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LETTER TO THE EDITOR

Charge ordering in electron-doped manganates

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Abstract. Electron-doped rare-earth manganates of the type $\text{Ca}_{1-x}\text{Ln}_x\text{MnO}_3$ ($\text{Ln} = \text{La, Nd, Gd}$ or Y) with $x = 0.2$ and 0.3 show charge ordering in the 150–270 K range, but the charge-ordering transition temperature, T_{CO} , generally decreases with the decrease in the size of the A-site cations, a trend exactly opposite to that for hole-doped manganates. On the other hand, T_{CO} increases with x or the electron concentration. These trends are also seen for $\text{Ca}_{1-x}\text{Bi}_x\text{MnO}_3$ compounds ($T_{CO} = 300$ K for $x = 0.3$) which show transitions to a more distorted orthorhombic structure below T_{CO} . In $\text{Ca}_{1-x}\text{Ln}_x\text{MnO}_3$, Cr doping does not melt the charge-ordered state, unlike the case for the hole-doped systems. $\text{CaMnO}_{2.82}$, for which electron doping is affected by anion vacancies, appears to show charge ordering at around 200 K.

Investigations of colossal magnetoresistance and related phenomena for the rare-earth manganates, reported extensively in the last few years, by and large pertain to solids of the composition $\text{Ln}_x\text{A}_{1-x}\text{MnO}_3$ ($\text{Ln} = \text{rare earth, A} = \text{Ca, Sr, } x \geq 0.5$), which involves hole doping [1, 2]. The hole-doped manganates exhibit charge ordering, particularly when $x = 4/8$ or $5/8$, and the charge-ordering transition is highly sensitive to the average radius of the A-site cations, $\langle r_A \rangle$ [2–4]. The charge-ordering transition temperature, T_{CO} , decreases with increase in $\langle r_A \rangle$, unlike the ferromagnetic Curie temperature, T_C , which increases with $\langle r_A \rangle$. Furthermore, the strain arising from the size mismatch between A-site cations affects T_C . It is found that T_C decreases with the variance, σ^2 , which is a measure of the mismatch between the A-site cations [5]. There has been some interest recently in studying the properties of electron-doped manganates where Ca is partly substituted for with a trivalent or a tetravalent cation. These studies [6] have shown that the electron concentration determines the magneto-transport properties of these materials. A study of $\text{Ca}_{1-x}\text{Bi}_x\text{MnO}_3$ ($x = 0.18$) has shown the occurrence of charge ordering accompanied by a structural transition [7]. We considered it important to investigate charge ordering in the electron-doped systems to examine the similarities, if any, with the hole-doped manganates. For this purpose, we have investigated manganates of the type $\text{Ca}_{1-x}\text{Ln}_x\text{MnO}_3$ ($\text{Ln} = \text{La, Nd, Gd}$ or Y), in particular the composition corresponding to $x = 3/8$ for which charge ordering should be favoured [8]. We have also studied the effect of electron doping on charge ordering in $\text{Ca}_{1-x}\text{Bi}_x\text{MnO}_3$ ($x = 0.2, 0.3$), paying attention to the structure changes at the charge-ordering transition. Lastly, we have examined the effect of electron doping in the parent CaMnO_3 , brought about by oxygen deficiency.

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Table 1. Properties of electron-doped manganates showing charge ordering.

