Cation disorder and size effects in magnetoresistive manganese oxide perovskites

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Large disorder effects due to size differences between A-site R^{3+} (R=La,Pr,Nd,Sm) and M^{2+} (M=Ca,Sr,Ba) cations have been found in magnetoresistive $(R_{0.7}M_{0.3})MnO_3$ perovskites. The ferromagnetic-metal–paramagnetic-insulator transition temperature T_m varies as $T_m = T_m(0) - pQ^2$ due to strain fields resulting from ordered or disordered oxygen displacements Q that are parametrized by the statistical mean and variance of the A cation radius, respectively. The value of p is related to the Mn-O force constant showing that Mn^{3+} Jahn-Teller distortions assist electron localization at T_m. The maximum possible T_m is estimated to be $\sim$530 K although experimentally observable values are $\leqslant$360 K. A large suppression of magnetoresistance due to cation disorder is also evidenced. [S0163-1829(96)51046-5]

The transition between ferromagnetic metallic and paramagnetic insulating states in $(R_{1-x}M_x)MnO_3$ perovskites is characterized by a maximum in the electrical resistivity ρ_m at the transition temperature T_m. ρ_m decreases greatly in an applied magnetic field B, and this giant negative magnetoresistance (MR) effect[1] may be quantified by the ratio of resistivities in zero and applied fields, $\rho(0)/\rho(B)$, which has a maximum value R_B at a temperature close to T_m. The magnitude of R_B increases greatly as T_m is shifted to lower temperatures, from values of 1–2 at room temperature up to, e.g., R_{5T}=250 000 in $Pr_{0.7}Sr_{0.05}Ca_{0.25}MnO_3$ at 85 K.[2]

The hole-doping x (giving an Mn oxidation state of $3+x$) and the average A-site cation radius $\langle r_A \rangle$ are found to be key chemical variables that control T_m,[3–7] giving a maximum T_m=360 K for x=0.3 and $\langle r_A \rangle$=1.23 Å.[4] Hole doping in the range $x \approx 0.2$–0.5 is needed to stabilize the low-temperature ferromagnetic metallic phase in which a ferromagnetic ''double exchange'' interaction between the localized t_{2g}^3 electron configurations on adjacent Mn ions is mediated by the itinerant, spin-polarized e_g electrons.[8] The strong dependence of T_m on $\langle r_A \rangle$ is shown in Fig. 1(a) using experimental values for $(R_{0.7}M_{0.3})MnO_3$ samples from the literature[2,4–6,9–11] and this study (Table I). This evidences a very strong coupling of electronic motion to lattice effects in $(R_{1-x}M_x)MnO_3$ perovskites. Supporting observations include the switching of a lattice distortion in $(La_{0.83}Sr_{0.17})MnO_3$ by an applied magnetic field,[12] striction-coupled MR in the $(Nd,Sm)_{0.5}Sr_{0.5}MnO_3$ system,[13] and a large oxygen isotope effect on the transition temperature in $(La_{0.7}Ca_{0.3})MnO_3$.[14] A further lattice effect whose influence has not been studied in detail, although it is inherent to almost all $(R_{1-x}M_x)MnO_3$ compositions, is the random disorder of R^{3+} and M^{2+} cations with different sizes distributed over the A sites in the perovskite structure. To quantify this effect, we use the *variance* (second moment) of the A-cation radius distribution, σ^2. For two or more A-site species with fractional occupancies y_i ($\Sigma y_i = 1$), the variance of the ionic radii r_i about the mean $\langle r_A \rangle$ is $\sigma^2 = \Sigma y_i r_i^2 - \langle r_A \rangle^2$. Standard ionic radii[15] with values 1.216–1.132 Å for R^{3+}=La-Sm and 1.18, 1.31, and 1.47 Å for M^{2+}=Ca, Sr, and Ba, respectively, were used to calculate $\langle r_A \rangle$ and σ^2.

