Charge ordering in the rare-earth manganates: the origin of the extraordinary sensitivity to the average radius of the A-site cations, $\langle r_A \rangle$

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Charge ordering in the rare-earth manganates: the origin of the extraordinary sensitivity to the average radius of the A-site cations, $\langle r_A \rangle$

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Abstract. The charge ordering in $Nd_{0.5}Sr_{0.5}MnO_3$ ($\langle r_A \rangle = 1.24$ Å), which occurs on cooling the ferromagnetic metallic ground state, is readily destroyed on application of a magnetic field of 6 T. For $Y_{0.5}Ca_{0.5}MnO_3$ ($\langle r_A \rangle = 1.13$ Å), for which the ground state is charge ordered, on the other hand, magnetic fields have no effect on the charge ordering. In order to understand such a marked difference in charge-ordering behaviour of the manganates, we have investigated the structure as well as the electrical and magnetic properties of $Ln_{0.5}Ca_{0.5}MnO_3$ compositions (Ln = Nd, Sm, Gd and Dy) wherein $\langle r_A \rangle$ varies over the range 1.17–1.13 Å. The lattice distortion index, D, and charge-ordering transition temperature, T_{CO}, for the manganates increase with the decreasing $\langle r_A \rangle$. The charge-ordered state is transformed to a metallic state on applying a magnetic field of 6 T in the case of $Nd_{0.5}Ca_{0.5}MnO_3$ ($\langle r_A \rangle = 1.17$ Å), but this is not the case with the analogous Sm, Gd and Dy manganates with $\langle r_A \rangle$ less than 1.17 Å. In order to explain this behaviour, we have examined the $\langle r_A \rangle$-dependence of the Mn–O–Mn bond angle, the average Mn–O distance and the apparent one-electron bandwidth, obtained from these structural parameters. It is suggested that the extraordinary sensitivity of the charge ordering to $\langle r_A \rangle$ arises from factors other than those based on the Mn–O–Mn bond angle and average Mn–O distances alone. It is possible that the competition between the covalent mixing of the oxygen O: 2pσ orbital with the A-site and B-site cation orbitals plays a crucial role. Strain effects due to size mismatch between A-site cations could also cause considerable changes in T_{CO}.

1. Introduction

Investigations of perovskite rare-earth manganates of the formula $Ln_{1-x}A_xMnO_3$ (Ln = rare earth, A = alkaline earth) have highlighted the important role played by the size of the A-site cations in determining the properties of these materials [1–3]. Thus, the ferromagnetic Curie temperature, T_C, of the $Ln_{0.7}A_{0.3}MnO_3$ compositions increases with the increase in the average radius of the A-site cations, $\langle r_A \rangle$. Increasing $\langle r_A \rangle$ causes an increase in the internal pressure which decreases the buckling of the MnO_6 octahedra. A plot of the ferromagnetic T_C against $\langle r_A \rangle$ for $Ln_{0.7}A_{0.3}MnO_3$ compositions shows an increasing trend up to ~1.24 Å and a saturation or decrease thereafter [4, 5]. It is recognized that while changing the size of the A-site cations, one has to ensure that there is little mismatch between the A-site cations

[6, 7]. The effect of the size of the A-site cations is seen to be even more profound on the charge-ordering behaviour of the manganates [1, 8]. Accordingly, for $Ln_{0.5}A_{0.5}MnO_3$, drastic changes in properties are seen over the small range of $\langle r_A \rangle$ of 1.13 Å–1.24 Å. $Nd_{0.5}Sr_{0.5}MnO_3$ with an $\langle r_A \rangle$ of ∼1.24 Å has a ferromagnetic metallic (FMM) ground state which changes to a charge-ordered antiferromagnetic state at around 158 K ($T_{CO} = T_N$), the transition being first order [9]. Application of magnetic fields melts this charge-ordered state, rendering it metallic even at a field strength of 6 T. Recent studies [8] of $Y_{0.5}Ca_{0.5}MnO_3$ ($\langle r_A \rangle = 1.13$ Å) show that it is a charge-ordered insulator with a high T_{CO} of ∼260 K. Furthermore, application of magnetic fields up to 6 T has no effect on the resistivity of this material. It appears that the characteristics of the charge-ordered state in the manganates with small $\langle r_A \rangle$, as for $Y_{0.5}Ca_{0.5}MnO_3$, are distinctly different from those with high $\langle r_A \rangle$, as for $Nd_{0.5}Sr_{0.5}MnO_3$.