Composition	$\langle r_A \rangle$ (Å)	σ^2 (Å ²)	Lattice parameters (Å)			%D(300 K)	T_{CO} (K) ^(a)
			<i>a</i>	<i>b</i>	<i>c</i>		
Ca _{0.8} La _{0.2} MnO ₃	1.187	0.0002	5.333	5.316	7.546	0.15	215 (170)
Ca _{0.64} La _{0.36} MnO ₃	1.193	0.0003	5.390	5.391	7.588	0.20	271 (254)
Ca _{0.8} Nd _{0.2} MnO ₃	1.177	0.0001	5.317	5.316	7.495	0.13	176 (154)
Ca _{0.64} Nd _{0.36} MnO ₃	1.174	0.0001	5.388	5.361	7.570	0.33	271 (253)
Ca _{0.8} Gd _{0.2} MnO ₃	1.165	0.0008	5.300	5.311	7.482	0.13	157 (139)
Ca _{0.64} Gd _{0.36} MnO ₃	1.154	0.0012	5.354	5.381	7.509	0.26	269 (252)
Ca _{0.8} Y _{0.2} MnO ₃	1.159	0.0017	5.262	5.339	7.437	0.65	182 (141)
Ca _{0.64} Y _{0.36} MnO ₃	1.142	0.0025	5.295	5.442	7.451	1.32	— (240)
Ca _{0.8} Bi _{0.2} MnO ₃	1.187	0.0002	5.326	5.329	7.531	0.03 ^b	210 (200)
Ca _{0.7} Bi _{0.3} MnO ₃	1.191	0.0003	5.349	5.396	7.537	0.47 ^b	300 (290)

^a From magnetization measurements; values in parentheses are from resistivity data.

^b Values above T_{CO} ; the values below T_{CO} are 0.3 and 0.85 respectively for $x = 0.2$ and 0.3 .

Polycrystalline samples of Ca_{1-x}Ln_xMnO₃ (Ln = La, Nd and Gd; $x = 0.1, 0.2$ and 0.36) were prepared by the ceramic route by heating stoichiometric proportions of the respective rare-earth oxides, CaCO₃ and Mn₃O₄. The mixtures were first heated at 900 °C for 12 hours in air and then ground thoroughly, pelletized and heated again at 1200 °C in air for 12 hours. The final sintering was carried out at 1400 °C. Ca_{1-x}Bi_xMnO₃ ($x = 0.2, 0.3$) samples were prepared by starting with a nitrate solution containing the appropriate ions in stoichiometric proportions. The solution was evaporated to dryness and decomposed. The mixture so obtained was preheated at 800 °C for six hours, pelletized and heated at 1200 °C for six hours in oxygen. CaMnO₃ was prepared by the oxidative decomposition of the calcite precursor CaMn(CO₃)₂ in air at 1000 °C. CaMnO_{2.82} was obtained by reducing CaMnO₃ in a hydrogen atmosphere at 350 °C for 35 minutes, maintaining the heating and cooling rates at 5 K min⁻¹. The phase purity of the samples was established by recording the x-ray diffraction (XRD) patterns with a SEIFERT 3000 TT diffractometer. Low-temperature XRD patterns of Ca_{1-x}Bi_xMnO₃ were recorded with a STOE/STADIP high-resolution x-ray diffractometer. The Mn⁴⁺ content was determined by redox titrations by employing ferrous ammonium sulphate. The electrical resistivity was measured from 300 K to 20 K by the four-probe method. The magnetization was measured by means of a vibrating-sample magnetometer (Lakeshore VSM 7300) by employing a field of 100 G. Magnetic susceptibility measurements were also carried out using a Lewis Coil Force Magnetometer. All of the manganates studied by us gave good x-ray diffraction patterns which could be indexed on the basis of an orthorhombic unit cell. In table 1, we list the unit-cell parameters along with the average A-site ion radius, $\langle r_A \rangle$, values of σ^2 [5] and the orthorhombic distortion index, %D [4].

The compounds Ca_{1-x}Ln_xMnO₃ with $x = 0.1$ do not show evidence for charge-ordering properties in the 120–300 K range, and instead exhibit ferromagnetic interactions akin to those in spin glasses [6]. The compounds with $x = 0.2$ show peaks in magnetization due to charge ordering at 215, 176 and 157 K for Ln = La, Nd and Gd respectively (figure 1(a)). At these temperatures, there is a marked increase in electrical resistivity as can be seen in figure 1(b). The compounds with compositions corresponding to the optimal 3/8 doping ($x = 0.36$) show interesting electrical and magnetic properties. Thus, the magnetization exhibits a broad maximum at around 270 K when Ln = La, Nd or Gd (figure 2(a)). Around this temperature, there is a small, but definitive, jump in resistivity (figure 2(b)). An examination of the variation of T_{CO} in Ca_{1-x}Ln_xMnO₃ suggests that T_{CO} increases with the increase in x or the electron