To determine how the properties of $(R_{1-x}M_x)MnO_3$ perovskites change with the A-site variance σ^2, we have prepared a series of eight samples (Table I) with fixed doping (x=0.3) and mean A-cation radius ($\langle r_A \rangle$=1.23 Å), but in which σ^2 is varied by use of different R and M combinations. The samples were prepared under identical conditions by solid-state reaction in air at 1350 °C. Powder x-ray diffraction showed all the samples to consist of a single perovskite phase with the orthorhombic $\sqrt{2}a_p \times 2a_p \times \sqrt{2}a_p$ $Pnma$ superstructure, where a_p is the cubic perovskite cell dimension.[12] The cell parameters a, b, and c were refined by the Rietveld method.[16] Resistivities [Fig. 2(a)] of sintered polycrystalline bars (approximate dimensions $1.5 \times 4 \times 8$ mm^3) were measured between 80 and 400 K using a standard four-probe technique and magnetizations M [shown as B/M in Fig. 2(b)] were recorded using a Quantum Design superconducting quantum interference device magnetometer with an applied field B=50 mT. The peak resistivity temperatures T_m are in good agreement with characteristic magnetic transition temperatures T_C defined by minima in dM/dT.[5]

The parameters in Table I all show a strong dependence on σ^2. The differences between the unit-cell parameters decrease smoothly with increasing σ^2 and the combined effects of disorder and inhomogeneity (discussed below) necessitated tetragonal or cubic cell parameter constraints at high values of σ^2. T_m shows a strong linear dependence upon σ^2 up to $\sim$0.015 $Å^2$ (Fig. 3) and then varies around an average value of $\sim$100 K above this limit. The latter behavior is due to segregation of the A cations as a result of the large disparities in size, so that the samples are no longer microscopically homogeneous, although they appear to be single phases by powder x-ray diffraction. There is a corresponding change in the low-temperature behavior of the inverse magnetizations [Fig. 2(b)] which, for the three samples with $\sigma^2 > 0.015$ $Å^2$, lie substantially above the Curie-Weiss

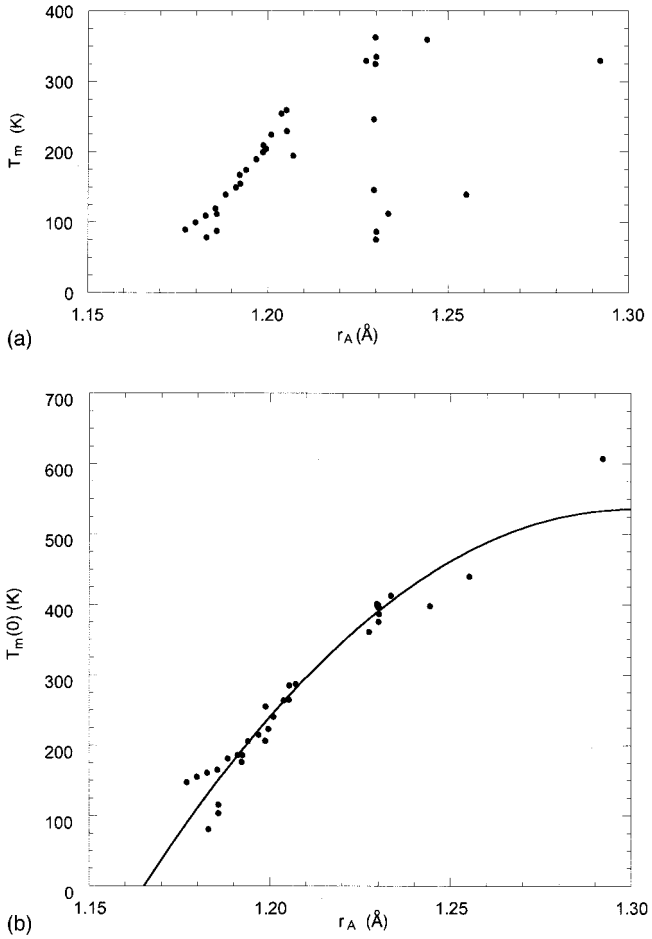

FIG. 1. Plots of (a) experimental T_m values, and (b) $T_m(\sigma^2=0)$ corrected for cation-size disorder using the procedure described in the text, against average A-cation radius for $Ln_{0.7}M_{0.3}MnO_3$ compositions. (b) shows the fit of Eq. (2).

