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A comparative study of ferromagnetic transition temperatures for some perovskite manganates

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Abstract. Three series of bulk samples, $\text{La}_{2/3}(\text{Ca}_{1-z}\text{Sr}_z)_{1/3}\text{MnO}_3$, $(\text{La}_{1-y}\text{Sm}_y)_{1/3}\text{Nd}_{1/3}\text{Sr}_{1/3}\text{MnO}_3$ and $\text{La}_{1/3}\text{Nd}_{1/3}(\text{Ca}_{1-x}\text{Sr}_x)_{1/3}\text{MnO}_3$, were carefully prepared. Paramagnetic insulator to ferromagnetic metal transitions were observed for all of the samples. Their T_c – $\langle r_A \rangle$ relation fell onto three distinct plots in the phase diagram, the sequence of which, from high to low values of T_c , is consistent with the increasing occupancy of A site magnetic rare earth ions. Close investigation into the data revealed that the large variance of T_c with common $\langle r_A \rangle$ could not be explained by the present understanding. In view of the fact that T_c is essentially related to A site magnetic rare earth contents, and the recent finding that the Mn–Re coupling might contribute to the overall magnetic structure in the perovskite manganates, we propose a site-percolation model in which the Mn–Re interaction could influence the ferromagnetic coupling between Mn ions. Before the content of A site magnetic Re^{3+} reaches the critical value of 0.311 for a simple cubic lattice, the effect could be negligible; otherwise, the effect could be significant, manifesting itself by the lowering of T_c , which would be enhanced by more A site magnetic Re^{3+} occupancy. Such description agrees well with our current study and some other previously reported ones.

1. Introduction

Perovskite manganates $\text{Re}_{1-x}\text{M}_x\text{MnO}_3$ (Re^{3+} is trivalent rare earth ion, M^{2+} is divalent alkaline ion) have triggered a great deal of interest since the discovery of the CMR phenomenon [1]. It is believed that a double-exchange mechanism is responsible for the ferromagnetic metallic ground state of this kind of material when it is properly doped with holes [2]. A close relationship between structure, magnetism and electronic properties has been revealed [3–5]. A magnetic and electronic phase diagram was established which shows that, with the hole density fixed at the optimum value of about 30%, the ferromagnetic transition temperature T_c is uniquely related to the average A site ionic radius $\langle r_A \rangle$ [4, 6]. It could be inferred from this picture that the same $\langle r_A \rangle$ results in the same T_c . It is rather intriguing since this simple relation only takes into account the average size effect on the A site. Recently, work on this question has revealed two influential factors, i.e., the A cation disorder [7] and the electropositivity of the alkaline ions [8], through which the constant $\langle r_A \rangle$ does not lead to a constant T_c . The authors of [7] argued that the local deformations of MnO_6 octahedra due to the A cation disorder and size effect act as ‘performed Jahn–Teller distortions’ which localize the e_g electrons, thereby lowering the metal–insulator transition temperature, and hence T_c . In [8], it was suggested that due to

the simultaneous sharing of the O $2p_{\pi}$ electrons by the Mn t_{2g} orbitals and the outer orbitals of the divalent alkaline M^{2+} , the covalent overlap of the M^{2+} -O bond might compete with the Mn(t_{2g})-O($2p_{\pi}$) hybridization. Thus the electropositivity of alkaline ions influences the effective ferromagnetic coupling and hence T_c . Both results deepen our understanding on this question. However, in this paper, through comparative A site ion substitution by magnetic rare earth ion and nonmagnetic alkaline ion respectively, as well as fine tuning of average A site ionic radii $\langle r_A \rangle$, we will show that, apart from the above two points, moments on the A site rare earth sublattice may also play a role in determining the electronic and magnetic properties.

