Effect of the cation size disorder on charge ordering in rare-earth manganates

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(Received 29 October 1998)

The effect of disorder arising from the mismatch between the average sizes of the A-site cations in the rare-earth manganates, $L_{0.5}A_{0.5}MnO_3$ (L=rare earth, A=alkaline earth), on their charge-ordering behavior has been investigated. Measurements on two series of manganates with a fixed average cation radius, $\langle r_A \rangle$, of 1.17 and 1.24 Å, reveal that the charge-ordering transition temperature, T_{CO}, is not very sensitive to the size mismatch unlike ferromagnetic T_C or metal-insulator transition data. Furthermore, T_{CO} is not affected greatly by the orthorhombic lattice distortion. The observed decrease in T_{CO} with increase in $\langle r_A \rangle$ is consistent with a quadratic dependence upon $(r_A^0 - \langle r_A \rangle)$ where $r_A^0 = 1.13$ Å. [S0163-1829(99)02218-3]

Two of the important features of the rare-earth manganates, $L_{1-x}A_xMnO_3$ (L=rare-earth; A=alkaline earth), are the ferromagnetic metallic and the charge-ordered states exhibited by them.[1,2] The ferromagnetic Curie temperature T_C around which an insulator-metal transition occurs in these manganates has been shown to be sensitive to the mismatch in the sizes of the A-site cations.[3-5] While the T_C and the insulator-metal transition temperature T_M increase with the increase in the average size of the A-site cation $\langle r_A \rangle$, the value saturates at high $\langle r_A \rangle$ values probably because many of these manganates have A-site cations with a large size mismatch.[6] In order to account for the effects due to the strain arising from the size mismatch of the A-site cations on T_C or T_M, Rodriguez-Martinez and Attfield[3,4] employed the variance in the distribution of $\langle r_A \rangle$. The variance σ^2 is defined by

$$\sigma^2 = \Sigma x_i r_i^2 - \langle r_A \rangle^2, \qquad (1)$$

where x_i is the fractional occupancy of A site ions and r_i is the corresponding ionic radii. Rodriguez-Martinez and Attfield[3,4] as well as Damay *et al.*[5] have studied several series of manganates of the type $L_{1-x}A_xMnO_3$ for fixed values of $\langle r_A \rangle$ and have found a linear relation between T_C and σ^2, with the T_C decreasing with the increase in σ^2. Since the charge-ordering behavior of the rare-earth manganates is very sensitive to $\langle r_A \rangle$,[2,7] we considered it important to quantify how the charge-ordering transition temperature T_{CO} depends on the size mismatch between the A-site cations. For this purpose, we have studied charge-ordering in several manganates of the type $L_{0.5}A_{0.5}MnO_3$. In order to understand the dependence of T_{CO} on σ^2, we have determined T_{CO} in two series of manganates with fixed $\langle r_A \rangle$ values of 1.24 and 1.17 Å, albeit in a few members of each series, because of the difficulty in realizing compositions which permit reliable measurements.

Polycrystalline samples of manganates of the composition $L_{0.5-x}L'_xA_{0.5-y}A'_yMnO_3$ with $\langle r_A \rangle = 1.24$ and 1.17 Å, as well as several manganates of the type $L_{0.5}A_{0.5}MnO_3$ with variable $\langle r_A \rangle$ were prepared by the ceramic route by heating stoichiometric quantities of the respective rare-earth oxide,

Mn_3O_4 and the carbonates of the alkaline-earth elements. The final sintering temperature in the preparations was 1400 °C. The Mn^{4+} content in all the compositions was close to 50% as determined by redox titrations.

The manganates with an $\langle r_A \rangle$ of 1.24 Å studied by us are akin to $Nd_{0.5}Sr_{0.5}MnO_3$ exhibiting distinct ferromagnetic and the charge-ordering transitions both in the magnetization and
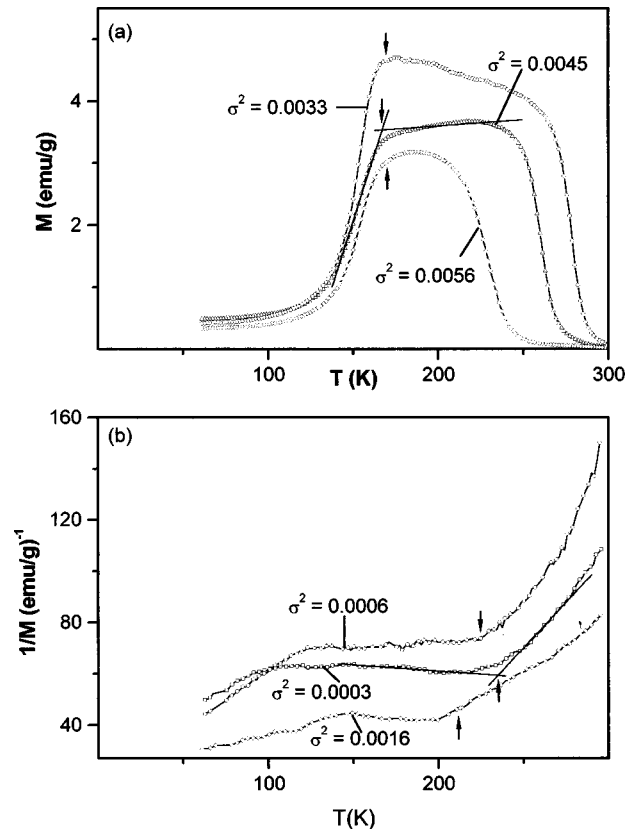