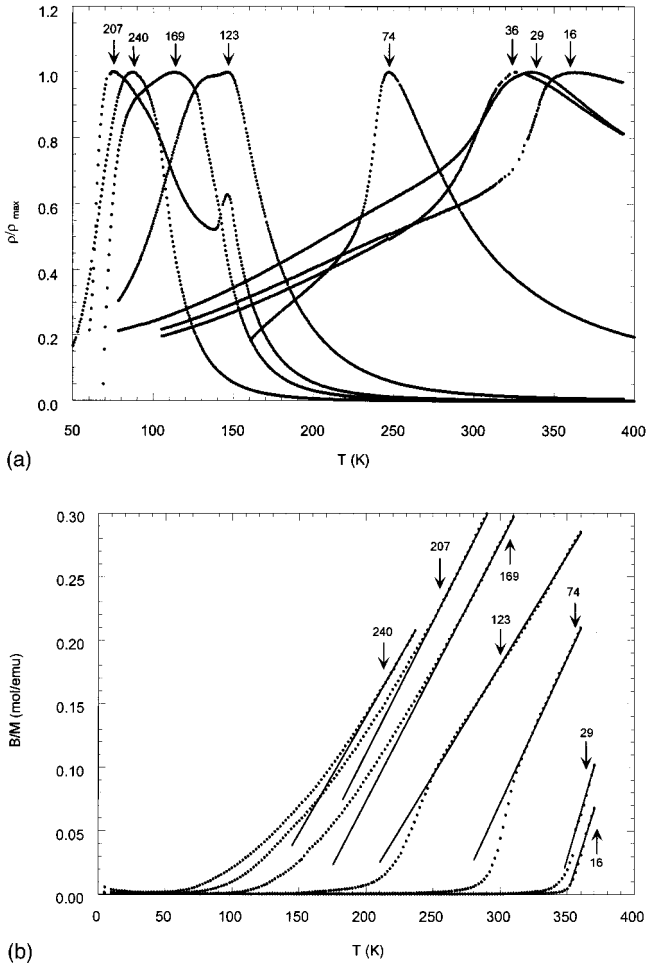

FIG. 2. Plots of (a) normalized resistivity, and (b) inverse magnetization as B/M, with the σ^2 ($\times 10^4$ Å^2) values labeled. The high-temperature Curie-Weiss limits are shown as full lines in (b). Data for the $\sigma^2=0.0036$ Å^2 sample have been omitted from (b) for clarity as they largely overlap the $\sigma^2=0.0029$ Å^2 data.

limit as T_C is approached from high temperatures, possibly reflecting a coexistence of antiferromagnetic and ferromagnetic regions.[17] Inhomogeneity is also evidenced by the presence of a second resistive transition in the $\sigma^2=0.0207$ Å^2 sample [Fig. 2(a)], and by the disparity between T_m and T_C for the $\sigma^2=0.0240$ Å^2 material (Table I). The nature of the phase segregation will depend upon the sizes of the individual A cations so that T_m is no longer a simple function of σ^2.

TABLE I. Variation of cell parameters a, b, and c, the resistivity maximum ρ_m, and the metal-insulator transition temperature measured from resistivity (T_m) and magnetization (T_C) data with cation-size variance σ^2 for a series of $(R_{0.7}M_{0.3})MnO_3$ perovskites with constant $\langle r_A\rangle = 1.23$ Å .