Two parallel series of samples were carefully prepared through the conventional solid state reaction method. One is $\text{La}_{1/3}\text{Nd}_{1/3}(\text{Ca}_{1-x}\text{Sr}_x)_{1/3}\text{MnO}_3$ with $x = 0.6, 0.7, 0.8$ and 0.9 (denoted as LNCS series), the other is $(\text{La}_{1-y}\text{Sm}_y)_{1/3}\text{Nd}_{1/3}\text{Sr}_{1/3}\text{MnO}_3$ with $y = 0.643, 0.464, 0.321$ and 0.178 (denoted as LSNS series). x and y are chosen to make the respective samples in the two series have the same average A site ionic radius $\langle r_A \rangle$. The $\langle r_A \rangle$ thus obtained was 1.212, 1.217, 1.221 and 1.225 Å using ninefold coordination values tabulated in [9]. To make a comparison, a third series of samples was also prepared, i.e., $\text{La}_{0.67}\text{Ca}_{0.33-z}\text{Sr}_z\text{MnO}_3$, with $z = 0.05, 0.1$ and 0.15 while $\langle r_A \rangle = 1.211, 1.217$ and 1.224 Å respectively (denoted as LCS series).

Dried stoichiometric mixtures of 99.99% pure La_2O_3 , Sm_2O_3 , Nd_2O_3 , SrCO_3 , CaCO_3 and MnO_2 were well mixed and calcined at 1373 K for 48 h. The powder obtained was reground, pelletized and sintered at 1473 K for another 72 h with intermediate grindings, then furnace cooled to room temperature. The phase purity was examined by x-ray powder diffraction using a D-max Rigaku system with rotating anode. Low-field ac susceptibility was measured above 77 K by means of a sensitive mutual inductance method with a frequency of 320 Hz. The resistivity was measured by a standard four-probe method in the same temperature range.

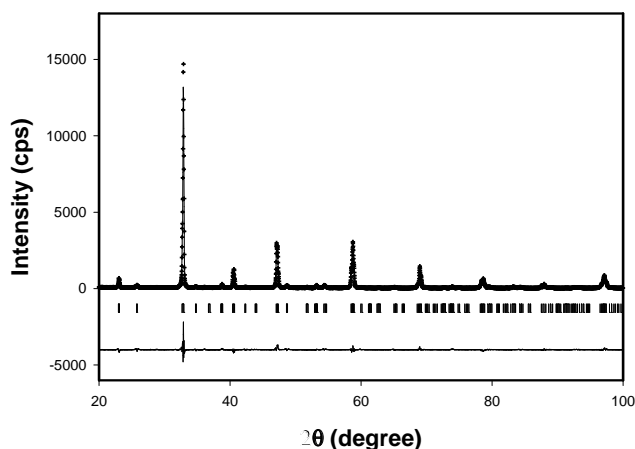


Figure 1. The experimental x-ray powder pattern (+) and best fit (continuous line) at room temperature for a selected sample $(\text{La}_{0.357}\text{Sm}_{0.643})_{1/3}\text{Nd}_{1/3}\text{Sr}_{1/3}\text{MnO}_3$. The bars denote the calculated Bragg reflections. The plot at the bottom shows the difference of the experimental and theoretical fits.

The x-ray powder diffraction patterns show the samples are of orthorhombic single phase with space group $Pnma$ (figure 1). The sharp peaks and good peak shape are indicative of the high quality of our samples. Figure 2 presents the ac susceptibility against temperature

