An investigation of the re-entrant ferromagnetic transition in rare earth manganates in the regime of competing charge-ordering and ferromagnetic interactions

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P V Vanitha and C N R Rao[1]

Chemistry and Physics of Materials Unit and CSIR Centre of Excellence in Chemistry, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore 560 064, India

E-mail: cnrrao@jncasr.ac.in

Abstract
Manganates of the compositions $Nd_{0.5-x}La_xCa_{0.5}MnO_3$ and $Pr_{0.5-x}La_xCa_{0.5}MnO_3$, with the average A-site cation radius, $\langle r_A \rangle$, in the range 1.17–1.20 Å, are charge ordered at ordinary temperatures ($T_{CO} \sim 240$ K), and undergo a re-entrant transition to a ferromagnetic state on cooling ($T_C < T_{CO}$). The ferromagnetic Curie temperature, T_C, of the re-entrant transition increases markedly with x or $\langle r_A \rangle$ in the two series of compounds. The plots of T_C and T_{CO} against $\langle r_A \rangle$ show that the two curves intersect around a $\langle r_A \rangle$ value of 1.195 Å, below which $T_{CO} > T_C$. Site disorder due to the size mismatch of the A-site cations, σ^2, has a marked effect on the re-entrant transition temperature, T_C. Thus, in a series of manganates of the type $Ln_{0.5}A_{0.5}MnO_3$ with a fixed $\langle r_A \rangle$ value of 1.185 Å, the T_C decreases markedly with increase in site disorder, suggesting that the re-entrant transition can be entirely suppressed at a sufficiently high value of σ^2. Between T_{CO} and T_C, the CO and FM states are likely to coexist, the coexistence temperature regime decreasing with increasing $\langle r_A \rangle$, and increasing with σ^2 at a fixed $\langle r_A \rangle$.

1. Introduction

Recent investigations of the rare earth manganates of the composition $Ln_{1-x}A_xMnO_3$ (Ln = rare earth, A = alkaline earth) have revealed several interesting properties and phenomena in these compounds such as charge ordering (CO) and phase segregation in addition to colossal magnetoresistance (CMR) [1, 2]. One of the important factors which affects the properties of the manganates is the average radius of the A-site cations, $\langle r_A \rangle$ [2–5]. Thus, the

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[1] Corresponding author.

ferromagnetic Curie temperature, T_C, as well as the CO transition temperature, T_{CO}, depend markedly on $\langle r_A \rangle$. In the charge-ordered manganates, the role of $\langle r_A \rangle$ is indeed profound in that those with very small $\langle r_A \rangle$ (say <1.18 Å) have a robust charge-ordered antiferromagnetic state which is not affected by magnetic fields or impurity doping at the B-site [2]. $Nd_{0.5}Sr_{0.5}MnO_3$ with a $\langle r_A \rangle$ of 1.24 Å has a ferromagnetic metallic (FMM) ground state ($T_C = 250$ K), which transforms to a charge-ordered CE-type antiferromagnetic state on cooling to 150 K. The CO state in this compound is readily transformed to a ferromagnetic metallic state by the application of a magnetic field or by doping the B-site with Cr or Ru [6,7]. $Nd_{0.5}Ca_{0.5}MnO_3$ with a $\langle r_A \rangle$ of 1.17 Å exhibits a T_{CO} of 240 K followed by a transition to the CE type antiferromagnetic state on cooling to 150 K and the CO state can be melted on application of high magnetic fields or doping at the B-site [8]. $La_{0.5}Ca_{0.5}MnO_3$ ($\langle r_A \rangle = 1.198$ Å) has a T_C of 225 K and undergoes a transition to the antiferromagnetic CO state (CE type) at 135 K. This transition coincides with a change from incommensurate to nearly commensurate CO [9]. There is a two-phase narrow temperature regime where the ferromagnetic and CO phases coexist. Clearly, the $\langle r_A \rangle$ regime between 1.17 and 1.22 Å is a complex one with competing ferromagnetic and CO interactions.