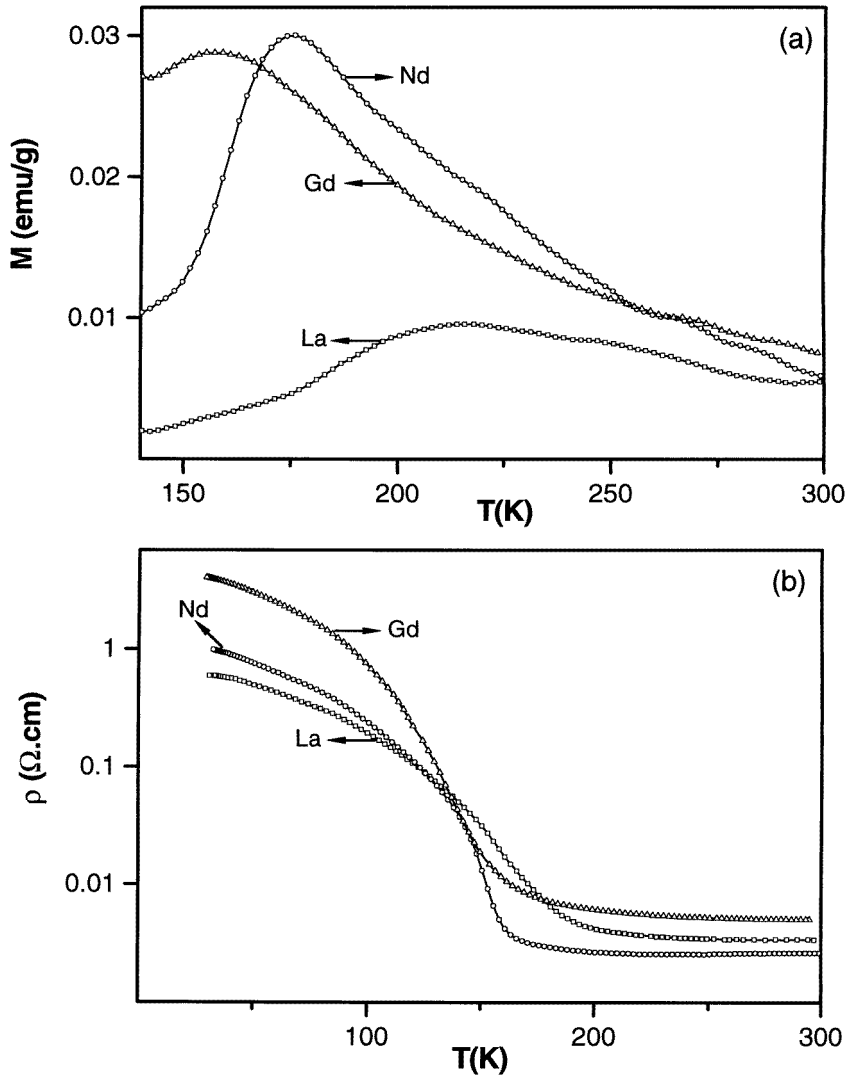


Figure 1. The temperature variation of (a) the magnetization and (b) the electrical resistivity of $\text{Ca}_{0.8}\text{Ln}_{0.2}\text{MnO}_3$ (Ln = La, Nd, Gd).