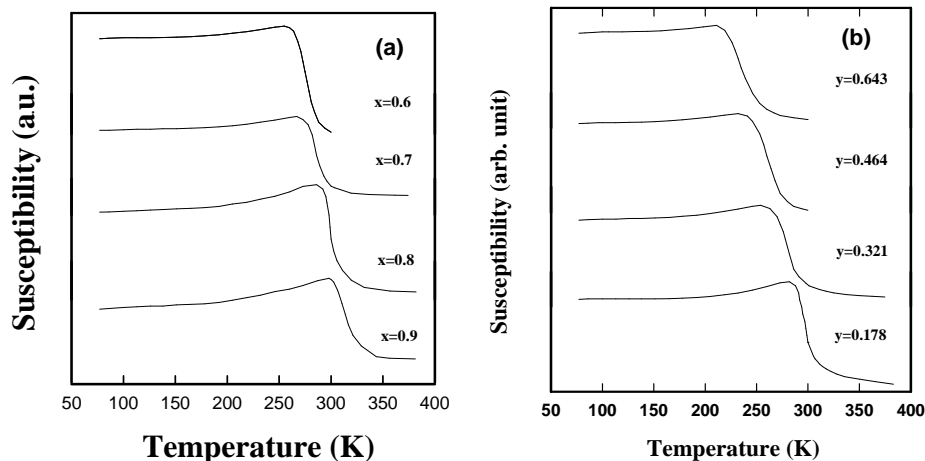


Figure 2. (a) Temperature dependence of ac susceptibility of LNCS series. x corresponds to Sr content. (b) Temperature dependence of ac susceptibility of LSNS series. y corresponds to Sm content.

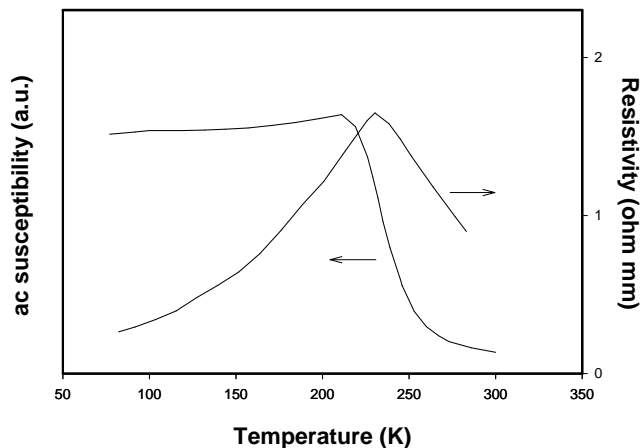


Figure 3. Resistivity and ac susceptibility against temperature for a selected sample $(\text{La}_{0.357}\text{Sm}_{0.643})_{1/3}\text{Nd}_{1/3}\text{Sr}_{1/3}\text{MnO}_3$.

for LNCS and LSNS series. As the temperature decreases, all samples show clearly a ferromagnetic transition while T_c (the temperature at which $d\chi/dT$ is minimum) decreases as the Sm content increases for LSNS series, or as the Sr content decreases for LNCS series. The metal-insulator transitions were observed for all the samples manifesting the strong correlation between electronic transport and magnetism as figure 3 shows, where the resistivity and ac susceptibility for $(\text{La}_{0.357}\text{Sm}_{0.643})_{1/3}\text{Nd}_{1/3}\text{Sr}_{1/3}\text{MnO}_3$ are presented as an example. Similar results are obtained for LCS series.

The relations between T_c and $\langle r_A \rangle$ for the LSNS and LNCS series as well as the LCS series are plotted in figure 4. We can see that, for each series, the T_c evolution with $\langle r_A \rangle$ is qualitatively in agreement with the phase diagrams [4, 6], i.e., as $\langle r_A \rangle$ decreases, T_c decreases. However, obviously, for each series, $T_c \sim \langle r_A \rangle$ displays a different functional

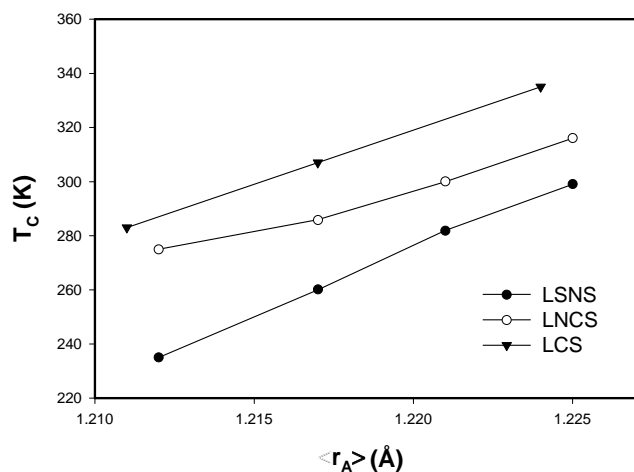


Figure 4. T_c against $\langle r_A \rangle$ for LCS, LNCS, LSNS series.

