

LETTER TO THE EDITOR

Distinction between Two Types of Charge-Ordered States in the Rare Earth Manganates, $Ln_{0.5}A_{0.5}MnO_3$, Based on Chemical Melting

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Effects of cation substitution in the manganese site of charge-ordered (CO) rare earth manganates have been studied to find out how the properties vary with the average radius of the A site cations, $\langle r_A \rangle$, and the substituent cation. The insulating CO state of $Ln_{0.5}Ca_{0.5}MnO_3$ ($Ln = Nd, Gd, \text{ or } Y$) is unaffected by substitution with Al^{3+} and Fe^{3+} , but the CO state in the Nd compound ($\langle r_A \rangle = 1.17 \text{ \AA}$) is converted into a ferromagnetic metallic state by Cr^{3+} substitution. Chemical conversion of the charge-ordered state in the insulating manganates by Cr^{3+} substitution seems to occur only when $\langle r_A \rangle \geq 1.17 \text{ \AA}$. Progressive substitution of Mn^{3+} in $Nd_{0.5}Sr_{0.5}MnO_3$ ($\langle r_A \rangle = 1.24 \text{ \AA}$) with Al^{3+} and Fe^{3+} renders the material an insulator. Substitution with Cr^{3+} , however, makes it a ferromagnetic metal from 250 K ($\sim T_C$) down to low temperatures, without the intervening CO state as in the parent manganate. © 1998 Academic Press

Charge-ordering in the rare earth manganates of the type $Ln_{0.5}A_{0.5}MnO_3$ ($Ln = \text{rare earth}, A = Ca, Sr$) has been a subject of intense investigation during the past two years. The charge-ordered state in these compounds is very sensitive to the average ionic radius of the A site cations, $\langle r_A \rangle$ (1, 2). In $Nd_{0.5}Sr_{0.5}MnO_3$ with $\langle r_A \rangle = 1.24 \text{ \AA}$, the ground state which is a ferromagnetic metal (FMM) ($T_C \sim 250 \text{ K}$) transforms to a charge-ordered (CO) state on cooling to $\sim 150 \text{ K}$ (3). When $\langle r_A \rangle$ is small, as in $Y_{0.5}Ca_{0.5}MnO_3$ ($\langle r_A \rangle = 1.13 \text{ \AA}$), the ground state is a charge-ordered insulator even at room temperature, and the material does not show ferromagnetism at any temperature (4). Furthermore, the charge-ordered states of $Nd_{0.5}Sr_{0.5}MnO_3$ and $Y_{0.5}Ca_{0.5}MnO_3$ show completely different sensitivities to magnetic fields. Thus, the application of a magnetic field of 6 T transforms the CO state in $Nd_{0.5}Sr_{0.5}MnO_3$ to a metallic state, but has no effect on the CO state of

$Y_{0.5}Ca_{0.5}MnO_3$. A recent study (5) has shown that the magnetic field effect ceases when $\langle r_A \rangle \leq 1.17 \text{ \AA}$; $Nd_{0.5}Ca_{0.5}MnO_3$ with $\langle r_A \rangle = 1.17 \text{ \AA}$, however, shows CO–FMM transition on applying a field of 6 T. Clearly there are two types of charge-ordered states in the manganates, depending on the $\langle r_A \rangle$ regime (1). Substitution of different ions in the A site varies the internal pressure and markedly affects the CO and FMM states; an increase in $\langle r_A \rangle$ or internal pressure lowers the T_{CO} and increases the ferromagnetic T_C (6, 7).

