

First-order transition at T_C in the orthomanganites

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The orthomanganites $L_{0.7}A_{0.3}\text{MnO}_3$, L =rare-earth or Y and A =alkaline earth, exhibit a first-order transition at a ferromagnetic Curie temperature T_C , where T_C drops with decreasing tolerance factor t from a high near 350 K at $t=0.98$ to a $T_C^*\approx 60$ K at $t\leq 0.96$. The paramagnetic phase is a polaronic conductor; the ferromagnetic phase contains mobile electrons in extended states for larger tolerance factors $t>t_c=0.96$, but remains polaronic for $t<t_c$. The temperature dependence of the thermopower is used to explore the polaron-extended state transition for five nominal compositions $(\text{La}_{1-x}\text{Nd}_x)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ designed to have tolerance factors near the critical value t_c . Comparison of the temperature dependence of the thermopower, $\alpha(T)$, as a result of chemical pressure, i.e., $t<1$, with that for hydrostatic pressure reveals an anomalously large compressibility of the Mn-O bonds, which is characteristic of a double-well potential at a crossover from an electronic state of lower mean kinetic energy to one of greater kinetic energy. It also reveals a trapping of mobile holes above T_C that increases with decreasing T_C . In the orthomanganites, the crossover is from polaronic- e to extended- σ^* electronic conduction at T_C , a crossover that is responsible for the ‘‘colossal’’ negative magnetoresistance observed in the orthomanganites. [S0163-1829(96)00521-8]

INTRODUCTION

The mismatch between the equilibrium bond lengths $A\text{-O}$ and $M\text{-O}$ of an AMO_3 cubic perovskite is given by the deviation from unity of the tolerance factor

$$t \equiv (A\text{-O})/\sqrt{2}(M\text{-O}). \quad (1)$$

The room-temperature, ambient-pressure value of t is calculated from the sums of the empirical ionic radii given in tables, e.g., those of Shannon and Prewitt.¹ A $t<1$ places the $M\text{-O}$ bonds under compression and the $A\text{-O}$ bonds under tension. These internal stresses are relieved by a cooperative rotation of the MO_6 octahedra that lowers the symmetry of the unit cell from cubic to, for example, rhombohedral ($R\bar{3}c$) or orthorhombic ($Pbnm$). The resultant bending of the $M\text{-O-M}$ bond angle from 180° to $(180^\circ - \phi)$ reduces the σ -bonding nearest-neighbor $M\text{-O-M}$ resonance integral²

$$b_\sigma \approx \epsilon_s \lambda_s^2 + \epsilon_\sigma \lambda_\sigma^2 \cos \phi \quad (2)$$

that enters the tight-binding expression $W_\sigma \approx 2z b_\sigma$ for the bandwidth; $z=6$ is the number of nearest-neighbor M atoms in the perovskite structure, ϵ_s and ϵ_σ are one-electron energies, and λ_s and λ_σ are covalent-mixing parameters. Substitution of a smaller isovalent cation reduces t , thereby increasing ϕ and reducing the bandwidth W_σ .

Since the covalent-mixing parameters $\lambda \equiv b^{ca}/\Delta E$ for O $2s$, $2p_\pi$, and $2p_\sigma$ electron transfer over an energy ΔE to an empty transition-metal d orbital have a $\Delta E_s > \Delta E_p$ and a p_π - t resonance integral b^{ca} smaller than the p_σ - e resonance integral, they have the relation

$$\lambda_s < \lambda_\pi < \lambda_\sigma. \quad (3)$$

The corresponding π -bonding resonance integral is $b_\pi \approx \epsilon_\pi \lambda_\pi^2$, and it follows that the relation

$$W_\pi < W_\sigma \quad (4)$$

holds where ϕ is not too large, as in the perovskites. Relation (4) allows retention of localized π -bonding electrons in the presence of a transition from polaronic- e to itinerant- σ^* electrons with increasing W_σ . Moreover, from the Virial theorem

$$2\langle T \rangle + \langle V \rangle = 0, \quad (5)$$

a discontinuous change in the mean electron kinetic energy $\langle T \rangle$ at a transition from polaronic- e to itinerant- σ^* electrons would be reflected in a compensating discontinuous change in the mean electron potential energy $\langle V \rangle$, so we can expect a first-order decrease in the mean Mn-O bond length on increasing W_σ through a transition from polaronic- e to extended- σ^* electrons.