dependence. Systematically, the PM–FM transition temperatures for the LCS series are larger than those for the LNCS series which, in turn, are higher than those of the LSNS series. This non-uniqueness of T_c versus $\langle r_A \rangle$ is beyond the prediction of the phase diagrams [4, 6]; however, it is consistent with recent reports [7, 8].

Table 1. The ferromagnetic transition temperatures T_c (K), the average A site ionic radii $\langle r_A \rangle$ (Å) and the A cation size variance σ^2 (Å²) for the samples of the LSNS and LNCS series.

$\langle r_A \rangle$		1.212	1.217	1.221	1.225
LSNS	σ^2	0.0046	0.0042	0.0038	0.0034
	T_c	235	260	282	299
LNCS	σ^2	0.0037	0.0023	0.0034	0.0044
	T_c	275	286	300	316

In [7], the authors defined A cation size variance $\sigma^2 = \sum y_i r_i^2 - \langle r_A \rangle^2$, in which y_i and r_i are the fractional occupancy and the ionic radius of the i th A site species, respectively, to quantify the A cation disorder and size effect. They found that, when $\sigma^2 < 0.015 \text{ \AA}^2$, T_c decreases monotonically as σ^2 increases, which can be attributed to the localization of charge carriers resulting from the strain field induced by the size mismatch of randomly distributed A cations. In [8], it was shown that Sr doped samples exhibit lower T_c than Ca doped ones due to the more electropositive nature of Sr. In table 1, we give the $\langle r_A \rangle$, T_c and the value of σ^2 for the samples of the LSNS and LNCS series. One can find the disagreement between the data and the two above-mentioned effects. When $\langle r_A \rangle = 1.225 \text{ \AA}$, the value of σ^2 for the sample of the LSNS series (0.0034 \AA^2) is considerably smaller than that of the sample belonging to the LNCS series (0.0044 \AA^2), while their Ca content is nearly equal, with the difference only about 0.03. Such a small variance of Ca content could make us ignore the difference of electropositivity of the alkaline ions. Then according to [7], the LSNS sample with smaller σ^2 should exhibit higher T_c than the corresponding LNCS one with bigger σ^2 . Obviously, this is not the case for our observation. In contrast, the T_c of the former (299 K) is much lower than that of the latter (316 K). The fact suggests that the

above-mentioned two effects are not sufficient to account for the large variance of T_c with common $\langle r_A \rangle$. Other mechanisms should be explored.

Careful investigation of the data shows that T_c is in fact closely related to the content of magnetic rare earth ions Re^{3+} . When $\langle r_A \rangle$ is fixed, the sample with more magnetic Re^{3+} shows lower T_c than the one with less magnetic Re^{3+} . For the LNCS series, their T_c values are lower than those of the LCS series due to the presence of Nd^{3+} , but at the same time higher than those of their counterparts in the LSNS series due to the absence of Sm^{3+} . The largest deviation (40 K) occurs for $\langle r_A \rangle = 1.212 \text{ \AA}$ when the difference in Sm^{3+} content is greatest, while the least deviation (17 K) occurs for $\langle r_A \rangle = 1.225 \text{ \AA}$ when the difference in Sm^{3+} content is smallest. As a result, we obtain three distinct T_c - $\langle r_A \rangle$ curves corresponding to three series of samples with different magnetic Re^{3+} contents (figure 4). Each curve qualitatively agrees with the proposed phase diagrams [4, 6], but, systematically, the curve with more magnetic Re^{3+} lies lower than the one with less magnetic Re^{3+} . Naturally, one can infer from the observation that magnetic rare earth ions on the A site probably play an important role in the underlying physics of perovskite manganates.

