x = 0$ shows two distinct regions. The first region, which occurs at low fields (≤ 1.5 T), is characterized by a steep increase in the MR. For higher fields, the MR shows only a gradual increase. Similar behaviour was observed earlier in some 3D perovskites [22]. The low-field region arises from the motion of domain walls, where a reorientation of the domains takes place. The gradual increase in MR in the high-field region is due to the gradual enhancement of the magnetization due to the application of the external field, which may be termed as increased ordering within the domains.

With the addition of Cr, the steep increase in the low-field region is suppressed and the MR increases only gradually. Increasing the Cr content decreases the magnetization and could alter the domain structure, which would cause only a gradual increase in the MR. Recently, Asano *et al* [23] have reported a detailed study of the magnetotransport in the $n = 2, 3$ and ∞ members and have shown that the low-field response of the MR is greatest for $n = 2$ and decreases with dimensionality. In the present discussion, the term ‘dimensionality’ refers broadly to the extent of the interactions and not just the number of planes in the layers. In the materials under study, the interactions are stronger within the bilayers but interactions also exist across the bilayers. A comparison of figure 6 with this result of Asano *et al* [23] seems to suggest that with increasing Cr the dimensionality increases, in the sense that there is an increase in the interactions across the bilayers. We would like to mention that preliminary results from electron spin resonance (ESR) measurements on these compositions [24] are consistent with this suggestion.

4. Conclusions

We have carried out a study of Cr doping in the $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ system. With increasing Cr, charge itinerancy gives way to charge localization. The ferromagnetic Curie temperature increases slightly and then decreases as the Cr content is increased. However,

the magnetoresistance ratio is not significantly affected, which suggests that the layered manganates are more accommodative to dopants than the three-dimensional perovskites.

Acknowledgments

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