Role of size mismatch of *A*-site cations on the first-order transition in manganates

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The effect of *A*-site ionic size mismatch σ^2 on perovskite manganates exhibiting a first-order phase transition at the ferromagnetic Curie temperature T_c as well as charge ordering temperature T_{co} is investigated. For a given average ionic radius $\langle r_A \rangle$ manganates with relatively small σ^2 seem to show first-order behavior. The occurrence of first-order paramagnetic insulator to ferromagnetic metal transition enhances magnetoresistance in the vicinity of T_c. Manganates with larger σ^2 are generally insulating and the nature of electronic conduction changes gradually from activated to variable range hopping with increasing σ^2. [S0163-1829(99)11829-0]

Perovskite manganates belong to a unique class of materials because of the large abundance of fascinating properties they contain. Among them are the wide variety of distinct phase transitions these oxides undergo as a function of temperature, pressure, magnetic and electric fields, and when subjected to radiation has drawn much attention.[1–7] In this study, we focus on two different kinds of first-order phase transitions induced by temperature variation which are characterized by thermal hysteresis in resistivity and magnetization at (1) the ferromagnetic Curie temperature T_c associated with the paramagnetic insulator (PMI) to ferromagnetic metal (FMM) transition and (2) the charge ordering temperature T_{co} corresponding to the transition from the paramagnetic insulator or ferromagnetic metal to the antiferromagnetic charge ordered insulator (AFMCOI).

It has been shown by Hwang *et al.*[8] for a series of $La_{1-x-y}Pr_xCa_yMnO_3$ with fixed $y \approx 0.3$ (fixed carrier concentration) that the ferromagnetic Curie temperature decreased and the PMI to FMM transition became increasingly first order with decreasing $\langle r_A \rangle$, the average radius of the *A*-site cations. Decreasing $\langle r_A \rangle$ reduces the Mn-O-Mn bond angle and hence the e_g electron transfer integral which in turn controls the T_c. The origin of the first-order transition at T_c remains a matter of speculation. Archibald *et al.*[9] have inferred from the thermopower measurements under varying pressures on $(La_{1-x}Nd_x)_{0.7}Ca_{0.3}MnO_3$ that a double well potential for the equilibrium Mn-O bond length exists as the system passes through the localized polaronic regime to the itinerant double exchange regime. This would suggest a structural origin with discontinuous changes in unit cell volume at T_c. The thermal expansion studies by Ibarra *et al.*[10] have shown the occurrence of a transition from the high volume (insulating) to low volume (metallic) state in the vicinity of T_c. $(La_{1-x}L_x)_{2/3}Ca_{1/3}MnO_3$ with $L = Gd$ or Dy (Refs. 11 and 12) which also shows appreciable hysteresis in the temperature dependence of resistivity and magnetization displays distinct features of a magnetically driven first-order transition. The low-temperature metallic phase in these systems appears to be canted ferromagnetic (CFM) and undergoes a metamagnetic transition to the colinear phase in presence of low applied fields with unusually large magnetoresistance.

Strong first-order effects near T_{co} have been observed in $L_{1-x}D_xMnO_3$ (L = rare earth or Y; D = divalent ion) with certain commensurate values of x and hence a Mn^{4+}/Mn^{3+} ratio. For example, $Nd_{1-x}Sr_xMnO_3$ with $x = 0.5$ orders ferromagnetically at 255 K and undergoes a first-order transition to an antiferromagnetic charge ordered state at 158 K.[13] Tokura *et al.*[14] have found that the thermal hysteresis associated with the first-order transition at T_{co} increases with decreasing $\langle r_A \rangle$ as Sm is progressively substituted for Nd in $Nd_{0.5}Sr_{0.5}MnO_3$.

It is now well established by the reports mentioned above that $\langle r_A \rangle$ has a critical role in controlling the first-order nature of the phase transitions at T_c as well as T_{co}. Rodriguez-Martinez *et al.*[15] recently demonstrated that for a given $\langle r_A \rangle$ the PMI to FMM transition temperature of $L_{0.7}D_{0.3}MnO_3$ could vary significantly depending on the size differences between the *A*-site cations of the perovskite structure. The size mismatch of the *A*-site cations leads to local lattice distortions via random displacements of oxygen ions coordinated to them. This microscopic effect has been parametrized as $\sigma^2 = \Sigma x_i r_i^2 - \langle r_A \rangle^2$, where x_i denotes the fractional occupancy of the *A*-site ions with radius r_i. In this paper, we report the dramatic effects of the *A*-site ionic mismatch on the phase transition and related transport properties of manganates exhibiting a first-order transition at T_c as well as T_{co}.