Since the sensitivity of the insulating charge-ordered states of the $Ln_{0.5}A_{0.5}MnO_3$ compositions to magnetic fields seems to depend on $\langle r_A \rangle$ [10], we considered it important to find out whether there was a critical $\langle r_A \rangle$-value below which magnetic fields have little effect on the charge-ordered states. We have therefore carried out a systematic investigation of the electrical and magnetic properties of several rare-earth manganates of the formula $Ln_{0.5}A_{0.5}MnO_3$ (Ln = Nd, Sm, Gd and Dy). The results show that the charge-ordered state ceases to be sensitive to magnetic fields when $\langle r_A \rangle$ is less than 1.17 Å. At the other extreme, an $\langle r_A \rangle$-value of 1.24 Å appears to define a limit around which a FMM ground state manifests itself, as in $Nd_{0.5}Sr_{0.5}MnO_3$. In order to understand the disparate behaviour of the charge-ordered manganates, we have related T_C and T_{CO} for the manganates to $\langle r_A \rangle$, and also to the apparent one-electron bandwidth, W_a, estimated on the basis of the knowledge of the Mn–O–Mn angles and the average Mn–O distances in these materials [11, 12].

Table 1. Properties of $Ln_{0.5}Ca_{0.5}MnO_3$ compositions.

Ln	$\langle r_A \rangle$ (Å)	Lattice parameters (Å)			T_{CO} (K)		Effect of
		a	b	c	χ	$d\log(\rho)/dT^{-1}$	H (6 T)
Nd	1.172	5.384	5.406	7.607	240	220	Yes†
Sm	1.156	5.356	5.418	7.548	260	240	No
Gd	1.143	5.345	5.460	7.523	260	250	No
Dy	1.132	5.317	5.483	7.457	260	255	No
Y	1.127	5.305	5.495	7.445	260	250	No

† 99.99% at 60 K.

2. Experimental procedure

$Ln_{0.5}Ca_{0.5}MnO_3$ (Ln = Nd, Sm, Gd and Dy) compositions were prepared by high-temperature solid-state reactions. Stoichiometric quantities of high-purity oxides of the rare earths (Ln) and Mn_3O_4 were mixed and the mixtures prefired at 1470 K for 12 hours and later sintered at 1670 K/1770 K for 12/24 hours. The phase purity of the samples was established by powder x-ray diffraction (XRD). The XRD patterns were recorded with a Rich–Scheifert instrument. The lattice parameters of the various compositions are listed in table 1 along with the respective $\langle r_A \rangle$-values based on ionic radii for ninefold coordination [13].

Electrical resistivity measurements were carried out from 300 K to 20 K by the four-probe method. Magnetoresistance was measured by the four-probe method over the
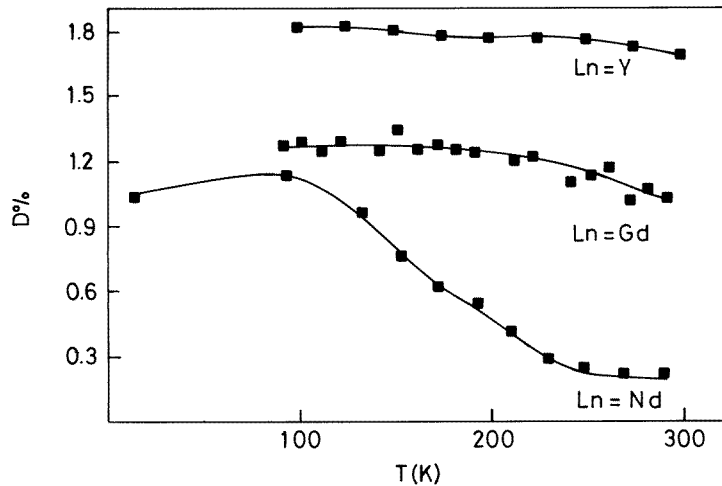
Figure 1. The temperature variation of the lattice distortion index D for $Ln_{0.5}Ca_{0.5}MnO_3$. $D = \sum |(a_i - a)|/3a_i$, where $a_1 = a, a_2 = b, a_3 = c/\sqrt{2}$ and $a = (a \times b \times c/\sqrt{2})^{1/3}$.

temperature range 4.2–300 K in a magnetic field of 6 T using a superconducting solenoid. The dc susceptibility measurements were made using a Lewis Coil Force Magnetometer.