It has been found that the magnetic rare earth ions might contribute strongly to the magnetic structure of the perovskite manganates, that is, the magnetic rare earth ions on the A site can form a magnetic sublattice which is antiparallel with the ferromagnetic $\text{Mn}^{3+}/\text{Mn}^{4+}$ sublattice, as was found in $\text{Dy}_{0.67}\text{Ca}_{0.33}\text{MnO}_{3\pm d}$ [10] and $\text{Ga}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ [11]. Due to the strong 3d exchange interaction compared to that of 4f, the Re-Re interaction could be neglected while Mn-Mn and Mn-Re interactions are responsible for the resultant magnetic structure with the former coupling stronger than the latter. As the Mn-Mn interaction is ferromagnetic, the observed ferrimagnetism must arise from a weaker, antiferromagnetic Mn-Re interaction [11]. Thus, the Mn ion is simultaneously coupled to the other neighbouring Mn ions and the magnetic rare earth ions. The latter can influence the effective ferromagnetic interaction between the Mn ions, which, in general, will lead to the weakening of the FM coupling, hence reducing T_c . As the Mn-Re interaction is weak, the Re ion would only influence its nearest-neighbouring Mn ions through their antiferromagnetic coupling. This effect would localize around the Re ion and would not extend across the whole lattice when the Re content is small, because the Re ions are randomly distributed on the A site and separated far apart as evidenced by the x-ray data. Then, in this case, the effect only acts as a perturbation and its influence on the Mn-Mn ferromagnetic coupling would be negligible. However, when the content of A site Re ions increases to some extent, the Re ions are getting closer, and the correlation of the Re induced effect increases. Then the effect of Mn-Re antiferromagnetic coupling on the Mn-Mn ferromagnetic coupling would extend across the whole lattice with the result of reducing T_c . It seems that this course can be interpreted in a site-percolation manner on a simple cubic lattice. As the critical concentration for site percolation on a simple cubic lattice is 0.311 [12], one could expect that, before the content of magnetic rare earth ions reaches this value, there is no discernible effect; otherwise, a significant effect which would be enhanced by increasing magnetic rare earth ions can be observed as manifested by a significant lowering of T_c . Our experimental results agree well with the above description. In addition, the significant lowering of T_c previously found (but ignored) for some other compounds, such as $\text{Nd}_{0.7}\text{M}_{0.3}\text{MnO}_3$ ($M = \text{Sr}, \text{Ba}$) [13] and $\text{Pr}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ [14], which are also located in the ferromagnetic metal region in the phase diagram, could be accounted for using our descriptions.

In summary, we prepared three series of samples with one of them free of magnetic rare earth ions, while the other two have different magnetic Re^{3+} contents. Their T_c - $\langle r_A \rangle$ relations lie on three different curves in the phase diagram, the sequence of which, from high

to low values of T_c , is consistent with the increasing magnetic rare earth ion content. Close investigation into the data revealed that not all the significant variance of T_c with common $\langle r_A \rangle$ could be explained by existing knowledge. Based on the fact that T_c is essentially related to the content of A site magnetic rare earth ions, as well as the recent finding that the Mn–Re coupling might contribute to the overall magnetic structure in perovskite manganates, we propose that the magnetic interaction between Mn and A site magnetic rare earth ions could influence the ferromagnetic Mn–Mn interaction in a site-percolation manner. If the occupancy of magnetic rare earth ions on the A site reaches the critical value 0.311 for the simple cubic lattice, the Mn–Mn ferromagnetic coupling is significantly weakened, hence T_c is reduced. The effect would be enhanced when more magnetic rare earth ions are introduced into the A site. Such a picture agrees well with our current study and some other previous reports.

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