FIG. 1. Temperature variation of (a) the magnetization M of the $L_{0.5}A_{0.5}MnO_3$ series with a fixed $\langle r_A \rangle$ of 1.24 Å and (b) of $1/M$ of the manganates of the series with a fixed $\langle r_A \rangle$ of 1.17 Å. T_{CO} is shown by an arrow.
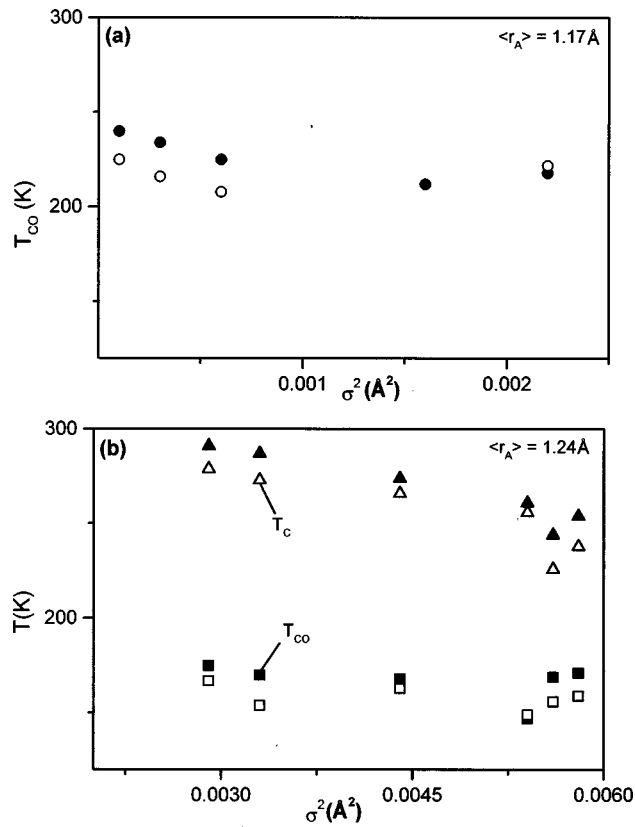
FIG. 2. Variation of the charge-ordering transition temperature T_{CO} with σ^2 in the $L_{0.5}A_{0.5}MnO_3$ series with (a) $\langle r_A \rangle = 1.17$ Å and (b) $\langle r_A \rangle = 1.24$ Å. Filled circles, triangles, and squares are from magnetic measurements and the corresponding open symbols are from resistivity measurements.

resistivity data. We have employed both the measurements to obtain T_{CO} values for these compositions. The T_{CO} data for manganates with $\langle r_A \rangle = 1.17$ Å were obtained from the minima in the inverse magnetization-temperature plots as well as from the maxima in $d(\ln \rho)/dT^{-1}$ plots. In Fig. 1, we show the typical magnetic behavior of the manganates with $\langle r_A \rangle = 1.24$ and 1.17 Å. The method employed to determine
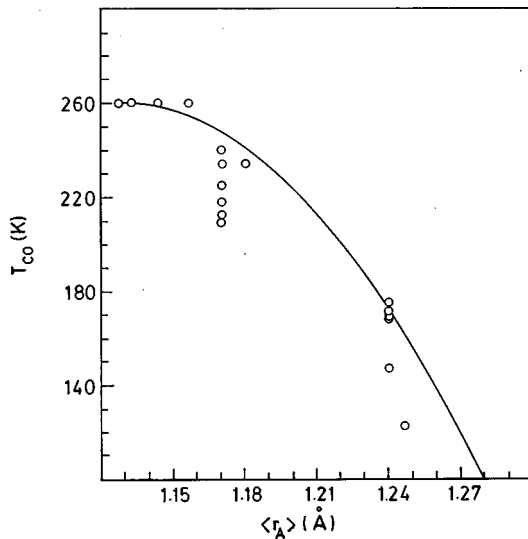

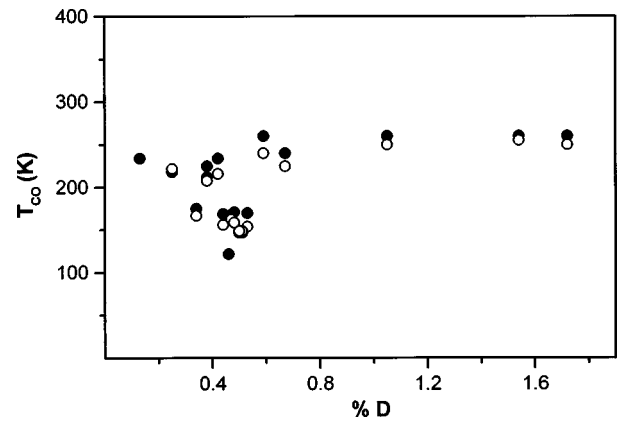FIG. 3. A plot of T_{CO} values against $\langle r_A \rangle$ in $L_{0.5}A_{0.5}MnO_3$.