$Nd_{0.25}La_{0.25}Ca_{0.5}MnO_3$ with a $\langle r_A \rangle$ of 1.185 Å has been investigated in some detail [10]. This manganate shows an incipient charge-ordered state below $\sim$200 K which becomes unstable on cooling to $\sim$150 K, with the material undergoing a transition to a charge-delocalized FM state [10]. The transition has been considered to be a re-entrant transition since the CO insulating state reverts back to an FMM state. This is in a direction opposite to that normally found in the CMR manganates, where an FMM state goes to a CO AFM state on cooling. It is noteworthy that the AFM correlations in this manganate are short range. At the CO–FM transition, there is a sharp decrease in the electrical resistivity and an increase in the magnetization characteristic of a ferromagnetic ordering. It appears that two phases exist over a region of at least 50 K near the transition. The $(La_{1-z}Nd_z)_{1-x}Ca_xMnO_3$ system has been studied by Moritomo [11], who finds that the ground state at a fixed x value changes the FMM state to a CO insulating state with increase in z. He reports an electronic phase separation which dominates in a wide x–z parameter regime around the FM–CO phase boundary. We considered it important to study the nature of the CO state and the re-entrant ferromagnetic state in the manganates in the $\langle r_A \rangle$ regime 1.17–1.20 Å where the competition between the two interactions is prominent, giving rise to interesting magnetic and electrical properties. In particular, we wanted to examine the role of $\langle r_A \rangle$ as well as of the site disorder arising from size mismatch of the A-site cations, on the ferromagnetism and CO in these manganates. It is indeed well established that both ferromagnetic T_C and the T_{CO} are strongly affected by site disorder [12–14]. Site disorder arising from the size mismatch of the A-site cations is quantified in terms of the variance, σ^2, as defined by

$$\sigma^2 = \sum x_i r_i^2 - \langle r_A \rangle^2$$

where x_i is the fractional occupancy of A ions and r_i is the corresponding ionic radii. For this purpose, we have investigated two series of manganates, $Nd_{0.5-x}La_xCa_{0.5}MnO_3$ and $Pr_{0.5-x}La_xCa_{0.5}MnO_3$, with $\langle r_A \rangle$ values in the range 1.172–1.198 Å. We have also examined a series of manganates with a fixed $\langle r_A \rangle$ value of 1.185 Å corresponding to $Nd_{0.25}La_{0.25}Ca_{0.5}MnO_3$ to examine the effect of size disorder, σ^2. The study delineates the effects of $\langle r_A \rangle$ and σ^2 on the re-entrant ferromagnetic transition in the manganates with $\langle r_A \rangle$ values in the complex regime of competing CO and FM interactions.

2. Experimental procedure

Polycrystalline samples $Nd_{0.5-x}La_xCa_{0.5}MnO_3$, $Pr_{0.5-x}La_xCa_{0.5}MnO_3$ and $Ln_{0.5-x}Ln'_xCa_{0.5-y}Sr_yMnO_3$ ($\langle r_A \rangle = 1.185$ Å) were prepared by the conventional ceramic method. Stoichiometric

Table 1. Structure and properties of $Ln_{0.5-x}La_xCa_{0.5}MnO_3$ (Ln = Nd, Pr).

