LETTER TO THE EDITOR

Bandwidth narrowing in bulk $L_{2/3}A_{1/3}MnO_3$ magnetoresistive oxides

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Abstract. The key structural factor governing the one-electron bandwidth (W) in $L_{2/3}A_{1/3}MnO_3$ (A = Ca, Sr) magnetoresistive oxides has been identified by a neutron study. Reducing the size (R_0) of the lanthanide, the Mn–O bondlength in MnO_6 octahedra does not change ($d_{Mn-O} \approx 1.960$ Å) and hence does not contribute to the narrowing of the $\sigma(e_g)$ conduction bandwidth. In contrast, the Mn–O–Mn angle (θ) bends at a rate $d\theta/dR_0 = 122.6$ Å^{-1}. The calculation of the bandwidth dependence on θ has been performed and it has been found to be proportional to the measured Curie temperature, both having almost a $T_c(\theta) \approx W(\theta) \approx \cos^2\theta$ dependence.

The electronic structure of transition metal (M) oxides has been a controversial topic during the last fifty years. Moreover, the discovery of colossal magnetoresistive effects (CMR) in hole-doped manganese oxides $L_{1-x}A_xMnO_3$ is attracting much attention since, in addition to their potential applications, their insulator-to-metal transition (T_C) is extraordinarily appealing [1]. Strong magnetostructural effects [2] and the double-exchange (DE) interaction are at the origin of the occurrence of ferromagnetism and metallic conduction. An essential step towards new technological applications is to discover all the structural factors governing the CMR.

When the atomic size of the lanthanide (R_0) is systematically reduced in manganites, resistivity, magnetic and neutron diffraction measurements [3, 4] have provided evidence of the following key features: (i) the Curie temperatures, where the CMR response is maximum, have been found to systematically lower in $(L_{1-x}L'_x)_{2/3}A_{1/3}MnO_3$ (A = Ca, Sr, Ba) samples when R_0 is reduced; (ii) the amplitude of the giant resistivity peak $\Delta\rho(T_C)/\rho$ ($= (\rho(T_C) - \rho(300 \text{ K}))/\rho(300 \text{ K})$) and the magnetoresistive response $\Delta\rho(H)/\rho$ ($= (\rho(H) - \rho(H = 0))/\rho(H)$) are also controlled by R_0, and they have enhanced values when T_C is shifted to lower temperatures [3]; (iii) the residual value ρ_0 of the resistivity at low temperature changes by 11 orders of magnitude when R_0 is increased from 1.09 to 1.20 Å [2–4]. Hence, it follows that the CMR response in manganese perovskites, having fixed the Mn^{3+}/Mn^{4+} ratio to the optimal value of two ($A_{1/3}$), can be tailored to great extent through variations of the L size. This structural tuning of the CMR has been proposed to be the result of changes in the Mn–O–Mn bond angles [3, 4] and the associated $\sigma(e_g)$ bandwidth (W) narrowing. Nevertheless, a systematic understanding of the microscopic structural features in these materials, necessary for an appropriate tailoring of the CMR response, is still lacking.

We have recently reported [5] a detailed structural analysis of the $L_{2/3}A_{1/3}MnO_3$ series, concentrating on the evolution with R_0 of the structural parameters governing the narrowing
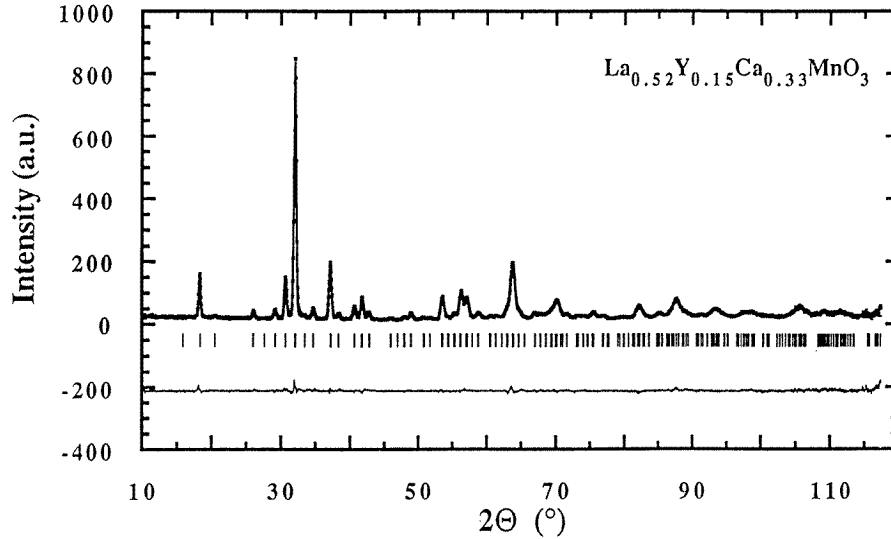
Figure 1.   Observed (+) and calculated (——) neutron diffraction patterns for La$_{0.52}$Y$_{0.15}$Ca$_{1/3}$MnO$_3$ at room temperature.