In the presence of localized t^3 configurations of spin $S=3/2$, the electrons of e -orbital parentage experience a strong intra-atomic-exchange interaction that would narrow the σ^* band of a ferromagnetic phase by a transition to a paramagnetic phase. Therefore, stabilization of a metallic relative to a polaronic phase at lower temperatures may be found at or near a ferromagnetic Curie temperature. Just such a transition appears to be responsible for the remarkable negative magnetoresistance and other physical properties of the $\text{Mn}^{4+}/\text{Mn}^{3+}$ mixed-valent orthomanganites $L_{1-x}A_x\text{MnO}_3$, where L is a rare-earth or Y and A is an alkaline earth.³ In this perovskite family, the electron transfer from a high-spin $\text{Mn}^{3+}:t^3e^1$ to a $\text{Mn}^{4+}:t^3e^0$ ion is responsible for the electronic conduction, and the conduction electrons (holes) may be either polaronic- e or itinerant- σ^* depending on the bandwidth W_σ whereas the t^3 configurations remain localized with a spin $S=3/2$. A recent study⁴ of the isoelectronic perovskites $L_{0.7}A_{0.3}\text{MnO}_3$ has revealed a remarkable dependence on t of the ferromagnetic Curie temperature T_C in an interval $0.96 < t < 0.98$, Fig. 1(a), where we use the tabulated ionic radii for 12-fold oxygen coordination of the A -site cations⁵ rather than the eightfold coordination

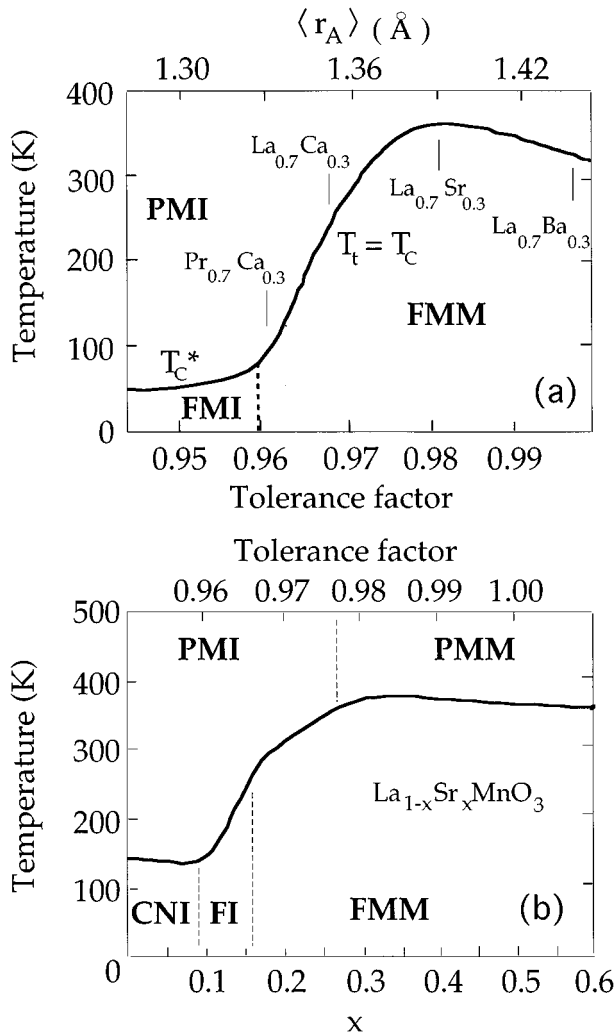


FIG. 1. (a) Phase diagram of Curie temperature T_C vs tolerance factor t for a ratio $\text{Mn}^{4+}/\text{Mn}=0.3$ adapted from Ref. 4, (b) Phase diagram of magnetic-ordering temperature vs x in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ adapted from Ref. 6. FMI=ferromagnetic insulator, FMM=ferromagnetic metal, PMI=paramagnetic insulator, PMM=paramagnetic metal, CNI=spin-canted insulator.