Composition	$\langle r_A \rangle$ (Å)	σ^2 (Å²)	Lattice parameter (Å)			T_C (K)	T_{CO} (K)	T_p (K)
			a	b	c			
$Nd_{0.5}Ca_{0.5}MnO_3$	1.172	0.0001	5.392	7.589	5.376	—	240	—
$Nd_{0.4}La_{0.1}Ca_{0.5}MnO_3$	1.177	0.0002	5.400	7.603	5.397	—	~245	~100
$Nd_{0.35}La_{0.15}Ca_{0.5}MnO_3$	1.179	0.0003	5.404	7.631	5.402	~118	~245	~115
$Pr_{0.5}Ca_{0.5}MnO_3$	1.1795	0.0000	5.401	7.630	5.391	~154[a]	235	—
$Nd_{0.3}La_{0.2}Ca_{0.5}MnO_3$	1.182	0.0003	5.409	7.633	5.404	118	237	125
$Nd_{0.25}La_{0.25}Ca_{0.5}MnO_3$	1.185	0.0004	5.416	7.636	5.410	127	239	137
$Pr_{0.35}La_{0.15}Ca_{0.5}MnO_3$	1.185	0.0002	5.411	7.647	5.410	138	239	136
$Nd_{0.2}La_{0.3}Ca_{0.5}MnO_3$	1.187	0.0004	5.417	7.637	5.413	136	242	144
$Pr_{0.25}La_{0.25}Ca_{0.5}MnO_3$	1.189	0.0002	5.413	7.657	5.401	150	237	148
$Nd_{0.15}La_{0.35}Ca_{0.5}MnO_3$	1.190	0.0004	5.416	7.635	5.418	155	226	155
$Pr_{0.15}La_{0.35}Ca_{0.5}MnO_3$	1.192	0.0003	5.417	7.665	5.403	185	234	168
$Nd_{0.1}La_{0.4}Ca_{0.5}MnO_3$	1.193	0.0004	5.416	7.649	5.427	177	—	176
$La_{0.5}Ca_{0.5}MnO_3$	1.198	0.0003	5.418	7.639	5.427	225	135	—

[a] Corresponds to T_N in this composition.

Table 2. Structure and properties of $Ln_{0.5-x}Ln'_xCa_{0.5-y}Sr_yMnO_3$ with a fixed $\langle r_A \rangle$ of 1.185 Å.

Composition	σ^2 (Å²)	Lattice parameter (Å)			T_C (K)	T_{CO} (K)	T_p (K)
		a	b	c			
$Pr_{0.35}La_{0.15}Ca_{0.5}MnO_3$	0.0002	5.411	7.647	5.410	138	239	136
$Nd_{0.25}La_{0.25}Ca_{0.5}MnO_3$	0.0004	5.416	7.636	5.410	127	239	137
$Sm_{0.15}La_{0.35}Ca_{0.5}MnO_3$	0.0008	5.414	7.636	5.408	105	238	108
$Nd_{0.3}Sm_{0.2}Ca_{0.35}Sr_{0.15}MnO_3$	0.0031	5.401	7.642	5.398	105	221	103
$Gd_{0.3}Nd_{0.2}Ca_{0.27}Sr_{0.23}MnO_3$	0.0055	5.423	7.641	5.401	79	220	78

mixtures of the respective rare earth oxides, alkaline earth carbonates and MnO_2 were ground and heated at 900 °C in air followed by heating at 1000 and 1200 °C for 12 h each in air. The powders thus obtained were pelletized and the pellets sintered at 1400 °C in air. The phase purity of the samples was established by recording the x-ray diffraction patterns in the 2θ range of 10°–100° with a Seiferts 3000 TT diffractometer. Electrical resistivity (ρ) measurements were carried out from room temperature to 20 K by the four-probe method. DC magnetization (M) measurements were made at 100 Oe using a vibrating sample magnetometer (Lakeshore 7300).