concentration. When $x = 0.2$, T_{CO} decreases significantly, although $\langle r_A \rangle$ decreases with only a marginal change in the σ^2 -value (table 1). When $x = 0.36$, T_{CO} is nearly constant despite the marked decrease in $\langle r_A \rangle$ and fairly high values of σ^2 when Ln = Gd. It appears that at optimal electron doping, $\langle r_A \rangle$ has no effect on T_{CO} . The yttrium-substituted materials with the smallest values of $\langle r_A \rangle$ fail to exhibit high values of T_{CO} and fall in line with the other manganates discussed above (table 1). These trends for the electron-doped $\text{Ca}_{1-x}\text{Ln}_x\text{MnO}_3$ compounds are different from those for the hole-doped $\text{Ln}_{1-x}\text{Ca}_x\text{MnO}_3$ compounds, where T_{CO} increases with decrease in $\langle r_A \rangle$ [4]. Interestingly, the decrease in T_{CO} with $\langle r_A \rangle$ when $x = 0.2$ is in the same direction as the decrease in ferromagnetic interaction.

The electron-doped manganates with $x = 0.36$ differ from the corresponding hole-

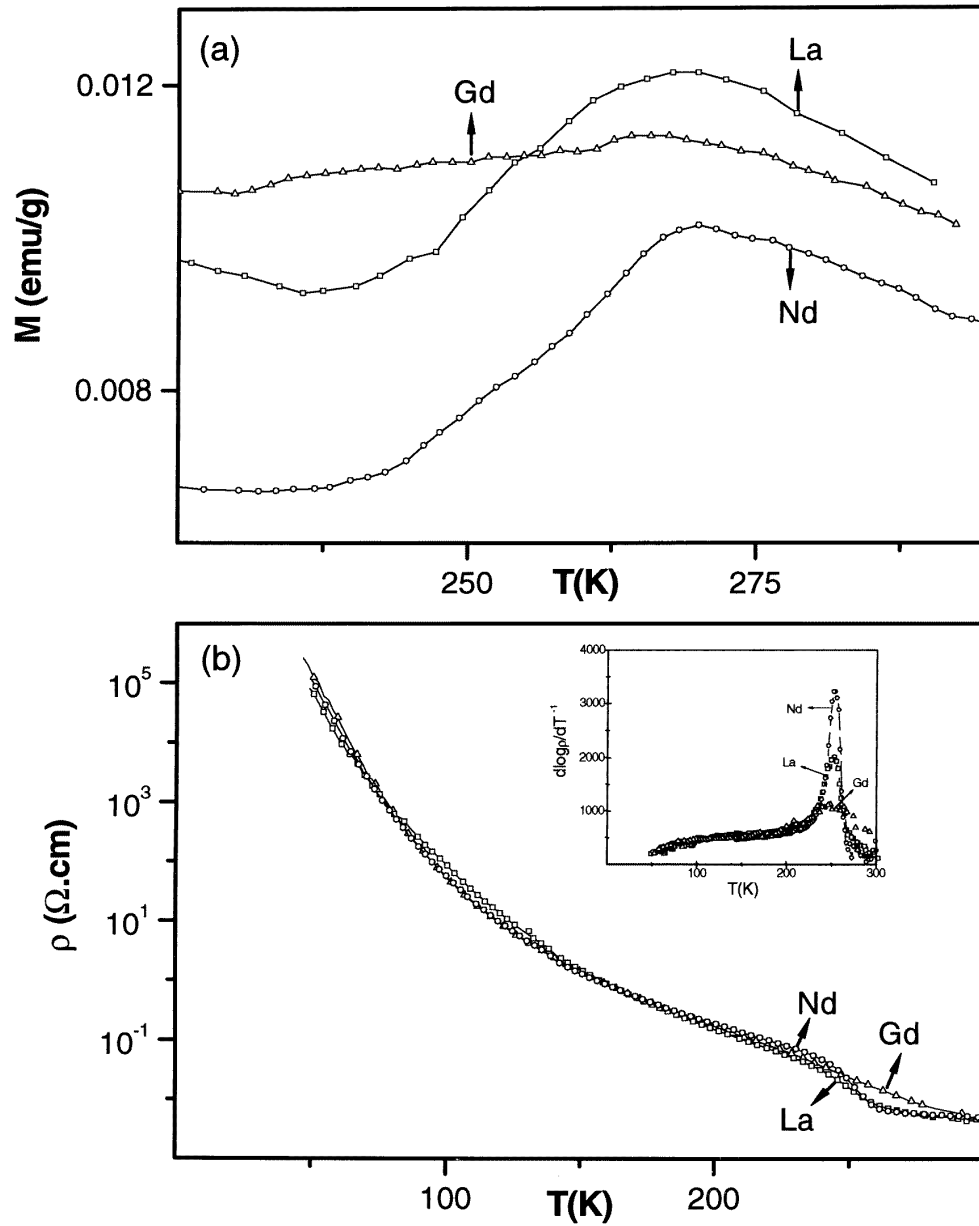


Figure 2. The temperature variation of (a) the magnetization and (b) the electrical resistivity of $\text{Ca}_{0.64}\text{Ln}_{0.36}\text{MnO}_3$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Gd}$). In the inset of (b), the temperature variation of $d(\log \rho)/dT^{-1}$ (or the activation energy) is shown.