A-site composition	σ^2 (Å^2)	a (Å)	b (Å)	c (Å)	ρ_m (Ω cm)	T_m (K)	T_C (K)
$La_{0.70}Ca_{0.11}Sr_{0.19}$	0.0016	5.5045(6)	7.7542(9)	5.4482(6)	1.22×10^{-2}	363	350
$La_{0.32}Pr_{0.38}Sr_{0.30}$	0.0029	5.5046(4)	7.7175(5)	5.4538(3)	1.58×10^{-2}	336	332
$La_{0.53}Sm_{0.17}Sr_{0.30}$	0.0036	5.5089(4)	7.7177(5)	5.4582(3)	1.84×10^{-2}	326	325
$Pr_{0.70}Sr_{0.23}Ba_{0.07}$	0.0074	5.4968(3)	7.7307(4)	5.4700(3)	1.13×10^{-1}	247	248
$Nd_{0.70}Sr_{0.16}Ba_{0.14}$	0.0123	5.4927(3)	7.7345(4)	5.4740(3)	7.96×10^{0}	146	148
$Nd_{0.41}Sm_{0.29}Ba_{0.20}Sr_{0.10}$	0.0169	5.4943(3)	7.7328(4)	5.4760(3)	9.94×10^{1}	87	98
$Nd_{0.15}Sm_{0.55}Ba_{0.25}Sr_{0.05}$	0.0207	5.4844(4)	7.7484(10)	5.4844[a]	2.32×10^{2}	76	72
$Sm_{0.70}Ba_{0.30}$	0.0240	5.4879(1)	7.7611[b]	5.4879[b]	6.67×10^{2}	113	60

[a] $a=c$ constrained to give stable refinement.

[b] $a=b/\sqrt{2}=c$ constrained to give stable refinement.

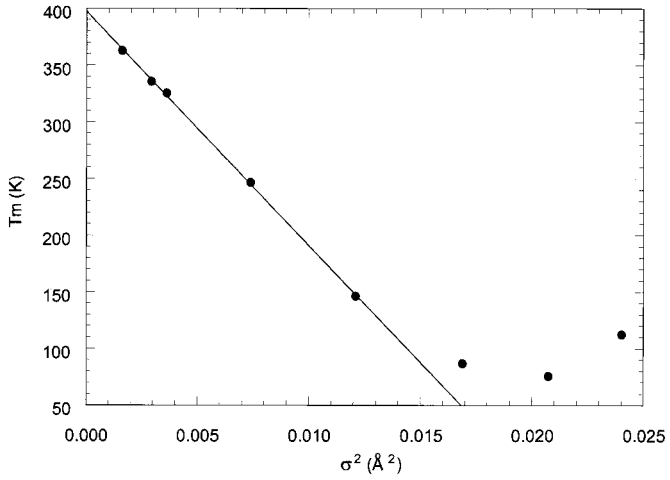

FIG. 3. Variation of T_m with A-cation size variance σ^2, showing the fit of Eq. (1) to data with $\sigma^2 < 0.015$ Å^2.

A fit to the linear region in Fig. 3,

$$T_m(\langle r_A\rangle,\sigma^2) = T_m(\langle r_A\rangle,0) - p_1\sigma^2, \qquad (1)$$

gives $T_m(\langle r_A\rangle,0) = 400$ K and $p_1 = 20\,600$ K Å^{-2} for our series of samples in which $\langle r_A\rangle = 1.23$ Å . $T_m(\langle r_A\rangle,0)$ is an estimate of the ideal metal-insulator transition temperature that would be observed if cation-size disorder were not present.[18] Equation (1) has been used to estimate the variation of T_m with $\langle r_A\rangle$ in the absence of cation-size disorder, shown in Fig. 1(b), by extrapolating $T_m(\langle r_A\rangle,0)$ from T_m for all the reported compositions with $\sigma^2 < 0.015$ Å^2 in Fig. 1(a), assuming the slope p_1 to be independent of $\langle r_A\rangle$. For the small number of samples with $\sigma^2 > 0.015$ Å^2 the cruder approximation $T_m(\langle r_A\rangle,0) \approx T_m + 300$ based on the inhomogeneous region of Fig. 3 has been used.