In tables 1 and 2, we have listed the values of $\langle r_A \rangle$, σ^2 and the lattice parameters along with those of the ferromagnetic Curie temperature, T_C, and the CO temperature, T_{CO}. The T_C values were obtained from M–T curves, taking the point where there is an abrupt increase in M as the T_C. T_{CO} values were obtained from the magnetization measurements by the procedure mentioned in our earlier paper [14]. We have not used the resistivity data since they do not give definitive values of T_{CO} in these materials. In the systems studied (other than in the parent $Nd_{0.5}(Pr_{0.5})Ca_{0.5}MnO_3$) we do not see a clear AFM transition since the CO state transforms to the FM state on cooling. In the two parent compounds, however, the CO state transforms to an AFM state and no FM state is found on cooling. In tables 1 and 2, we have also listed the insulator–metal transition temperature, T_p, as obtained from the electrical resistivity measurements. The value of T_p corresponds to the maximum in the ρ–T curve.
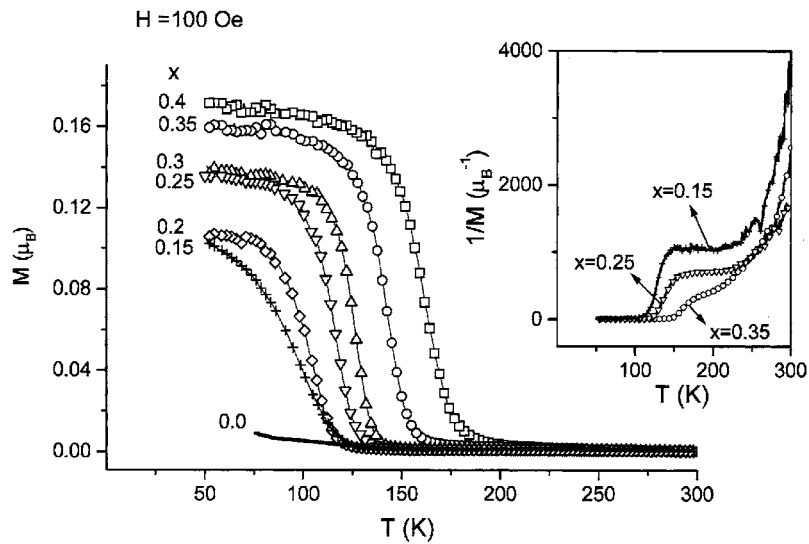
Figure 1. Temperature variation of the magnetization, M, of $Nd_{0.5-x}La_xCa_{0.5}MnO_3$. The inset shows the variation of inverse magnetization with temperature.

3. Results and discussion

In figure 1, we show the temperature variation of the magnetization, M, of the $Nd_{0.5-x}La_xCa_{0.5}MnO_3$ series of manganates. The material becomes ferromagnetic even for $x = 0.15$. The ferromagnetic Curie temperature, T_C, as well as the saturation magnetization of the material increase with increase in x from $\sim$118 K for $x = 0.15$ to 177 K when $x = 0.4$. The plot of inverse magnetization versus temperature in the inset of figure 1 shows how the CO transition temperature, T_{CO}, as evidenced from the broad minimum in the curve, varies with x. The T_{CO} of 240 K for the $x = 0.0$ composition changes only slightly as the x value is increased to 0.35.

In figure 2, we show the electrical resistivity data of $Nd_{0.5-x}La_xCa_{0.5}MnO_3$ to demonstrate the effect of substitution of La in place of Nd. The $x = 0.0$ composition is an insulator down to low temperatures. As the value of x is increased, an insulator–metal (I–M) transition manifests itself. The I–M transition temperature, T_p, increases with x from $\sim$100 K for $x = 0.1$ to 176 K when $x = 0.4$. The I–M transition temperature is close to the ferromagnetic Curie temperature, T_C.

The magnetic and electrical properties of the $Pr_{0.5-x}La_xCa_{0.5}MnO_3$ series of manganates are shown in figure 3. Here again, the material becomes ferromagnetic on substitution of La in place of Pr, with the T_C varying from 138 K for $x = 0.15$ to 185 K for $x = 0.35$. The inset in figure 3(a) shows how the T_{CO} varies with x in this series of manganates. The resistivity data in figure 3(b) show that the I–M transition temperature, corresponding to the peak in the resistivity–temperature curve, T_p, increases with increase in x just as in the case of the $Nd_{0.5-x}La_xCa_{0.5}MnO_3$ system, with the T_p values lying close to those of T_C.