of the electronic bandwidth, i.e. the e$_g$(Mn)–2p$_\sigma$(O)–e$_g$(Mn) orbital overlapping: the Mn-to-O distance (d_{Mn-O}) and the Mn–O–Mn angle (θ). It has been shown that the mean d_{Mn-O} distance is not significantly modified in this series, despite the samples exhibiting very different values of T_C whereas the mean angle $\theta = \langle$Mn–O–Mn$\rangle$ subtended systematically increases with increasing ionic radius R_0. In this letter, the correlation between the ferromagnetic ordering temperature T_C and θ is examined and it is found that T_C increases almost linearly with $\cos^2 \theta$. We have evaluated the $\sigma(\text{e}_g)$ bandwidth as a function of θ and the proportionality between $W(\theta)$ and T_C has been proved for the first time.

Ceramic samples of (L, L')$_{2/3}$A$_{1/3}$MnO$_3$ composition (L, L' = Nd, Pr, Y, La; A = Ca, Sr) were synthesized by solid-state reaction, mixing stoichiometric amounts of the appropriate high-purity oxides at 1100 °C for 24 h, with intermediate grindings and a final sintering process at 1400 °C. The as-prepared materials were characterized by x-ray and neutron diffraction [3, 5, 6]. Magnetization and transport measurements have been extensively discussed in [3], [6] and [7]. Neutron diffraction data of high resolution were obtained at the Reactor Orphée of the Laboratoire Léon Brillouin on 3T2 ($\lambda = 1.227$ Å). All of the samples were single phase and the oxygen content was found to be 3.00 from neutron data, within the calculated standard error ($\approx$1%). We applied the Rietveld method to the diffraction patterns by using the Fullprof program [8]. As an example, one of the fitted patterns is shown in figure 1. The transition temperatures determined from neutron, magnetic and resistivity measurements [3, 5–7] confirm the strong dependence of T_C on R_0 or, equivalently, on the tolerance factor t, defined as

$$t = d_{L-O}/\sqrt{2}(d_{Mn-O}). \tag{1}$$

On the basis of the diffraction data, the key parameters that determine the e$_g$(Mn)–2p$_s$(O) orbital have been analyzed [5]. For the completeness of the forthcoming discussion we recall briefly the main results and signal their relevance for the electronic coupling. First, it is found that the mean d_{Mn-O} distance is not significantly modified in this series.

In figure 2 we show the mean Mn–O distance in the MnO_6 octahedra of Ca and Sr samples with mean ionic radii R_0 varying within the interval 1.10–1.25 Å. This figure illustrates that the mean Mn–O distance is the same, $\langle d_{Mn-O} \rangle \approx 1.960(2)$ Å, in all the members of the series. At this point we call to mind that in this type of transition metal perovskites, a different effective doping of the M–O bond brings about a systematic variation of the M–O bondlength, as has been recently observed in isostructural $L_{1-x}A_xNiO_3$ perovskites (A = Sr, Ca, ...) [9] (where $\Delta d_{M-O}/\Delta x_{effec} \approx 10\%$ Å). Hence, the above result implies that the effective incorporation of extra carriers (holes) into the e_g $2p_\sigma$ bands does not depend significantly on the degree of distortion of the structure. Two additional conclusions are thus inferred from figure 2. (i) The similar $\langle$Mn–O$\rangle$ bondlength in $L_{2/3}A_{1/3}MnO_3$ compounds reflects identical hole doping of the bond. The efficiency in the hole injection process into the lower $\sigma(e_g)$ band is therefore not modified by changes in R_0. (ii) The data in figure 2 also confirm that the efficiency of such incorporation does not depend on the bivalent cation used for doping (Ca or Sr).
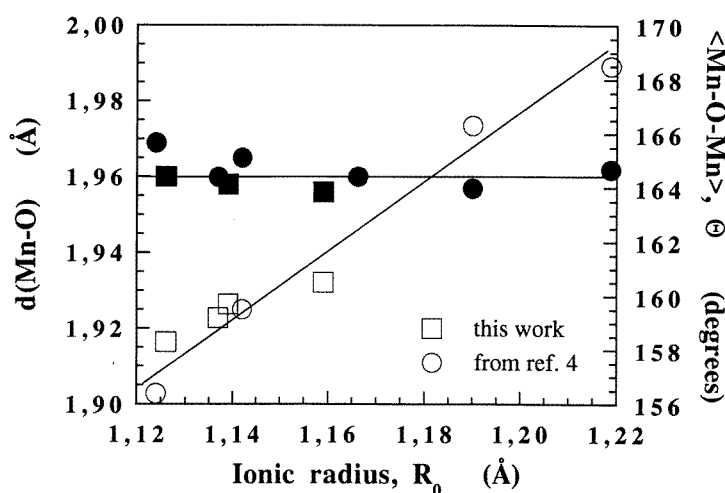
Figure 2. The average Mn–O distance (left-hand axis–solid symbols) and average Mn–O–Mn angle (θ) (right-hand side–empty symbols) in the MnO_6 octahedra of the $L_{2/3}A_{1/3}MnO_3$ series as a function of the ionic radius of the L_1A ions (R_0).