3. Results and discussion

All of the $Ln_{0.5}Ca_{0.5}MnO_3$ compositions (Ln = Nd, Sm, Gd and Dy) have the orthorhombic O′ structure ($c/\sqrt{2} \leqslant a \leqslant b$) as given in table 1. We have measured the dimensionless lattice distortion index, D, for the compositions with Ln = Nd, Gd and Y as a function of temperature. We show the temperature variation of $D\%$ in figure 1. In the case of Nd, the distortion increases as the temperature decreases, reaching a value of 1 around 100 K. The value of $D\%$ increases significantly as we go from Nd to Y. In the case of Y, the distortion is around 1.8% over the entire range of 100–300 K. The lattice distortion in $Ln_{0.5}Ca_{0.5}MnO_3$ clearly increases with decrease in $\langle r_A \rangle$. This has consequences on the charge-ordering behaviour as well.

In figure 2, we show the magnetic susceptibility data for three $Ln_{0.5}Ca_{0.5}MnO_3$ compositions (Ln = Nd, Sm and Gd), to illustrate that the susceptibility shows a maximum around 240 K or 260 K due to charge ordering just as for $Pr_{0.6}Ca_{0.4}MnO_3$ and other systems [14, 15]. The values of the charge-ordering transition temperature, T_{CO}, obtained from the susceptibility data are listed in table 1. In figure 2, we have also shown the temperature variation of the activation energy for conduction, in the form of plots of $d \log \rho/dT^{-1}$ against temperature. The plots show maxima due to charge ordering, just as for other charge-ordered manganates [15]; the maxima are in the range 220–255 K, the values being somewhat lower than the T_{CO}-values obtained from magnetic susceptibility measurements. We see however that T_{CO} is higher for Sm, Gd, Dy and Y derivatives than for $Nd_{0.5}Ca_{0.5}MnO_3$ (table 1).

In figure 3, we show the effect of a magnetic field of 6 T on the electrical resistivity of four $Ln_{0.5}Ca_{0.5}MnO_3$ compositions (Ln = Nd, Sm, Gd and Dy). For $Nd_{0.5}Ca_{0.5}MnO_3$ ($\langle r_A \rangle = 1.17$ Å), a magnetic field of 6 T significantly affects the resistivity and nearly makes it metallic below ∼120 K. The magnetic field has however no effect on the resistivity of
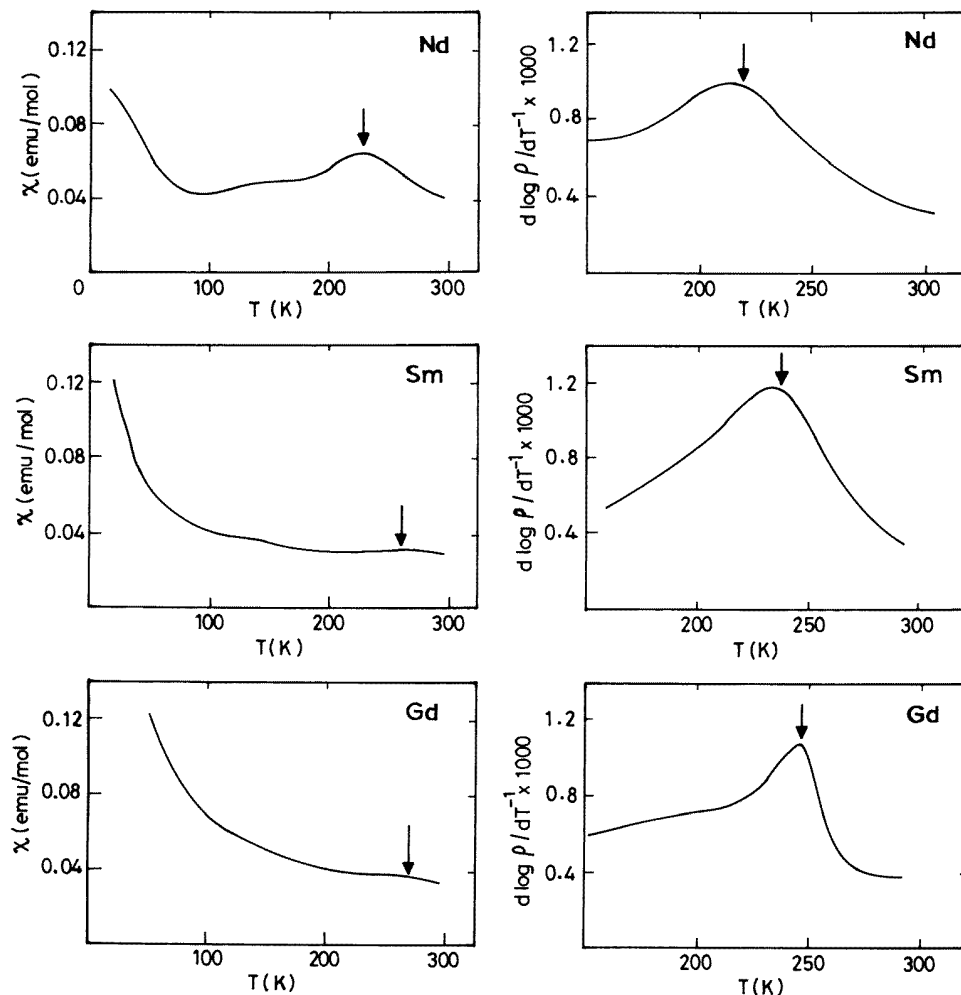
Figure 2. The temperature variation of the magnetic susceptibility, χ, and the activation energy for conduction, $d \ln \rho / dT^{-1}$, for $Ln_{0.5}Ca_{0.5}MnO_3$ (Ln = Nd, Sm and Gd).