In the $Nd_{0.5-x}La_xCa_{0.5}MnO_3$ and $Pr_{0.5-x}La_xCa_{0.5}MnO_3$ series of manganates (table 1) studied by us, the ferromagnetic transition occurs below the CO transition just as in $Nd_{0.25}La_{0.25}Ca_{0.5}MnO_3$. This is unlike the situation in the manganates with $\langle r_A \rangle > 1.20$ Å, where T_C is almost always greater than T_{CO}. We have plotted the T_C and T_{CO} values as well as the I–M transition temperature, T_p, against $\langle r_A \rangle$ in figure 4. The T_C increases with increase in
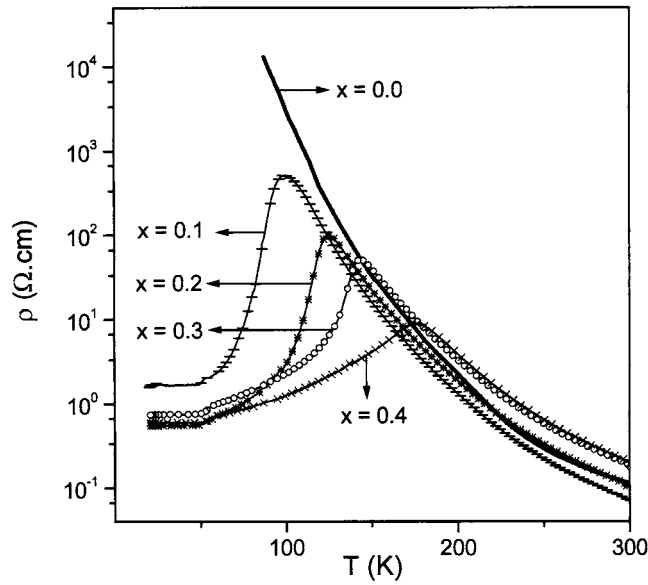
Figure 2. Temperature variation of the resistivity, ρ, of $Nd_{0.5-x}La_xCa_{0.5}MnO_3$.

$\langle r_A \rangle$ as expected. The CO transition temperature, T_{CO}, does not vary significantly with $\langle r_A \rangle$ in this regime. When $\langle r_A \rangle$ is slightly higher, say $\geqslant 1.19$ Å as in $La_{0.5}Ca_{0.5}MnO_3$, the CO transition occurs below the FM transition. In other words, the T_{CO}–$\langle r_A \rangle$ and T_C–$\langle r_A \rangle$ curves intersect around a $\langle r_A \rangle$ of 1.195 Å. This would mean that the nature of the ground state changes across this $\langle r_A \rangle$. This is indeed a fascinating feature of the rare earth manganates. Depending on the $\langle r_A \rangle$, the CO or the FM state can be the ground state, giving rise to $T_{CO} > T_C$ or $T_C > T_{CO}$ behaviour. That there is a critical cross-over point around $\langle r_A \rangle = 1.195$ Å is noteworthy.

$Nd_{0.5}Ca_{0.5}MnO_3$ has been found to exhibit ferromagnetic excitations at low temperatures even in the AFM regime [8], even though it has been considered to be a pure CO material [11]. In $Nd_{0.25}La_{0.25}Ca_{0.5}MnO_3$, there would be a coexistence region between the T_{CO} ($\sim$240 K) and the T_C ($\sim$140 K). A similar coexistence region is known to occur in $La_{0.5}Ca_{0.5}MnO_3$. The temperature range of the coexistence regime appears to decrease with the increase in x in $Nd_{0.5-x}La_xCa_{0.5}MnO_3$, accompanying an increase in $\langle r_A \rangle$, as can be surmised from figure 4. Moritomo [11] found the so-called phase separation regime in $Nd_{0.5-x}La_xCa_{0.5}MnO_3$ in the composition regime of $x = 0.2$–0.5. The systems studied by us (table 1) are, by and large, in this regime, although we find the $T_{CO} > T_C$ behaviour in a wider composition regime (0.1 < x < 0.5).