A-site cation disorder results mainly in random displacements of oxide ions from their average crystallographic positions. In a close-packed, hard-sphere ionic model of the structure, the mean random displacement is $Q_r \approx \sigma$ ($\sigma = \sqrt{\sigma^2}$ is the standard deviation in the distribution). Changing the mean A-cation radius $\langle r_A\rangle$ results in analogous, ordered oxide displacements for which the mean value is $Q_0 \approx r_A^0 - \langle r_A\rangle$, where the ideal radius for an undistorted cubic perovskite is $r_A^0 = 1.30$ Å for $(R_{0.7}M_{0.3})MnO_3$ compositions.[19] Hence, following Eq. (1), the disorder-corrected variation of T_m with $\langle r_A\rangle$ should be of the form

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

with $p_2 \sim p_1$. This expression is found to give a good fit to the extrapolated data in Fig. 1(b) with refined parameters $T_m(r_A^0,0) = 530 \pm 20$ K and $p_2 = 29\,000 \pm 1000$ K Å^{-2}. $T_m(r_A^0,0)$ is an experimental estimate of the metal-insulator transition temperature for an ideal, disorder-free $(R_{0.7}M_{0.3})MnO_3$ perovskite.

These results show that both the average radius $\langle r_A\rangle$ [Fig. 1(b)] and the size variance σ^2 of the A-site cations (Fig. 3) are key chemical parameters that can be used to tune the metal-insulator transition in $(R_{1-x}M_x)MnO_3$ perovskites at a constant doping x. In homogeneous samples, the dependence of T_m upon both parameters is described to a good approximation by equations $T_m = T_m(0) - pQ^2$, where the oxide ion displacements Q in the strain term are random due to A-site disorder [$Q_r \approx \sigma$ in Eq. (1)] or ordered due to the changing average A-cation radius [$Q_o \approx r_A^0 - \langle r_A\rangle$ in Eq. (2)]. The experimental T_m values for $x = 0.3$ [Fig. 1(a)] fall into two regions. For $\langle r_A\rangle < 1.22$ Å , the cation-size variance is small and the true variation of T_m with $\langle r_A\rangle$ is observed. As $\langle r_A\rangle$ increases above 1.22 Å , the disparity in R and M (=Sr and Ba) radii gives rise to an increasing σ^2 effect which offsets the increase in $T_m(0)$, resulting in approximately constant T_m values. $La_{0.7}Ba_{0.3}MnO_3$ has the maximum observable $\langle r_A\rangle$ of 1.29 Å but also a large value of $\sigma^2 = 0.0135$ Å^2 so that T_m is only 320 K although the extrapolated value for an ideal $(R_{0.7}M_{0.3})MnO_3$ perovskite is $T_m \approx 530$ K.

Our results are in agreement with recent mean-field treatments of the metal-insulator transition in $(R_{1-x}M_x)MnO_3$ perovskites.[20] Calculations based upon the double exchange interaction alone give unrealistically high values of $T_m \approx 2500$–5000 K,[21] but including electron-localizing (polaron) effects due to Jahn-Teller distortions of $Mn^{3+}O_6$ octahedra gives estimates of $T_m \sim 500$ K for small e_g electron hopping energies ~ 0.2 eV,[20] in agreement with our extrapolated $T_m(r_A^0,0)$ of 530 K. The Jahn-Teller part of the Hamiltonian contains the lattice strain term $(K/2)\Sigma Q_b^2$ summed over changes in Mn-O bond lengths Q_b where K is the harmonic force constant for these bonds. Assuming the changes in the T_m to be due principally to this strain energy, then an approximate expression for T_m is

$$T_m(\langle r_A\rangle,\sigma^2) = T_m(r_A^0,0) - \frac{K}{2\Delta S_m}\sum Q_b^2, \qquad (3)$$