We investigated whether it is possible to melt the charge-ordered states in the manganates by ion substitution in the B site and if so, whether the two types of CO states show differences. In this context, we noticed the work of Raveau *et al.* (8) who reported that the antiferromagnetic insulator $Pr_{0.5}Ca_{0.5}MnO_3$ shows an insulator–metal (I–M) transition on the substitution of Mn by Cr and Co. Damay *et al.* (9) substituted $Pr_{0.6}Ca_{0.4}MnO_3$ and found that the metallic state is induced when Mn is substituted by Fe^{3+} , Al^{3+} , Ga^{3+} , and Mg^{2+} . Barnabe *et al.* (10), on the other hand, have reported recently that an I–M transition is induced in charge-ordered $Ln_{0.5}Ca_{0.5}MnO_3$ most effectively by Cr. Maignan *et al.* (11) report a similar disappearance of charge-ordering in $Ln_{0.5}Ca_{0.5}MnO_3$ substituted by Ni. We felt that it should be possible systematically to examine the two different types of CO states, in the different $\langle r_A \rangle$ regimes, by investigating the effect of appropriate ion substitutions in the B site. For this purpose, we have studied the effect of substitution of Mn^{3+} by Al^{3+} , Fe^{3+} , and Cr^{3+} in $Ln_{0.5}A_{0.5}MnO_3$ compositions, with widely differing $\langle r_A \rangle$ values. The manganates investigated are $Y_{0.5}Ca_{0.5}MnO_3$ ($\langle r_A \rangle = 1.13 \text{ \AA}$), $Gd_{0.5}Ca_{0.5}MnO_3$ ($\langle r_A \rangle = 1.14 \text{ \AA}$), $Nd_{0.5}Ca_{0.5}MnO_3$ ($\langle r_A \rangle = 1.17 \text{ \AA}$), and $Nd_{0.5}Sr_{0.5}MnO_3$ ($\langle r_A \rangle = 1.24 \text{ \AA}$). Only the last manganate, showing FMM–CO transition, is sensitive to magnetic fields (3), while amongst the other three CO insulators, a magnetic field of 6 T melts the CO state only in the case of $Nd_{0.5}Ca_{0.5}MnO_3$ (5).

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Polycrystalline samples of the various manganate compositions were prepared by the ceramic route by heating stoichiometric proportions of the respective rare earth oxide, manganese oxides $\text{MnO}_2/\text{Mn}_3\text{O}_4$, oxides of the other transition metals, and the carbonates of the alkaline earth elements. The mixtures were first heated at 900°C for 12 h in air and then ground thoroughly, pelletized, and heated again at 1200°C in air for 12 h. The final heating was carried out at 1500°C . The gadolinium samples were finally heated at $1300^\circ\text{C}/1350^\circ\text{C}$. The phase purity of the samples was established by recording the X-ray diffraction patterns with a SEIFERT 3000 TT diffractometer. All materials studied here had an orthorhombic structure. The Mn^{4+} content was determined by redox titration using standard potassium permanganate and ferrous sulfate solution. Electrical resistivity was measured from 300 to 20 K by the four-probe method. Magnetization was measured in this temperature range by means of a vibrating sample magnetometer (Lakeshore VSM 7300).

In Fig. 1a, we show the effect of substitution of $M = \text{Al}^{3+}$, Fe^{3+} , and Cr^{3+} in the Mn site on the resistivity of $\text{Y}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$. We see that there is almost no effect of such substitution on the resistivity of $\text{Y}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-x}\text{M}_x\text{O}_3$ ($x = 0.03$) for all M . A decrease in the extent of substitution to $x = 0.01$ or an increase up to $x = 0.1$ showed no difference in behavior. We found a similar result with $\text{Gd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ (see inset of Fig. 1a), where substitution of Al^{3+} or Cr^{3+} for Mn^{3+} had no effect on the resistivity. Thus, both $\text{Y}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-x}\text{M}_x\text{O}_3$ and $\text{Gd}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-x}\text{M}_x\text{O}_3$ remain insulating from room temperature down to the lowest temperature, independent of the cation substitution on the Mn site. Since $\langle r_A \rangle$ is small ($< 1.15 \text{ \AA}$) in these two manganates, cation substitution on the Mn site may have had no effect. When we substituted the Mn site with Al or Fe in $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ ($\langle r_A \rangle = 1.17 \text{ \AA}$), there was no significant effect on the resistivity (Fig. 1b). Substitution by Cr^{3+} ($x = 0.03$ or 0.05), however, led to I–M transition around 140 K. The resistivity data on $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-x}\text{M}_x\text{O}_3$ are corroborated by the magnetization data (Fig. 2). Accordingly, when $M = \text{Cr}$ and $x = 0.03$, a FMM state emerges around 140 K. When $M = \text{Al}$ ($x = 0.03$), a CO transition occurs around 235 K, just as in the parent manganate. These results suggest that the melting of the charge-ordered state by cation substitution in the Mn site becomes possible only when $\langle r_A \rangle \geq 1.17 \text{ \AA}$, and further that only Cr^{3+} substitution gives the desired result. We may recall here that magnetic fields also affect the CO state in the manganates only when $\langle r_A \rangle \geq 1.17 \text{ \AA}$ (5). It appears that $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ with a $\langle r_A \rangle$ of 1.17 \AA is in the critical region where we observe the effect of the magnetic field, as well as with Cr^{3+} substitution in the Mn site. The question then arises as to why Cr^{3+} induces a metal–insulator transition in $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$, while Al^{3+} and Fe^{3+} do not.