One may suspect that the results discussed above are partly from site disorder. It is to be noted, however, that, in the manganates studied (table 1), the value of σ^2 is in the range of 0.0001–0.0004 Å^2. We can, therefore, consider the observed variation in T_C and T_{CO} in figure 4 to be almost entirely due to the effect of $\langle r_A \rangle$. In order to examine the effect of size mismatch on the magnetic and electrical properties on the re-entrant FM transition, we have studied a series of manganates with a fixed $\langle r_A \rangle$ value of 1.185 Å (table 2). We show the temperature variation of magnetization and electrical resistivity for these manganates in figures 5(a) and (b) respectively. It is remarkable that the saturation magnetization as well as the T_C decrease markedly with increase in σ^2 as shown in figure 5(a). Thus, the T_C of 138 K for $\sigma^2 = 0.0002$ Å^2 decreases to 79 K for $\sigma^2 = 0.0055$ Å^2. Accompanied by this change,
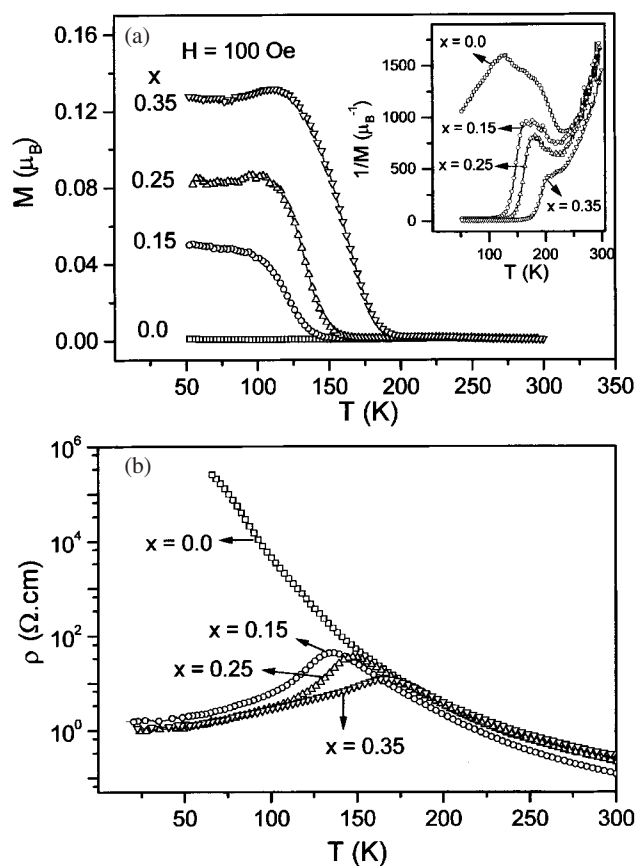
Figure 3. Temperature variation of (a) the magnetization M and (b) the resistivity ρ of $Pr_{0.5-x}La_xCa_{0.5}MnO_3$. The inset in (a) shows the variation of inverse magnetization with temperature.
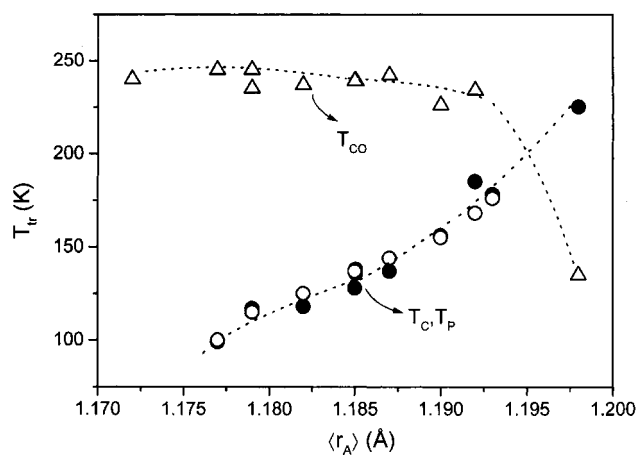