doped manganates in another respect. The charge-ordered states in hole-doped manganates such as $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ and $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ are melted by Cr substitution, giving rise to a ferromagnetic metallic state, provided that $\langle r_A \rangle \geq 1.17 \text{ \AA}$ [9]. In $\text{Ca}_{1-x}\text{Ln}_x\text{MnO}_3$ ($x = 0.36$, $\text{Ln} = \text{La}, \text{Nd}$ or Gd), however, 3% doping with Cr does not completely destroy the charge ordering. We do not observe an insulator-metal transition on Cr doping as in the case of some of

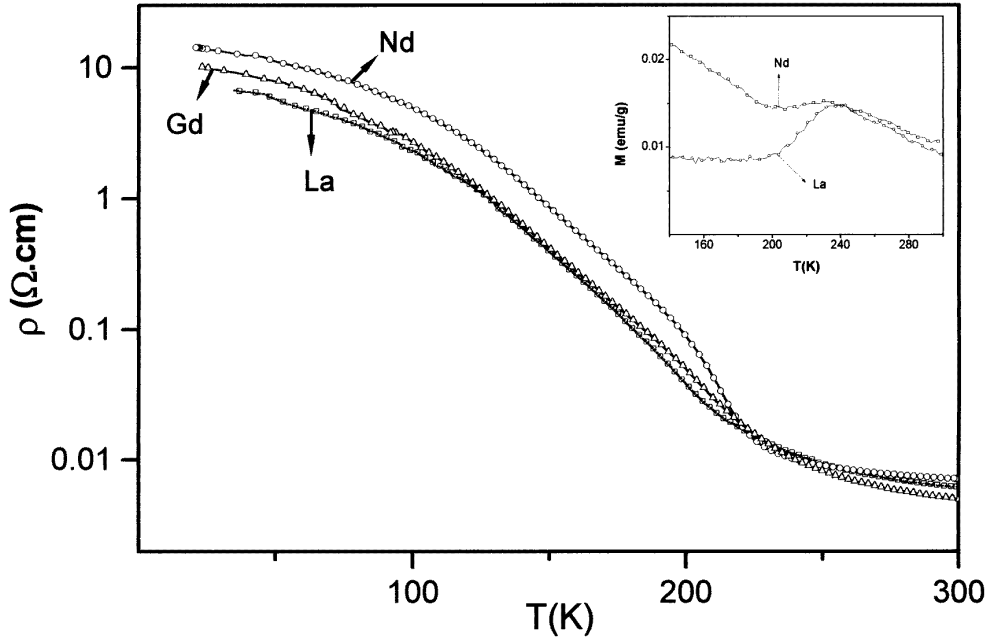


Figure 3. The effect of 3% Cr doping on the electrical resistivity of $\text{Ca}_{0.64}\text{Ln}_{0.36}\text{MnO}_3$ (Ln = La, Nd, Gd). In the inset, typical magnetization data showing charge-ordering transitions are shown.

the hole-doped charge-ordered materials (figure 3). Furthermore, magnetization measurements show that charge ordering persists, with the transition occurring at a slightly lower temperature (~ 240 K) as shown in the inset of figure 3. Increasing the Cr content to 10% makes the materials more insulating down to low temperatures. The absence of any significant effect of Cr doping in the electron-doped manganates, even when $\langle r_A \rangle \geq 1.17 \text{ \AA}$ (table 1) is to be contrasted with the marked effect found at similar doping levels in the case of hole-doped manganates [9].