On the other hand, we have considered the other structural parameter governing the strength of the hopping integral between $e_g(Mn)$–$2p_\sigma(O)$–$e_g(Mn)$ orbitals: θ. There are two Mn–O–Mn angles in the *Pbnm* symmetry that are very similar (for instance $\theta_1 = 158.8(3)°$ and $\theta_2 = 158.2(7)°$ in $La_{0.52}Y_{0.15}Ca_{1/3}MnO_3$) and only one if the symmetry is $R-3c$ (when $t \gtrsim 0.93$ [4]). In figure 2 we show how the mean angle $\theta = \langle$(Mn–O–Mn)$\rangle$ subtended in $L_{2/3}A_{1/3}MnO_3$ systematically increases with increasing ionic radius R_0, or equivalently, t. The t parameter in figure 2 has been calculated taking $d_{Mn-O} = 1.960$ Å and the d_{L-O} values tabulated in [10] (proportional to R_0). Consequently, a central result of our study is that, by contrast with the evolution of d_{Mn-O} in figure 2, the distortion in the skeleton of MnO_6 octahedra is found to decrease with increasing R_0 at a rate $d\theta/dR_0 = 122.6°$ Å^{-1}.

In an attempt to obtain further insight into the crucial role of θ, we have examined the dependence of T_C on the Mn–O–Mn bond angle of the studied samples. It is found that within the interval 1.125 Å $< R_0 <$ 1.16 Å T_C increases with θ. For larger radii some saturation of $T_C(\theta)$ is observed. This is shown in figure 3. The solid line is a fit to a law
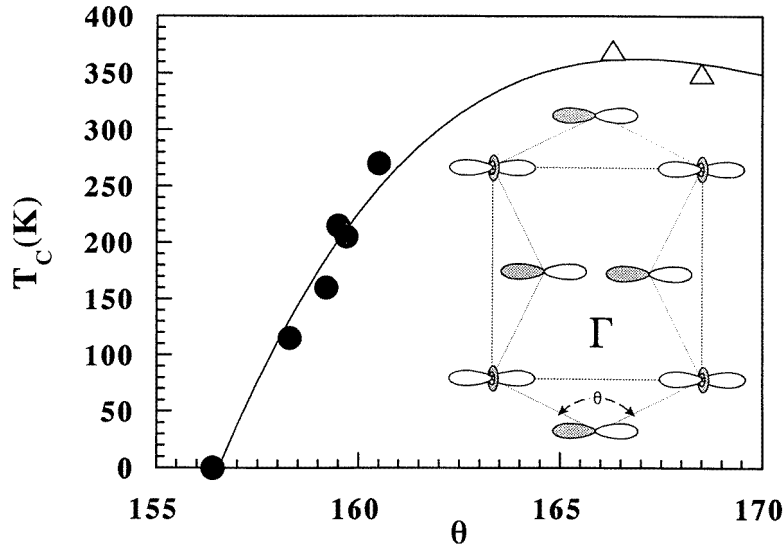
Figure 3. T_C against θ in the optimally doped $L_{2/3}A_{1/3}MnO_3$ series of magnetoresistive perovskites. The open triangles on the right ($Sr_{1/3}$, $(Ba, Sr)_{1/3}$) are from [4]. The solid line is a fit to $\alpha \cos(\theta) + \beta \cos^2(\theta) + \gamma \cos^3(\theta)$ as described in the text. The inset shows an schematic representation of the relevant orbitals necessary for the bandwidth calculation along Γ–X.