Figure 4. Variation of ferromagnetic Curie temperature, T_C, the I–M transition temperature, T_p, and the CO transition temperature, T_{CO}, with $\langle r_A \rangle$ in the manganates $Ln_{0.5-x}La_xCa_{0.5}MnO_3$ (Ln = Nd, Pr). Closed and open circles represent T_C and T_p respectively. Dotted lines are guides to the eyes.
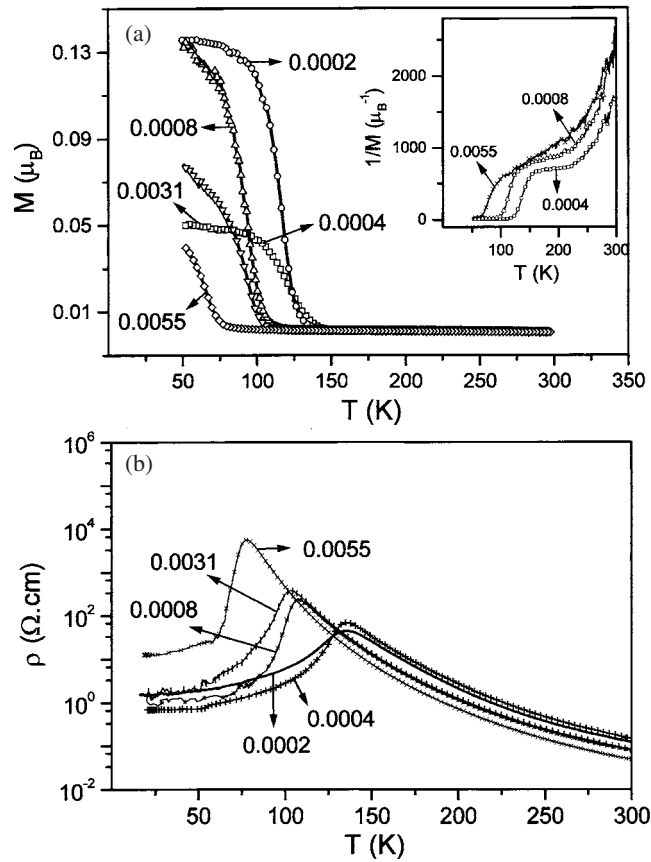
Figure 5. Temperature variation of (a) the magnetization and (b) the resistivity of the $Ln_{0.5}A_{0.5}MnO_3$ series of manganates with a fixed $\langle r_A \rangle$ of 1.185 Å. The inset in (a) shows the variation of inverse magnetization with temperature.

we also see a decrease in the temperature corresponding to the I–M transition, T_p, from 136 K for $\sigma^2 = 0.0002$ Å^2 to 78 K when $\sigma^2 = 0.0055$ Å^2. It appears that the re-entrant ferromagnetic transition can be entirely suppressed by increasing σ^2 sufficiently around a $\langle r_A \rangle$ of 1.19 Å. The variation of inverse magnetization as a function of temperature shown in the inset of figure 5(a) shows how T_{CO} decreases slightly with increase in σ^2.

In figure 6, we have plotted the variation of T_C (T_p) and T_{CO} against σ^2 for the series of manganates with a fixed $\langle r_A \rangle$ of 1.185 Å. There is a fairly good linear relationship of T_C (T_p) and T_{CO} with σ^2. The T_C (T_p)–σ^2 plot has a slope of $10\,000 \pm 2600$ K Å^{-2} with an intercept (T_C^0) of 132 ± 7 K. The T_{CO}–σ^2 plot has a slope of 4110 ± 870 K Å^{-2} with an intercept (T_{CO}^0) of 240 ± 2 K. The T_C^0 and T_{CO}^0 values represent the experimental estimates of the ideal ferromagnetic and charge-ordering transition temperatures that would be observed in the manganates with $\langle r_A \rangle$ of 1.185 Å in the absence of size mismatch. We have carried out studies on a few manganates with a fixed $\langle r_A \rangle$ of 1.189 Å and find that the variations of T_C and T_{CO} with σ^2 in this series follow trends similar to those in figure 6. Thus, for σ^2 values of 0.0007 and 0.0030 Å^2 (for $\langle r_A \rangle = 1.189$ Å), the T_C values are 136 and 68 K respectively while the corresponding T_{CO} values are 230 and 220 K. The estimates of T_C^0 and T_{CO}^0 found by us for $\langle r_A \rangle$ of 1.185 Å are in line with the results of earlier studies on the $Ln_{0.5}A_{0.5}MnO_3$ systems