where ΔS_m is the entropy change at the transition. If the mean-squared displacements Q^2 ($=Q_r^2$ or Q_o^2) due to changes in the cation variance or average size are assumed to be isotropic then $Q_b^2 = Q^2/3$ and for six Mn-O bonds per cation, Eq. (3) becomes

$$T_m(\langle r_A\rangle,\sigma^2) = T_m(r_A^0,0) - \frac{KQ^2}{\Delta S_m} \qquad (4)$$

so that the experimental coefficients p_1 and p_2 in Eqs. (1) and (2) are $\approx K/\Delta S_m$. Estimating $\Delta S_m \approx k\ln(2\langle S\rangle + 1)$ with $\langle S\rangle = 1.85$ and taking the range of $p \approx 21\,000$–$29\,000$ K Å^{-2} from the experimental fits of Eqs. (1) and (2) gives $K \approx 45$–65 N m^{-1}. This is of the correct magnitude for the Mn-O force constant, given the approximate nature of the calculation, and lies within the range 30–300 N m^{-1} estimated for K in $LaMnO_3$.[22] Hence, the local deformations of the MnO_6 octahedra due to A-cation disorder and size effects act as ''preformed Jahn-Teller distortions'' that promote the localization of e_g electrons thereby lowering T_m.

Consideration of A-cation size disorder through the variance σ^2 also accounts for variations in MR properties of $(R_{1-x}M_x)MnO_3$ perovskites with similar T_m values. Negligible disorder ($\sigma^2 < 10^{-6}$ Å^2) can be realized in the $Pr_{1-x}Ca_xMnO_3$ system due to the exact size matching of Pr^{3+} and Ca^{2+}, which enables a variety of charge and spin ordered states to be observed.[23] These phases are nonmetallic due to the small $\langle r_A\rangle$ of 1.18 Å , although a transition to the

ferromagnetic metallic state of $Pr_{0.7}Ca_{0.3}MnO_3$ can be induced by applied pressure,[6] magnetic fields (resulting in very large MR),[6,23] or chemical substitutions with La or Sr which increase $\langle r_A \rangle$.[2,5,24] The latter materials have very high magnetoresistance peaks, up to $R_{5T}=250\,000$ at 85 K in $Pr_{0.7}Sr_{0.05}Ca_{0.25}MnO_3$.[2] Phases with comparable $\langle r_A \rangle$ and T_m values, but significant A-cation size disorder, have much smaller MR peaks, e.g., $La_{0.6}Y_{0.1}Ca_{0.3}MnO_3$ with $\sigma^2=0.0022$ Å^2 has R_{5T} of only 40 at 120 K,[11] showing that A-cation disorder strongly reduces the magnitude of the magnetoresistive effect. Smaller reductions due to disorder are observed at higher temperatures, e.g., $La_{0.525}Pr_{0.175}Ca_{0.3}MnO_3$ ($\sigma^2=0.0003$ Å^2) has $R_{5T}=10$ at 210 K,[5] whereas $Nd_{0.7}Sr_{0.3}MnO_3$ ($\sigma^2=0.0044$ Å^2) has $R_{6T}=1.5$ at 195 K.[4]

In summary, the metal-insulator transition temperature and the magnitude of the MR in $(R_{1-x}M_x)MnO_3$ perovskites are dependent upon the hole-doping x, the mean A-cation radius $\langle r_A \rangle$, and the A-site disorder quantified by the size variance σ^2. The latter two effects are both described by equations $T_m=T_m(0)-pQ^2$ in which Q is the mean ordered and random oxide ion displacement, respectively, and p is related to the Mn-O force constant. These strain fields reduce T_m considerably from an estimated maximum value of 530 ± 20 K for $x=0.3$ which is in good agreement with recent theoretical estimates. Maximum MR effects are found in materials having a low value of $\langle r_A \rangle$, and hence a low T_m, and a small σ^2, such as $Pr_{1-x}Ca_xMnO_3$-based compositions.

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