FIG. 4. Variation of T_{CO} with the orthorhombic lattice distortion index, %D. Filled circles are from magnetic measurements and the corresponding open circles are from resistivity measurements.

T_{CO} is also indicated in the figure. In the other $L_{0.5}A_{0.5}MnO_3$ compositions with variable $\langle r_A \rangle$, T_{CO} values were obtained from the magnetization data.

In Fig. 2(a), we have shown the variation of T_{CO} with σ^2 of the $L_{0.5}A_{0.5}MnO_3$ series with $\langle r_A \rangle = 1.17$ Å. In Fig. 2(b), we have plotted the ferromagnetic T_C as well as T_{CO} values of the manganate series with $\langle r_A \rangle = 1.24$ Å against σ^2. Although we could properly characterize the charge-ordered states only in a few members of each series, the data show discernible trends. The T_{CO} values from electrical resistivity data generally tend to be somewhat lower than those from magnetization data. In the $\langle r_A \rangle = 1.17$ Å series, the T_{CO} values up to a σ^2 of 0.0006 Å^2, obtained from both the magnetization and electrical resistivity data, give a slope, $p_1 = 32\,000 \pm 3000$ K Å^{-2}. This slope is comparable to that obtained in the metal-insulator transition data in earlier studies.[3-5] For higher values of σ^2, there is no statistically significant dependence of T_{CO} on σ^2 in the manganates of the $\langle r_A \rangle = 1.17$ Å series. Within the accuracy of our measurements, the $T_{CO}-\sigma^2$ slope is less than 4000 K Å^{-2} when $\sigma^2 \geq 0.0006$ Å^2. In effect therefore, for moderate and high values of σ^2, T_{CO} appears to be essentially independent of σ^2. This may be because there may be no long-range orbital ordering when $\langle r_A \rangle = 1.17$ Å for $\sigma^2 \geq 0.0006$ Å^2, suggesting that below this value of σ^2 the dependence of T_{CO} on σ^2 reflects the effect of cation size mismatch on the long-range structural distortion at T_{CO}. This could also make the transition rather broad as found in the many manganates with $\langle r_A \rangle = 1.17$ Å [see Fig. 1(b)]. Similarly, there is no significant dependence of T_{CO} on σ^2 in the manganates with $\langle r_A \rangle = 1.24$ Å, unlike the ferromagnetic T_C values in these materials [Fig. 2(b)].

For the insulator-metal transition in the manganates, it has been proposed[3,4] that

$$T_M^0 = T_M^* - p_2(r_A^0 - \langle r_A \rangle)^2, \qquad (2)$$

where p_2 is analogous to p_1, the value of r_A^0 corresponds to that of the ideal perovskite having maximum T_M^0 value and a perovskite tolerance factor of 1. Oxygen atom displacements proportional to $(r_A^0 - \langle r_A \rangle)$ lead to suppression of T_M^0 through a changing strain energy.[8] Unlike in metal-insulator

transitions, it is difficult to fix the ideal value of $\langle r_A \rangle$ for the charge-ordered state. Experimentally, the variation of T_{CO} with $\langle r_A \rangle$ suggests that the charge-ordered state is favored for small $\langle r_A \rangle$,[2,7] as the bending of the Mn-O-Mn bond angle and the associated distortion of the MnO_6 octahedra facilitate the localization of separate Mn^{3+} and Mn^{4+} states. If we take the value of r_A^0 to be the minimum observed value of $\langle r_A \rangle$ $= 1.127$ Å, we can describe the T_{CO} data by using an expression similar to (2). The variation of T_{CO} seems to be best described by the curve given in Fig. 3 with $T_{CO}^* = 260$ K and $p_2 = 6900$ K Å^{-2}.

We have explored the relationship between T_{CO} and the orthorhombic lattice distortion index, which is strongly dependent on $\langle r_A \rangle$ or $(r_A^0 - \langle r_A \rangle)^2$. The lattice distortion index, %D, is defined as

$$\%D = 1/3 (\Sigma |a_i - a'|/a_i) \times 100, \qquad (3)$$

where $a' = (a \times b \times c/\sqrt{2})^{1/3}$. In Fig. 4, we have plotted the experimental T_{CO} values obtained for all the manganates studied by us against %D. We see that T_{CO} does not vary much, particularly when the distortion is high; the dependence of T_{CO} appears to be significant at best for small values of %D.

In conclusion, the present study indicates that the charge-ordering transition in the rare-earth manganates is not very sensitive to the mismatch between the sizes of the A-site cations or to the orthorhombic lattice distortion arising from the small cation size. The decrease in the charge-ordering transition temperature at high $\langle r_A \rangle$ (Refs. 2 and 7) is consistent with the observed quadratic dependence upon $(r_A^0 - \langle r_A \rangle)$ where $r_A^0 \approx 1.13$ Å.

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