$Sm_{0.5}Ca_{0.5}MnO_3$ ($\langle r_A \rangle = 1.16$ Å). The same is true of $Gd_{0.5}Ca_{0.5}MnO_3$ ($\langle r_A \rangle = 1.143$ Å) and $Dy_{0.5}Ca_{0.5}MnO_3$ ($\langle r_A \rangle = 1.132$ Å). It has already been shown that the resistivity of $Y_{0.5}Ca_{0.5}MnO_3$ ($\langle r_A \rangle = 1.127$ Å) is not affected by a magnetic field of 6 T [8]. It appears, therefore, that an $\langle r_A \rangle$ of 1.17 Å is a critical value below which magnetic fields (up to 6 T) have no effect on the charge-ordered manganates (table 1). The charge-ordered state in the manganates with $\langle r_A \rangle$ less than 1.17 Å is robust, being dominated by the cooperative Jahn–Teller effect [16]. We also note that high T_{CO}-values of 240 K and above occur for $Ln_{0.5}Ca_{0.5}MnO_3$ with $\langle r_A \rangle$ less than 1.17 Å. T_{CO} becomes zero when $\langle r_A \rangle$ is greater than 1.24 Å. It is likely that the $\langle r_A \rangle$-values of 1.17 Å and 1.24 Å define two different regimes of charge ordering in the manganates. In figure 4, we show the variation of the ferromagnetic Curie temperature, T_C, as well as that of T_{CO} with $\langle r_A \rangle$ for $Ln_{0.5}A_{0.5}MnO_3$. The value of T_C rises quite sharply when $\langle r_A \rangle$ is greater than 1.24 Å. What is surprising is that such small changes in value of $\langle r_A \rangle$ give rise to drastic differences in the properties of these
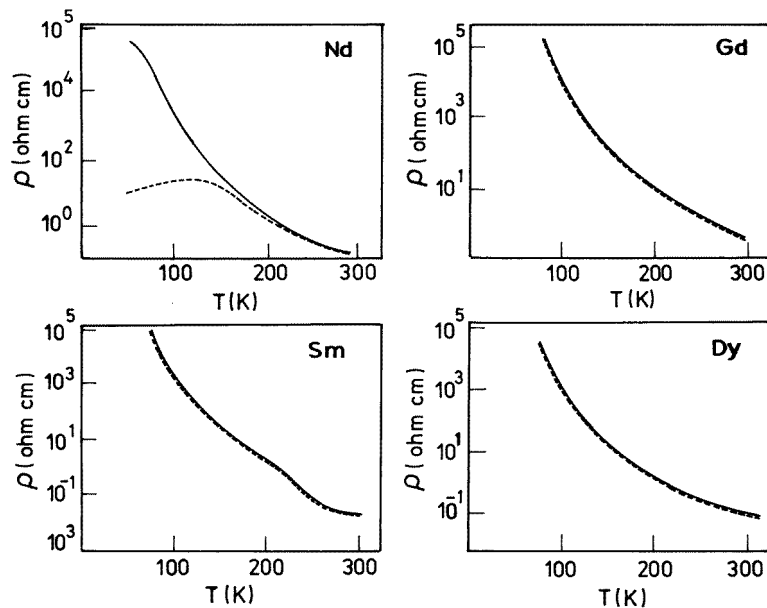
Figure 3. The electrical resistivity of $Ln_{0.5}Ca_{0.5}MnO_3$ (Ln = Nd, Sm, Gd and Dy) in the absence (full line) and presence of a magnetic field of 6 T (broken line). It has been recently found that exactly stoichiometric $Nd_{0.5}Ca_{0.5}MnO_3$ may require fields higher than 6 T to melt the CO state.
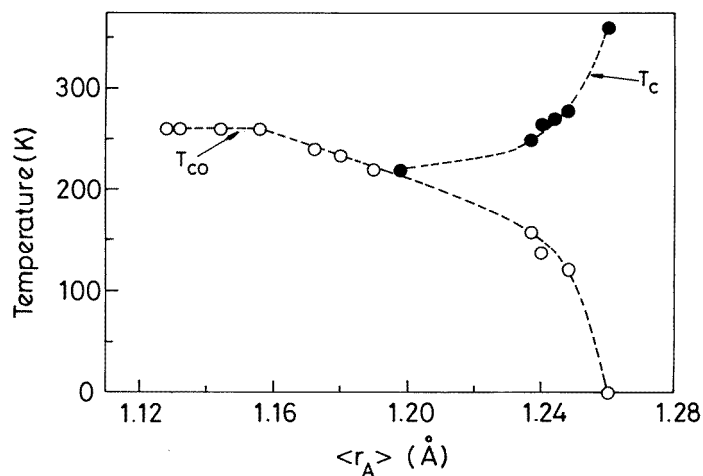