$T_C(\theta) = \alpha \cos(\theta) + \beta \cos^2(\theta) + \gamma \cos^3(\theta)$ with $\alpha = 1.15 \times 10^5$ K, $\beta = 2.4 \times 10^5$ K and $\gamma = 1.2 \times 10^5$ K. Because $\beta > \alpha$, γ, to first order $T_C \sim \cos^2(\theta)$. The qualitative meaning of this picture is that when increasing R_0 the Mn–O–Mn bond angle opens and thus the $\sigma(e_g)$ bandwidth increases.

In order to obtain an estimate of the expected dependence of $W(\theta)$, we have modelled the effects of bond bending on the $\sigma(e_g)$ band corresponding to the Γ–X direction using the LCAO approach of Harrison [11]. To keep the analysis simple, we have included only nearest-neighbour interactions, and only rotation (of angle θ) of the oxygen octahedra along the c-axis has been included. In figure 3 (inset) we show some of the orbitals involved in the calculations: d_{z^2}, p_z, p_x and p_y. This seems to be a reasonable starting point due to the fact that the Jahn–Teller distortion in the parent compound $LaMnO_3$ leads to a significant depression of the d_{z^2} orbitals with respect to the $d_{x^2-y^2}$ orbitals [12]. It is clear that in doped compounds the carrier delocalization should lead to a softening of the in-plane Mn–O bond-length distortion, as experimentally observed [5], and thus the splitting between the d_{z^2} bandwidth should not be substantially different. The atomic term energies for O(2p) and Mn(3d) ($E_p = -14.13$ eV and $E_d = -11.6$ eV respectively) and the overlap integrals ($V_{pd_\sigma} = -1.68$ eV and $V_{pd_\pi} = 0.77$ eV) have been calculated according to [11] using an averaged $d_{Mn-O} = 1.96$ Å distance (according to the data of figure 2).

In figure 4 we show the angular dependence of the $\sigma(d_{z^2})$ band. This picture clearly reveals the pronounced effect of the bond bending on W, which is the key physical parameter of the DE mechanism. The calculated $W(\theta)$ values, shown in figure 4 (inset), again can be expressed as $W(\theta) = A \cos(\theta) + B \cos^2(\theta) + C \cos^3(\theta)$ (solid line) with $A = -9.8$ eV, $B = -22.3$ eV and $C = -12.7$ eV. In fact this functional dependence originates from the angular dependence of the Slater interatomic matrix elements. For instance, $\langle p_z | d_{z^2} \rangle = n[n^2 - (l^2 + m^2)/2]V_{pd_\sigma} + 3^{1/2}n(l^2 + m)V_{pd_\pi}$ where (l, m, n) are the
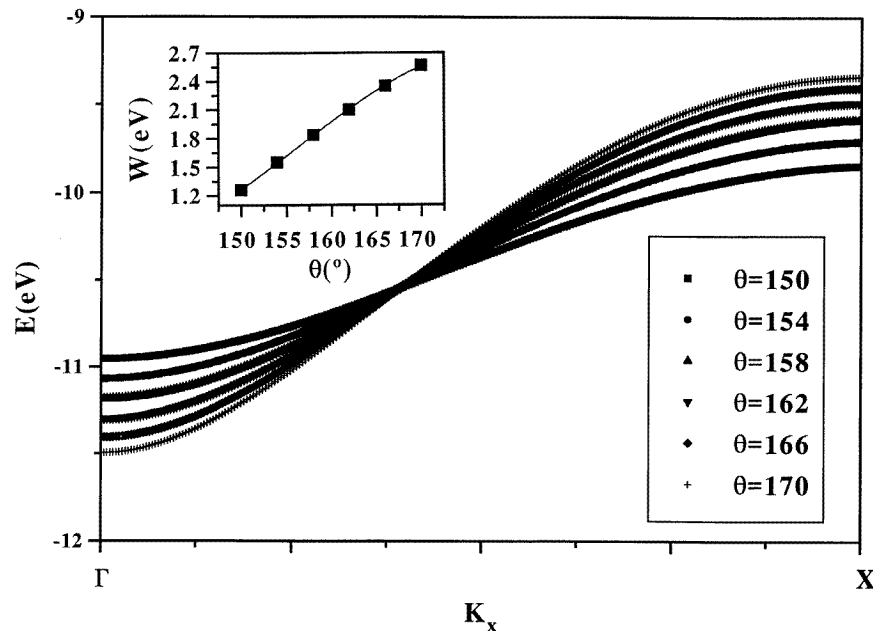
Figure 4. The conduction band $\sigma(e_g)$ along the Γ–X direction as a function of the Mn–O–Mn angle θ. Inset, the angular dependence of the bandwidth $W(\theta)$. The solid line is a fit to $A\cos(\theta) + B\cos^2(\theta) + C\cos^3(\theta)$ as described in the text.