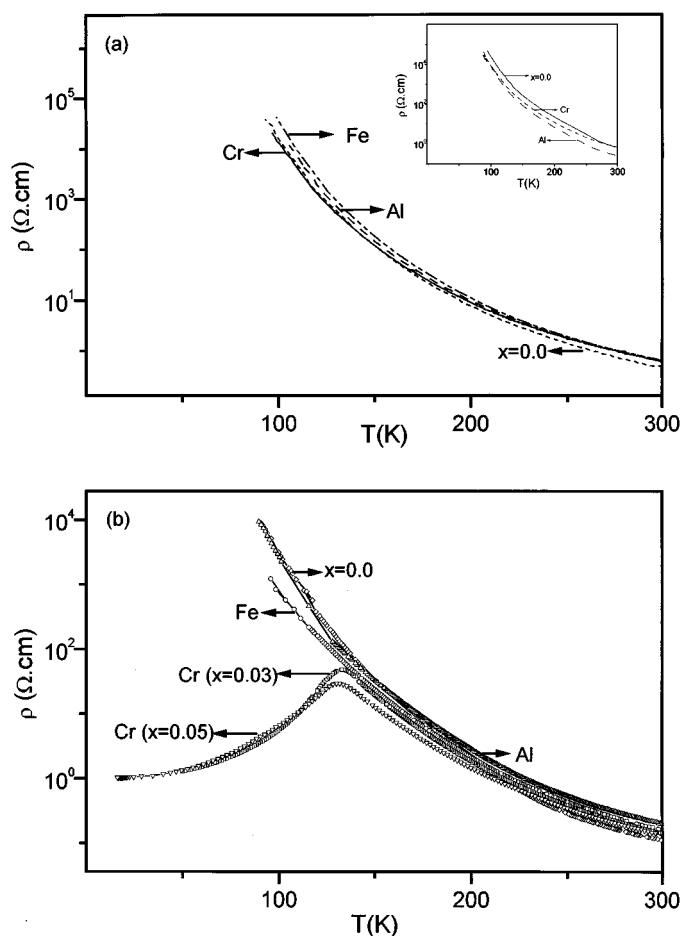


FIG. 1. Temperature variation of the resistivity of $\text{Ln}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-x}\text{M}_x\text{O}_3$: (a) $\text{Ln} = \text{Y}$; for the different cation substitutions, $x = 0.03$, (b) $\text{Ln} = \text{Nd}$, $x = 0.03$ for Al and Fe substitutions. The inset in (a) shows the data for $\text{Ln} = \text{Gd}$ ($x = 0.03$) for Al and Cr substitutions.

The six-coordination ionic radii of Fe^{3+} , Cr^{3+} , and Al^{3+} are 0.645, 0.615, and 0.535 \AA , respectively, the ionic radius of Mn^{3+} and Mn^{4+} being respectively 0.645 and 0.530 \AA . Mere cation disorder in the B site created by such substitution cannot be responsible for the observed effects, since the disorder would not vary from one cation to another. Substitution by Al^{3+} (d^0) would, however, exert a negative pressure effect, the ion being very small compared to Mn^{3+} . Fe^{3+} (d^5) is nearly the same size as Mn^{3+} and does not have any specific interaction with Mn^{3+} or Mn^{4+} . Cr^{3+} (d^3), on the other hand, can form $\text{Mn}^{3+}\text{--O--Cr}^{3+}$ units, which are analogous to $\text{Mn}^{3+}\text{--O--Mn}^{4+}$, since Mn^{4+} and Cr^{3+} have the same electronic configuration. The $\text{Mn}^{3+}\text{--O--Cr}^{3+}$ interaction is ferromagnetic, while the $\text{Mn}^{4+}\text{--O--Cr}^{3+}$ interaction is antiferromagnetic by the superexchange mechanism (12). Clearly, the presence of Cr^{3+} in the $\text{Mn}^{3+}\text{--O--Mn}^{4+}$ network perturbs the charge-ordering in the Mn network, favoring electron hopping from Mn^{3+} to