The compounds $\text{Ca}_{1-x}\text{Bi}_x\text{MnO}_3$ show certain distinctive features as regards charge ordering. In $\text{Ca}_{0.82}\text{Bi}_{0.18}\text{MnO}_3$ a regime of ferromagnetic spin fluctuations due to double exchange changes to a regime of antiferromagnetic spin fluctuations at around T_{CO} [7]. Below T_{CO} , the magnitude of the ferromagnetic interaction decreases. We have studied the charge-ordering characteristics of $\text{Ca}_{1-x}\text{Bi}_x\text{MnO}_3$ with $x = 0.2$ and 0.3 by measuring various properties. The magnetic susceptibilities of $\text{Ca}_{1-x}\text{Bi}_x\text{MnO}_3$ show distinct maxima at 210 and 300 K respectively when $x = 0.2$ and 0.3 (figure 4(a)), while the resistivity shows increases at these temperatures (see the inset of figure 4(a)). When $x = 0.2$, the parameters a , b and $c/\sqrt{2}$ are close to one another at 300 K, but diverge below 210 K. The compound with $x = 0.3$ undergoes marked changes in the orthorhombic unit-cell parameters at around 300 K. Above these transition temperatures, the structures are close to being cubic and, accordingly, the orthorhombic distortion index, % D , increases markedly below T_{CO} (figure 4(b)). Here again, T_{CO} increases with x even though $\langle r_A \rangle$ increases. It is also noteworthy that the composition with $x = 0.3$ in the Bi system shows one of the highest T_{CO} -values found (300 K) to date in the manganates. What appears to be true of all of the electron-doped manganates is that T_{CO} generally increases with the increase in % D . We may recall that % D is a measure of the deviation from the ideal cubic structure. Also noteworthy is the fact that σ^2 , which is a measure of the A-site ion-size mismatch [5], has little or no effect on T_{CO} in the electron-doped