Figure 4. The variation of the charge-ordering transition temperature, T_{CO}, and ferromagnetic transition temperature, T_C, with the average radius of the A-site cation, $\langle r_A \rangle$.

manganates.

It is known that $\langle r_A \rangle$ directly affects the Mn–O–Mn angle as well as the average Mn–O distance in the manganates. In figure 5, we have plotted the known values of the Mn–O–Mn angle and the average Mn–O distances in $Ln_{0.7}A_{0.3}MnO_3$ [11] and $Ln_{0.5}A_{0.5}MnO_3$ [12] against $\langle r_A \rangle$. The Mn–O–Mn angle increases with $\langle r_A \rangle$ smoothly in the manganates,
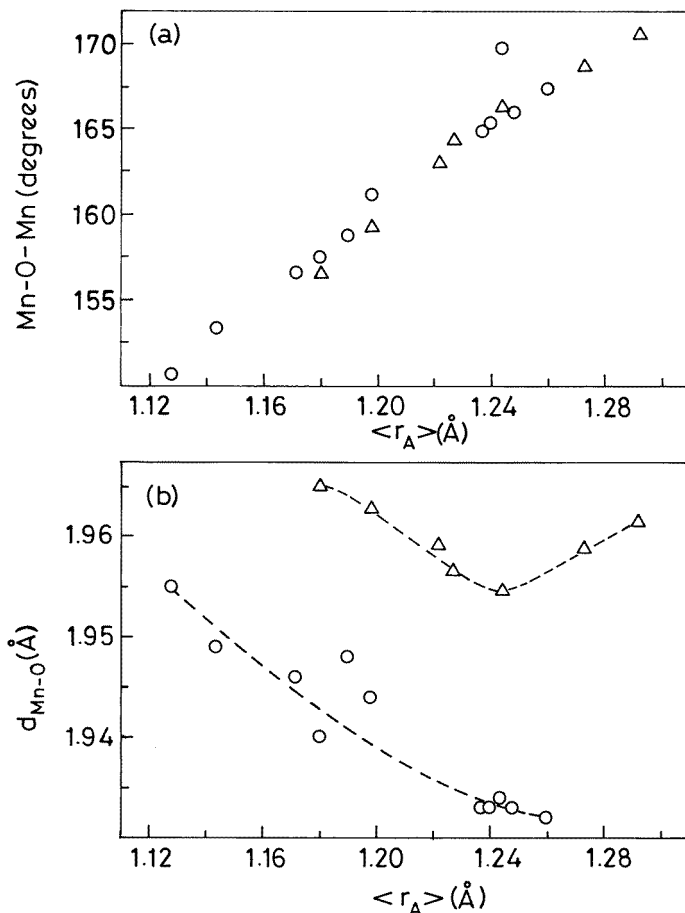
Figure 5. The variation of (a) the Mn–O–Mn angle and (b) the average Mn–O bond length with $\langle r_A \rangle$: $Ln_{0.5}A_{0.5}MnO_3$ (circles); $Ln_{0.7}A_{0.3}MnO_3$ (triangles).