Two sets of samples with $Mn^{4+} \sim 30\%$ and $\langle r_A \rangle \sim 1.19$ Å (hereafter referred to as S30) and $Mn^{4+} \sim 50\%$ and $\langle r_A \rangle \sim 1.236$ Å (S50) were prepared by the ceramic method by heating the component metal oxides and carbonates at 1273, 1473, and 1673 K for 24 h each with intermediate grindings. The samples were finally sintered at 1773 K for 12 h and slowly cooled to room temperature over 10 h. The nominal compositions of the two sets of samples are given in Table I along with the orthorhombic lattice parameters. The lattice parameters of the samples were determined using high purity silicon powder (99.999%) as an internal standard. The samples within each set S30 or S50 differ only in the *A*-site ionic size mismatch σ^2. The ionic radii used to determine the various compositions are La (1.216 Å) Nd (1.163 Å), Y (1.075 Å), Ca (1.18 Å), Sr (1.31 Å), and Ba (1.47 Å). The resistivity measurements were carried out on all the samples using the standard four-probe technique in the temperature range 10–300 K. Magnetoresistance measurements were carried out on S30 samples up to a maximum field of 5 T.

TABLE I. Composition and structure details of the various manganates investigated.

Sample	Composition	$\langle r_A \rangle$ (Å)	Mn^{4+} (%)	σ^2 (Å²)	Lattice parameters		
					a (Å)	b (Å)	c (Å)
S30 A	$(La, Nd)_{0.7}(Ca, Sr)_{0.3}MnO_3$			0.00196	5.443(3)	5.454(5)	7.693(5)
S30 B	$(La, Y)_{0.7}(Ca, Ba)_{0.3}MnO_3$	1.190	30	0.00652	5.442(3)	5.431(3)	7.720(9)
S50 A	$La_{0.5}(Ca, Sr)_{0.5}MnO_3$			0.00245	5.416(5)	5.405(7)	7.719(9)
S50 B	$Nd_{0.5}Sr_{0.5}MnO_3$			0.00540	5.427(4)	5.432(8)	7.686(5)
S50 C	$La_{0.5}(Ca, Ba)_{0.5}MnO_3$	1.236	50	0.00773	5.433(1)	5.409(3)	7.708(8)
S50 D	$(La, Y)_{0.5}Sr_{0.5}MnO_3$			0.00853	5.426(5)	5.423(9)	7.709(8)
S50 E	$Nd_{0.5}(Ca, Ba)_{0.5}MnO_3$			0.01580	5.434(1)	5.416(7)	7.709(1)

In Fig. 1(a) we show the temperature dependence of resistivities of samples S30 A and B. At 0 T, both samples undergo insulator-metal (I-M) transitions with transition temperatures 150 K (S30 A) and 132 K (S30 B), respectively. The lower T_{I-M} and higher peak resistivity of S30 B could be attributed to the larger σ^2 (see Table I).[15] The sample S30 B with smaller σ^2 exhibits marked thermal hysteresis in resistivity near $T_{I-M}(\sim T_c)$ which is a characteristic
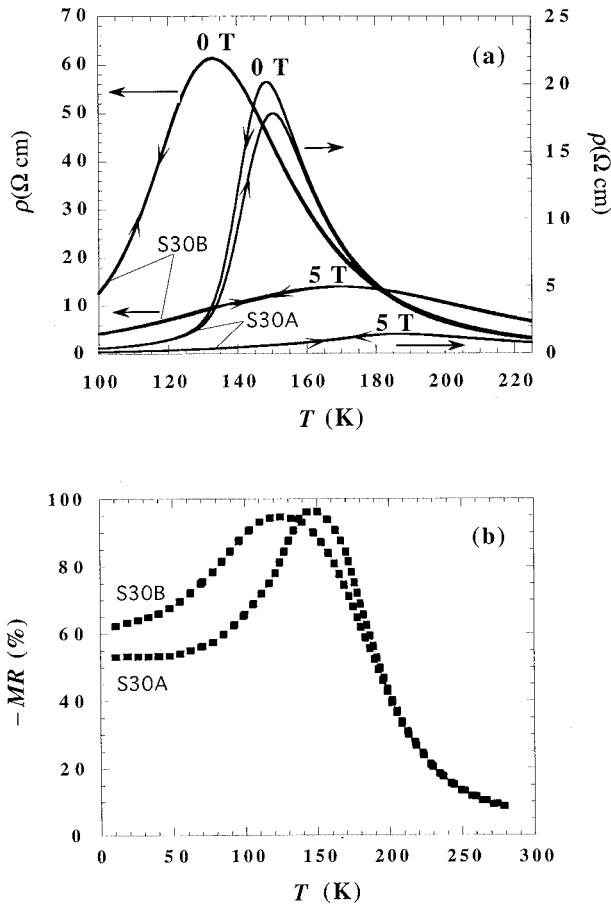