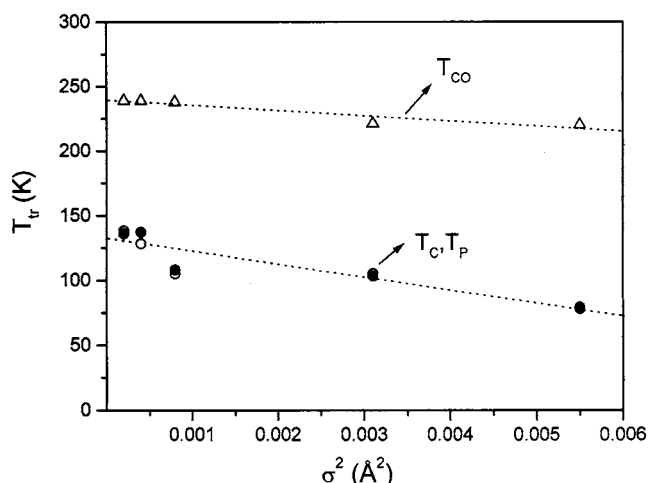**Figure 6.** Variation of ferromagnetic Curie temperature, T_C, I–M transition temperature, T_p, and CO temperature, T_{CO}, with σ^2 in the $Ln_{0.5}A_{0.5}MnO_3$ series of manganates with a fixed $\langle r_A \rangle$ of 1.185 Å.

with different fixed $\langle r_A \rangle$ values [12–14]. Thus, the value of T_C^0 for a fixed $\langle r_A \rangle$ value of 1.24 Å is 331 ± 13 K and the corresponding value of the slope is $15\,000 \pm 2800$ K Å^{-2}. The T_{CO}^0 value for a fixed $\langle r_A \rangle$ of 1.24 Å is 174 ± 13 K with a slope of 2840 ± 270 K Å^{-2}. The values of the slopes and the intercepts appear to be greater in a bonafide ferromagnet with large $\langle r_A \rangle$.

4. Concluding remarks

We have studied a series of rare earth manganates with an average A-site cation radius, $\langle r_A \rangle$, in the range 1.17–1.20 Å, where charge ordering and ferromagnetism are competing interactions. These manganates show charge ordering around 240 K and become ferromagnetic and metallic on cooling, characteristic of a re-entrant behaviour. Interestingly, the plots of T_{CO} and T_C against $\langle r_A \rangle$ intersect at a value of 1.195 Å, indicating a change in the relative stabilities of the ground states. Below a $\langle r_A \rangle$ of 1.195 Å, $T_{CO} > T_C$ and it is likely that the CO and FMM states coexist in the temperature range between T_{CO} and T_C. It is noteworthy that the width of the regime ($T_{CO}-T_C$) decreases with increase in $\langle r_A \rangle$, becoming rather small in $La_{0.5}Ca_{0.5}MnO_3$.

Site disorder arising from size mismatch has a profound effect on the T_C corresponding to the re-entrant transition in this $\langle r_A \rangle$ regime of the manganates. Accordingly, a change in σ^2 from 0.0002 to 0.0055 Å^2 at a fixed $\langle r_A \rangle$ of 1.185 Å brings about a vast change in T_C, although the T_{CO} is affected to a much smaller extent. Unlike the case for $\langle r_A \rangle$, the coexistence regime ($T_{CO}-T_C$) increases with increase in σ^2.

Acknowledgment

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