director cosines of the unit vector from the left-hand state to the right-hand state. In our particularly simple example of figure 3 $l = -\cos(\theta/2)$, $m = 0$, $n = \sin(\theta/2)$. We note that the ratios of the coefficients A/B and C/B are similar to those of α/β and γ/β obtained from the $T_C(\theta)$ dependence. It is very significant that the same function describes the measured $T_C(\theta)$ because it reflects the fact that T_C and W are closely related.

To emphasize this close relationship between the ferromagnetic ordering temperature and the bandwidth, we plot in figure 5 the measured $T_C(\theta)$ against the calculated $W(\theta)$. The linear $T_C(W)$ behaviour observed provides a clear picture of the dominant role of the bandwidth in the magnetic coupling. In addition, this figure makes evident that for larger θ angles, that is for larger R_0 (>1.16 Å) the measured $T_C(\theta)$ falls below the calculated $W(\theta)$, reflecting the fact that (A, B, C) and (α, β, γ) coefficients are not strictly proportional. This effect cannot be attributed to a change of the Mn–O distance because, as shown in figure 2, d_{Mn-O} remains constant. This is a very intriguing point that should be further investigated. We notice that all measured materials having $R_0 > 1.16$ Å are doped with Sr or Ba, whereas those having shorter radii have been doped with Ca. Therefore one can speculate that the behaviour of the Sr and Ba based samples when compared to those of Ca, having lower ferromagnetic temperature, that the bandwidth contribution alone would predict, reflects the higher electropositivity of Ba and Sr against Ca [13]. In this case the strength of the underlying antiferromagnetic interactions between the filled $\pi(t_{2g})$ orbitals would be reinforced and thus the Curie temperature reduced. In fact, comparison of transport and magnetic measurements [14] on $(L, L')_{2/3}A_{1/3}MnO_3$ compounds having the same average R_0 show that T_C of the Sr doped compounds is systematically lower than T_C of the Ca doped oxides.

In summary, we have shown that the evolution of $\theta(t)$ in figure 2, and not possible
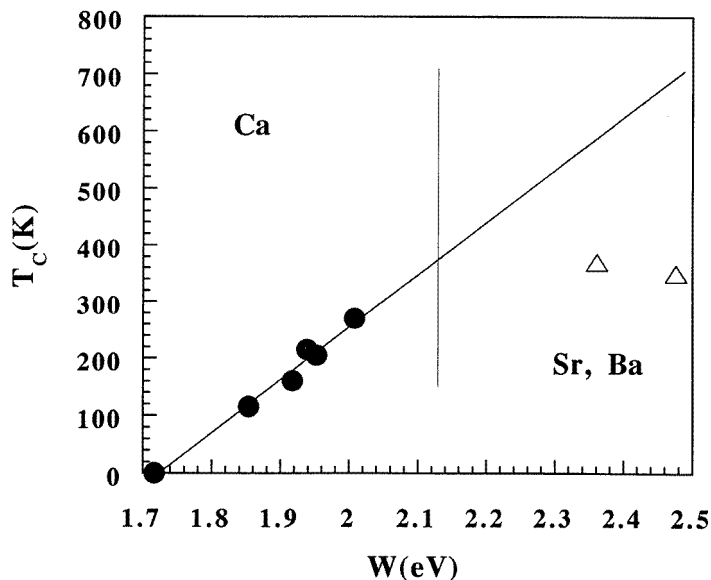
Figure 5. The dependence of the measured Curie temperature on the calculated bandwidth for samples having different bond bendings. The open triangles on the right ($Sr_{1/3}$, $(Ba, Sr)_{1/3}$) are from [4].

changes in the d_{Mn-O} distance, is at the origin of the reduction of W and the tuning in the electromagnetic response previously observed in these materials. The consequences of the $\theta(R_0)$ evolution depicted in figure 2 are extraordinary: the efficiency of the DE mechanism weakens with a narrower bandwidth. We have explicitly proved that $T_c(\theta) \sim W(\theta)$. Further work is needed to understand the weaker dependence of the Curie temperature on W in the compounds having larger alkalines.

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