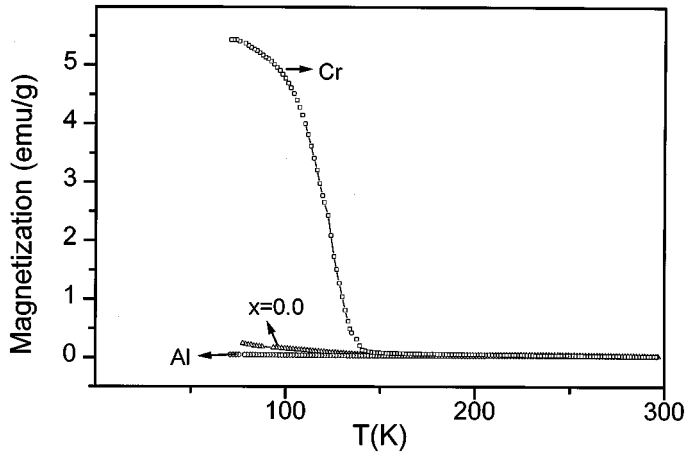


FIG. 2. Magnetization data of $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-x}\text{M}_x\text{O}_3$ ($M = \text{Cr}, \text{Al}$) with $x = 0.03$. Data for the $x = 0.0$ composition is shown for comparison.

Mn^{4+} sites, and giving rise to a FMM state due to double exchange. We should also note that there can be subtle compositional dependencies of the magnetotransport properties in such materials, showing some anisotropy as well (13).

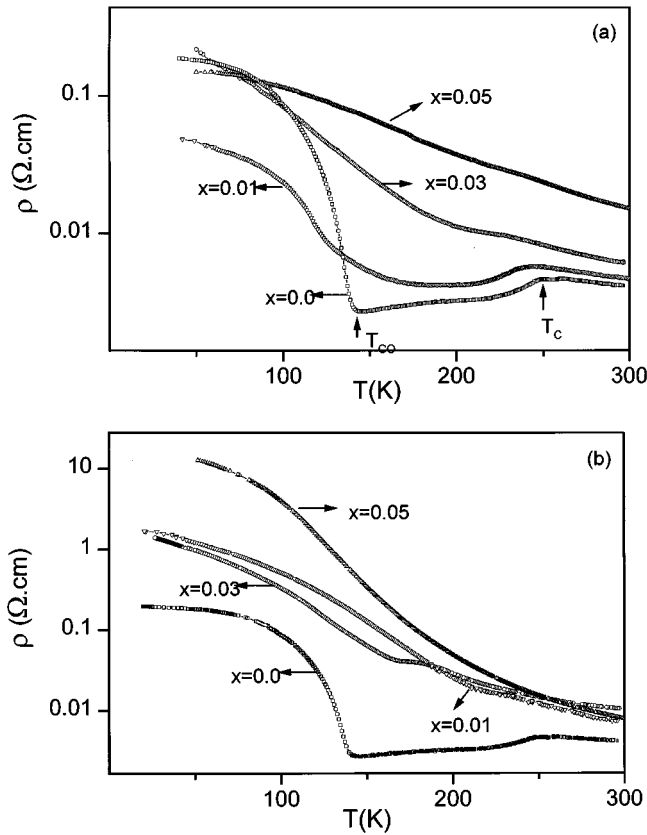


FIG. 3. Temperature variation of resistivity if $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{M}_x\text{O}_3$: (a) $M = \text{Al}$; (b) $M = \text{Fe}$. The x values are indicated.