FIG. 1. Temperature variation of (a) resistivities of samples S30 A and B at 0 and 5 T. The direction of arrows on the curves distinguish the cooling and warming curves. (b) Magnetoresistance (MR) at an applied field of 5 T for samples S30 A and B. The magnetoresistance is calculated from the data collected on warming.
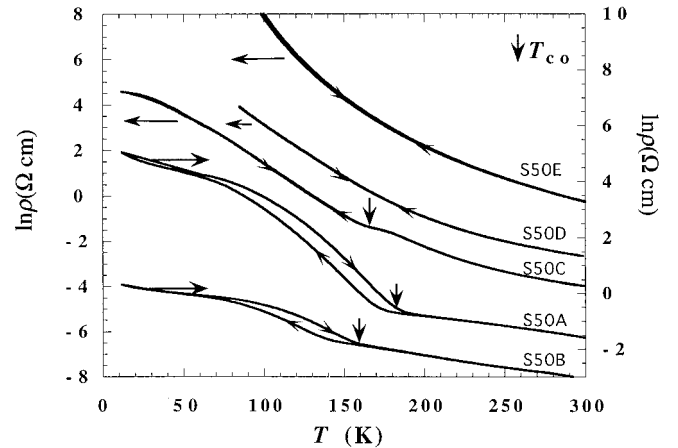
of a first-order transition. The physical origin of this transition is beyond the scope of this report. Application of magnetic field of 5 T has decreased the peak resistivity appreciably in both samples giving rise to a magnetoresistance as high as $\sim$95% [Fig. 1(b)]. The magnetic field has completely suppressed the first-order transition in S30 A. The suppression of hysteresis in resistivity under high magnetic fields in similar manganates can be found in the literature.[8]

The above observation brings out many interesting features of manganates with regard to σ^2 which are previously unnoticed. A smaller σ^2 and hence low A-site ionic size disorder favors the occurrence of a first-order transition at T_c. The increase in the width of hysteresis in resistivity and hence first-order behavior as Pr is substituted for La in $La_{0.7}Ca_{0.3}MnO_3$ by Hwang et $al.$[8] thus could arise from the combined effect of decreasing $\langle r_A \rangle$ and σ^2. The decrease in $\langle r_A \rangle$ produces the counter effect of decreasing T_c. Since the effect of $\langle r_A \rangle$ and σ^2 on T_c are opposite to each other, the maximum hysteretic effect is found in Pr-rich samples. A further decrease of $\langle r_A \rangle$ by the substitution of Y by these authors, however, did not yield first-order behavior probably due to the enhanced σ^2. The combined effect of decrease in $\langle r_A \rangle$ and increase in σ^2 causes the disappearance of T_c in their Y-substituted samples. The present investigation also unambiguously reveals the role of the first-order transition at