nearly independently of the composition, giving a common curve for the $Ln_{0.5}A_{0.5}MnO_3$ and $Ln_{0.7}A_{0.3}MnO_3$ systems. The plot of the average Mn–O distance (d_{Mn-O}) against $\langle r_A \rangle$, however, shows a minimum at 1.24 Å for $Ln_{0.7}A_{0.3}MnO_3$ [11]. In $Ln_{0.5}A_{0.5}MnO_3$, the Mn–O distance becomes nearly constant when $\langle r_A \rangle$ is greater than 1.24 Å [12]. Such a non-monotonic variation of the bond distance is geometrically consistent with the observed variations of the cell size, a, and of the Mn–O–Mn bond angle, θ, with $\langle r_A \rangle$. From the simple relation $a = 2d_{Mn-O} \sin \theta/2$, we would expect a minimum in d_{Mn-O} given by

$$\cot \theta/2 = (2/3)(\partial \ln a^3 /\partial \langle r_A \rangle)/(\partial \theta /\partial \langle r_A \rangle). \tag{1}$$

The observed dimensional variations of the cell volume (a^3) and of the bond angle with $\langle r_A \rangle$ verify the calculated minimum fairly accurately. Indeed, for $\partial a/\partial \langle r_A \rangle$ greater than 0, and $\partial \theta /\partial \langle r_A \rangle$ greater than 0 (i.e., the reduction of the buckling of the MnO_6 octahedra with $\langle r_A \rangle$), we necessarily have a minimum for d_{Mn-O}. We can estimate the apparent one-electron bandwidth, W_a, of the manganates by using the relation [17]

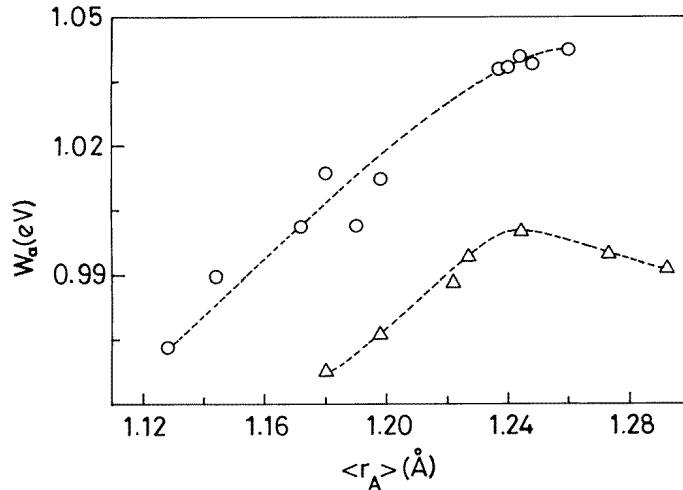$$W_a \propto \cos \omega / d_{Mn-O}^{3.5} \tag{2}$$

Figure 6. The variation of the apparent one-electron bandwidth W_a, calculated from the experimental Mn–O–Mn angle and average Mn–O distance in the manganates, with $\langle r_A \rangle$: $Ln_{0.5}A_{0.5}MnO_3$ (circles); $Ln_{0.7}A_{0.3}MnO_3$ (triangles).