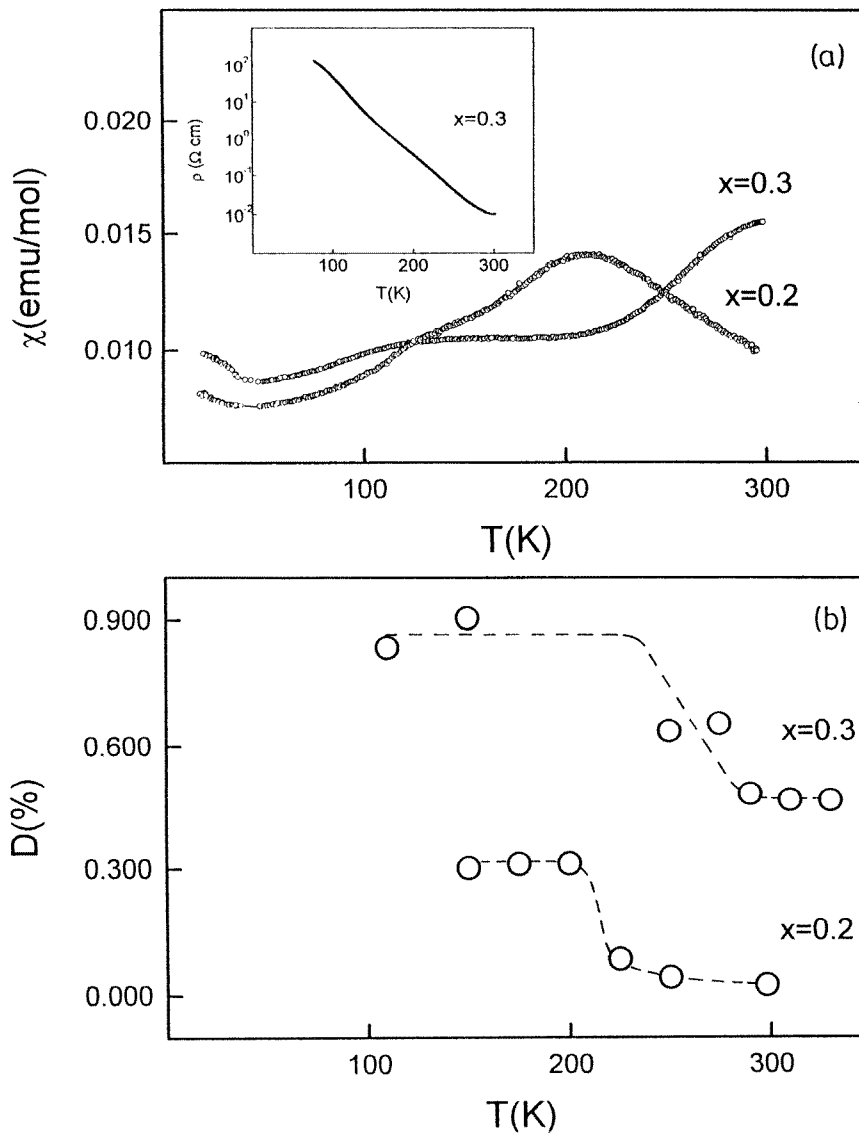


Figure 4. The temperature variation of (a) the magnetic susceptibility and (b) the orthorhombic lattice distortion index of $\text{Ca}_{1-x}\text{Bi}_x\text{MnO}_3$. In the inset of (a), typical electrical resistivity data for the composition with $x = 0.3$ are shown.

manganates (table 1). The increase in T_{CO} with x or $\langle r_A \rangle$ found in all of these manganates (table 1) suggests that the magnitude of the ferromagnetic interaction ($T > T_{CO}$) may play a role in determining the charge-ordering characteristics.

A comment on oxygen-deficient $\text{CaMnO}_{3-\delta}$ is now in order. These compounds show oxygen vacancy ordering at $\delta = 0.2, 0.25$ etc [10, 11]. The composition with $\delta = 0.18$ corresponds to the optimal $3/8$ doping which should give rise to charge ordering. We have studied the electrical and magnetic properties of $\text{CaMnO}_{2.82}$. Although we encountered some difficulty in obtaining exactly reproducible behaviour, we have observed a broad magnetic

susceptibility anomaly centred at around 200 K. While it is difficult to delineate the effects due to vacancy ordering and charge ordering, we believe that the similarity between the magnetic anomaly observed in $\text{CaMnO}_{2.82}$ and that for the compounds $\text{Ca}_{1-x}\text{Ln}_x\text{MnO}_3$ (table 1, figure 2) is noteworthy. The value of $\langle r_A \rangle$ for $\text{CaMnO}_{2.82}$ (1.182 Å) is comparable to those for $\text{Ca}_{0.8}\text{Bi}_{0.2}\text{MnO}_3$ and $\text{Ca}_{0.8}\text{La}_{0.2}\text{MnO}_3$ with T_{CO} -values of 210 K and 215 K respectively.

In conclusion, the present study demonstrates that the charge ordering in electron-doped manganates is distinctly different from that in the analogous hole-doped systems. In a given family of manganates, the charge-ordering transition temperature increases with the electron concentration and the magnitude of the ferromagnetic interaction, rather than with decrease in $\langle r_A \rangle$. In fact, T_{CO} decreases with decrease in $\langle r_A \rangle$, unlike in the case for the hole-doped manganates, where it increases.

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