The effect of cation substitution in the Mn site on the CO state in $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ ($\langle r_A \rangle = 1.24 \text{ \AA}$) is really interesting. In Fig. 3a, we show the resistivity behavior of $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Al}_x\text{O}_3$. When $x = 0.0$, the charge-ordering transition (T_{CO}) is at $\sim 150 \text{ K}$ and the resistivity increases markedly at this temperature. Substitution of Al in the Mn site with $x = 0.01$ slightly increases T_{CO} and decreases T_{C} . These changes are in a direction opposite to that of external pressure or substitution by large A-site cations (6, 7). Substitution of Al^{3+} in place of Mn^{3+} appears to have a negative pressure effect. When $x = 0.03$, we do not clearly see any distinction between T_{C} and T_{CO} in the resistivity data; the $x = 0.05$ composition is an insulator. The magnetization data (Fig. 4b) show that when $M = \text{Al}$ ($x = 0.03$), T_{C} is close to 250 K , but the value of magnetization gradually decreases from 200 K down, and it is difficult to pin down a value for T_{CO} . When Fe^{3+} is substituted ($x = 0.01$) in place of Mn^{3+} , there appears to be a CO transition around $\sim 200 \text{ K}$ in the resistivity curve (Fig. 3b), but we do not see a distinct FMM state, as with the Al^{3+} substitution (Fig. 3a). When $x = 0.03$ and 0.05 , the behavior of the Al^{3+}

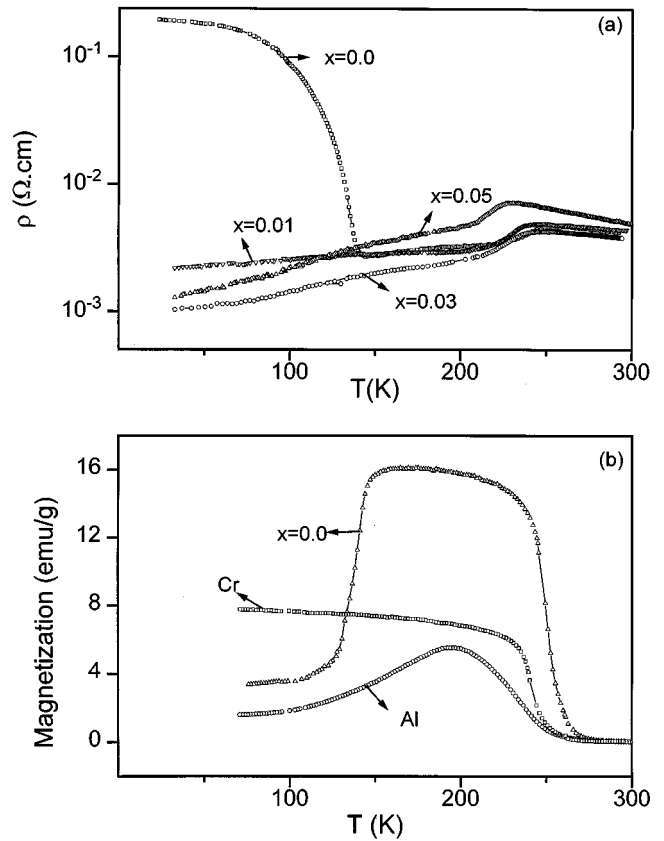


FIG. 4. (a) Temperature variation of resistivity of $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$. (b) Magnetization data of $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{M}_x\text{O}_3$ ($x = 0.03$) with $M = \text{Cr}, \text{Al}$. Data for the $x = 0.0$ composition is shown for comparison.

and Fe^{3+} compositions are comparable; the system becomes an insulator when $x = 0.05$.

The effect of Cr^{3+} substitution on the properties of $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ is indeed marked. Thus, in $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$, when $x = 0.01$, there is a slight decrease in the T_C but we do not see the resistance anomaly at T_{CO} as in the parent compound (Fig. 4a). The material is metallic below T_C , down to low temperatures. It seems that 1% Cr substitution suffices to destroy the CO state in $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$. The resistivity behavior of the $x = 0.03$ composition is similar, and the FMM state occurs from room temperature down to the lowest temperature. Such behavior is also found when $x = 0.05$. When $x = 0.1$, T_C appears to be around 210 K, but there is also a slight hump in the resistivity around 140 K in the metallic regime. The resistivity data on $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{M}_x\text{O}_3$ are nicely corroborated by the magnetization data (Fig. 4b). Accordingly, when $M = \text{Cr}$, the $x = 0.03$ and 0.05 compositions show a ferromagnetic T_C around 250 K with the sample remaining ferromagnetic down to 50 K. There is no charge-ordering transition around 150 K, as in the parent compound ($x = 0.0$).

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