where $\omega = \frac{1}{2}(\pi - \langle Mn\text{–}O\text{–}Mn \rangle)$. In order to obtain realistic values of W_a, we have normalized the values from equation (1), by setting the value of the bandwidth to 1 eV when $\langle r_A \rangle \sim 1.24$ Å. The manganate corresponding to an $\langle r_A \rangle$ of 1.24 Å is $La_{0.7}Sr_{0.3}MnO_3$. Furukawa and others have indeed taken W_a to be around 1 eV for the manganates with the FMM ground state [18–20]. In figure 6, we show the variation of W_a with $\langle r_A \rangle$ for both $Ln_{0.7}A_{0.3}MnO_3$ and $Ln_{0.5}A_{0.5}MnO_3$. This figure represents the variation of the apparent bandwidth with $\langle r_A \rangle$, based on purely geometrical factors, as defined by equation (1). The bandwidth shows a maximum in the case of $Ln_{0.7}A_{0.3}MnO_3$ around an $\langle r_A \rangle$ of 1.24 Å and a plateau above this $\langle r_A \rangle$-value in the case of $Ln_{0.5}A_{0.5}MnO_3$. What is noteworthy is that the change in W_a over the entire $\langle r_A \rangle$-range is rather small, although T_{CO} and T_C vary significantly with $\langle r_A \rangle$ (figure 4). Thus, the variation of the ferromagnetic Curie temperature and of the 'real' e_g-level bandwidth W of $Ln_{1-x}A_xMnO_3$ with the average A-site cationic radius $\langle r_A \rangle$ pose a problem. Note that, for $\Delta \langle r_A \rangle \cong 1.26$ Å–1.24 Å $= 0.02$ Å, we have $\Delta T_C \cong 350$ K–250 K $= 100$ K. In as much as both T_C and W scale with the orbital overlap of O: $2p\sigma$ with Mn: $3d_{x^2-y^2}$, which in turn is an increasing function of the Mn–O–Mn bond angle Θ ($=\pi - \omega$), and therefore of $\langle r_A \rangle$, we expect T_C and hence W to increase with $\langle r_A \rangle$ more drastically than is depicted in figure 6, in the case of W_a-values. The angular variation of the orbital overlap $\sim(1 - \cos \omega/2)$ is too small ($\leqslant 5\%$) to account for the relatively large observed change of T_C, which scales as $(1 - \cos \omega/2)^2$ due to double exchange, or of W, which scales as $1 - \cos \omega/2$.

The inadequacy of the Mn–O–Mn bond-angle variation for explaining the changes in T_C with $\langle r_A \rangle$, as observed, prompts us to consider covalent mixing effects associated with the changes in $\langle r_A \rangle$. Our reasoning is along the lines employed by Goodenough [21] in the context of $Ca_{1-x}Sr_xMnO_3$. Goodenough explained the enhancement of T_N for $Ca_{1-x}Sr_xMnO_3$ with increasing x successfully in terms of the lower covalent mixing of the larger A-site cation Sr. The covalent mixing of the A-site cation with the anion O: $2p\pi$ would normally compete with that between the anion and the B-site cation Mn: $3d\ t_{2g}$, thus reducing the superexchange coupling. In the case of $Ln_{1-x}A_xMnO_3$ with the electronically

mobile Mn^{3+}–O–Mn^{4+} units, in contrast to $Ca_{1-x}Sr_xMnO_3$ with the immobile Mn^{4+}–O–Mn^{4+} units, we can invoke the covalent mixing, but of the anion O: $2p\sigma$ with the A-site cation as competing against its covalent mixing with the B-site cation Mn: 3d e_g. Thus, with increasing $\langle r_A \rangle$, and hence decreasing A-site covalent mixing, we would expect an increasing e_g bandwidth W as well as the double-exchange coupling T_C. This covalent mixing effect is expected to be intrinsically much larger than the geometric (angular) effect (discussed earlier in relation to W_a). Furthermore, the effect of covalent mixing on W and T_C (double exchange) is considerably stronger than that on the superexchange (antiferromagnetic T_N), as the latter is of higher (fourth) order in the orbital overlap involved. We note that when $\langle r_A \rangle \sim 1.24$ Å, the Mn–O bond is shorter and more covalent, becoming increasingly ionic as $\langle r_A \rangle$ decreases (figure 5). When $\langle r_A \rangle$ is less than 1.17 Å, the Mn–O bond is close to being ionic, the distance closely corresponding to the sum of the ionic radii.

An important factor determining the magnitude of the charge-ordering temperature and its dependence on $\langle r_A \rangle$ is likely to be the strain resulting from the size mismatch between the A-site cations. In the absence of sufficient data, we cannot comment on how T_{CO} varies with the variance in the size distribution, σ^2, for a fixed $\langle r_A \rangle$. It is known however that the ferromagnetic Curie temperature, T_C, decreases significantly with the increase in σ^2 or size mismatch [6, 7]. With the available data, we find that high T_{CO}-values generally occur when σ^2 is small.

Acknowledgments

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