FIG. 2. Temperature variation of resistivities of S50 samples (A–E) at 0 T. Only S50 A and B samples with relatively smaller σ^2 show thermal hysteresis corresponding to the first-order transition at T_{co}.
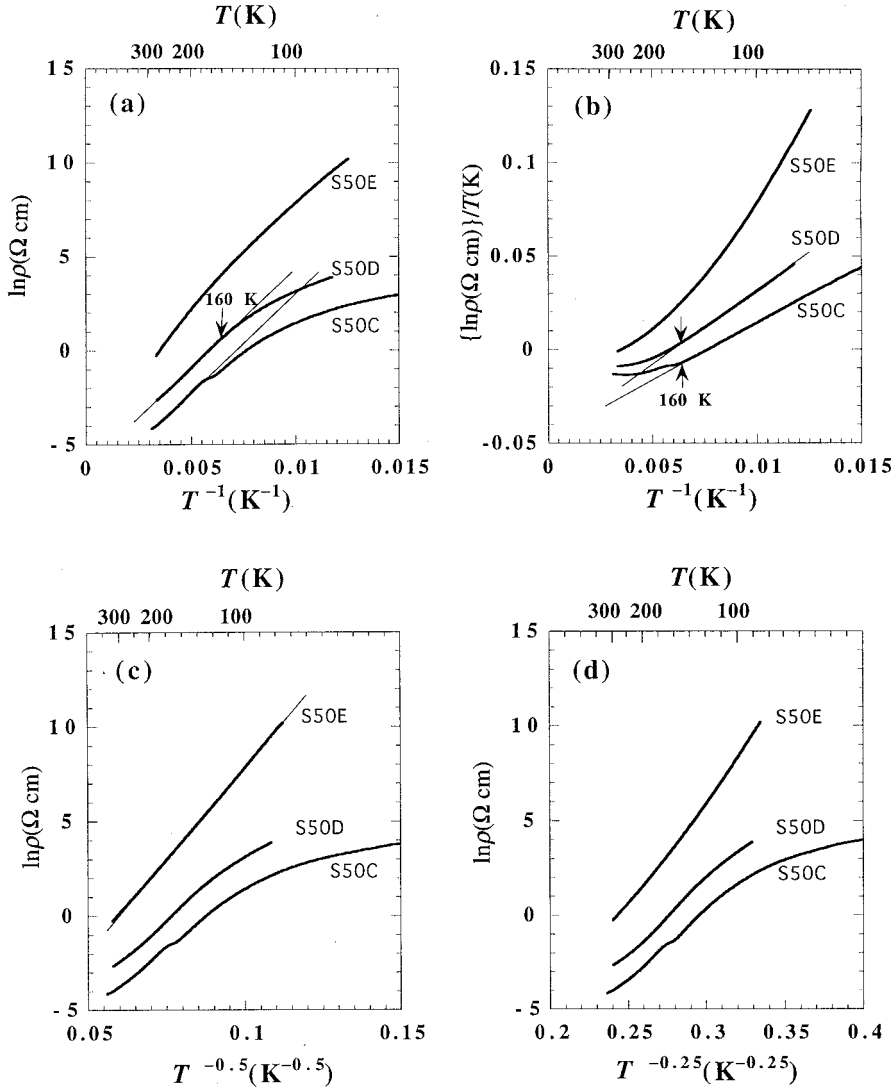
FIG. 3. Temperature variation of resistivities of samples S50 C, D, and E and their fits to the various models for electronic conduction (see text).

T_c on the magnetoresistance. A lower T_c and higher peak resistivity has been found indispensable for high magnetoresistance in manganates.[16] Hence S30 A with a relatively higher T_c and lower peak resistivity is expected to show a lower value of magnetoresistance compared to S30 B. The equally high magnetoresistance of S30 A derives the additional contributions from those factors responsible for the first-order hysteretic behavior.

The effect of σ^2 on the first-order transition at the charge ordering temperature T_{co} in manganese perovskites is illustrated in Fig. 2. As σ^2 increases, the hysteresis in the temperature variation of resistivity decreases and eventually vanishes at S50 C with $\sigma^2 = 0.00773 \, \text{Å}^2$. The sample S50 C shows weak charge ordering with a resistivity anomaly near 160 K. The application of a low magnetic field <0.5 T melts the charge ordered state[17] in S50 C unlike S50 B with a slightly lower $\sigma^2 = 0.0054 \, \text{Å}^2$ which requires a magnetic field as high as 12 T.[13] S50 D and E samples with larger σ^2 did not show a first-order transition. Thus, the present study leads to the conclusion that a lower σ^2 favors first-order transitions at T_c as well as T_{co} in manganates with fixed $\langle r_A \rangle$.

We have also noticed that the nature of electronic conduc-

tion in the insulating S50 C, D, and E samples are remarkably affected by A-site ionic size mismatch. In Figs. 3(a)–3(d) we plot the temperature variation of resistivities of these samples so as to fit with the various known conduction mechanisms. The S50 C and D samples show a good fit with the $\ln \rho \alpha T^{-1}$ law corresponding to the nearest-neighbor hopping of charge carriers or activation beyond mobility edge into extended states above 160 K. Below 160 K, these samples seem to follow the $\ln \rho / T \alpha T^{-1}$ law proposed by Emin and Holstein[18] for adiabatic small polaron hopping. The resistivity data of S50 E with the largest σ^2 did not fit well with the above power laws. However, it shows an extremely good fit in the entire temperature range with the variable range hopping law ($\ln \rho \alpha T^{-0.5}$) with a soft gap due to the modification of the density of states by the Coulomb interaction near the Fermi level. None of the samples in this study gave a satisfactory fit with the $\ln \rho \alpha T^{-0.25}$ law for variable range hopping proposed by Mott[19] for uncorrelated carriers.

The size mismatch of A-site cations in manganese perovskites gives rise to local spin- and position-dependent potential fluctuations. The value of σ^2 is a measure of this mis-

match and hence the degree of spin and Coulomb potential fluctuations. We assume that the origin of the first-order transition at T_c as well as T_{co} has its contributions from both crystallographic as well as magnetic phase changes. The sample with larger σ^2 has a higher degree of local deformation and could not sustain a first-order transformation. The large variations in the local spin and Coulomb potentials with increasing σ^2 also affect the electron motion in the lattice significantly.

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