given by Shannon and Prewitt.¹ For $t > 0.98$, a relatively high value of T_C reflects an important ferromagnetic contribution from the dominant e -electron indirect-exchange (or double-exchange) component of the Mn-O-Mn interatomic-exchange coupling between localized t^3 configurations; the superexchange t^3 -O- t^3 component is antiferromagnetic. In the interval $t_c \approx 0.96 \leq t < 0.98$, a transition at T_t from extended states to polaronic conduction coincides with T_C and is first order;⁴ stabilization of double-exchange coupling via extended- σ^* electrons below T_t introduces ferromagnetic order. For $t < t_c \approx 0.96$ the double-exchange component of the ferromagnetic coupling becomes suppressed because the time for a polaron to hop to a neighbor is long compared to the spin-lattice relaxation time. The Curie temperature T_C^* is determined by superexchange interactions, and the weak ferromagnetic component appears to reflect a spin canting of an antiferromagnet by antisymmetric Dzialoshinskii exchange. Figure 1(b) shows a similar variation of T_C with t for differ-

ent dopings.⁶ The four transition temperatures T_t , T_C , T_C^* , and T_C' are defined at the beginning of our Discussion section.

In order to demonstrate that the origin of the first-order transition resides in a double-well potential for the equilibrium Mn-O bond length at a crossover from polaronic- e to extended- σ^* electronic conduction, we have undertaken measurements of the temperature dependence of the thermopower $\alpha(T)$ made under different pressures. These measurements also reveal the influence on $\alpha(T)$ of the removal of the spin degeneracy of the σ^* band on cooling to $T_t = T_C$ as well as a trapping out of mobile holes in what appear to be superparamagnetic clusters below room temperature.

EXPERIMENTAL

In keeping with Hwang *et al.*,⁴ we have chosen to study the pressure dependence of $\alpha(T)$ as a function of bandwidth for a fixed Mn^{4+}/Mn ratio of 0.3 both because the largest negative magnetoresistance has been observed for this ratio and because of the study of Fig. 1(a). We have selected bandwidths W_σ that are characterized by tolerance factors that were intended to span the critical value $t_c \approx 0.96$, which was found⁴ for $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ in Fig. 1(a). For this purpose we have taken five values of x from the system $(\text{La}_{1-x}\text{Nd}_x)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ in the range $0.2 \leq x \leq 1$ such that three ($x=0.2, 0.4, 0.55$) have $t > 0.96$ and two ($x=0.75, 1.0$) have $t \leq 0.96$.

Polycrystalline samples were prepared by conventional solid-state reaction from stoichiometric mixtures of La_2O_3 (dried), Nd_2O_3 (dried), CaCO_3 , and Mn_2O_3 . The mixtures were calcined at 1250 °C, then reground, pressed into pellets, and sintered at 1350 °C. All products were found to be single-phase to x-ray powder diffraction. Measurements of the temperature dependence of the thermoelectric power $\alpha(T)$ and resistance $\rho(T)$ at atmospheric pressure were made with a homemade apparatus as described elsewhere.⁷ Measurements of $\alpha(T)$ under pressure were made with a self-clamping pressure cell as also described elsewhere.⁸ The lead contributions to $\alpha(T)$ and $\rho(T)$ were subtracted from all measurements.

RESULTS

Figure 2 shows $\alpha(T)$ at atmospheric pressure for the five chosen compositions; Figure 3 shows the corresponding resistivity data for $x=0.55$. Each sample showed a positive enhancement of $\alpha(T)$ as the temperature was lowered to T_C or T_C^* . Above 600 K, the resistivity shows a polaronic temperature dependence and $\alpha(T)$ saturates at a temperature-independent, negative value of $-15 \pm 5 \mu\text{V}/\text{K}$. On cooling through T_t , $\alpha(T)$ drops abruptly, but it reaches a small value only in the three samples with $t > 0.96$ (the detailed temperature dependence of the low-temperature phase deserves further investigation). Although $\alpha(T)$ drops sharply on cooling through T_C^* in the other two samples, it becomes unmeasurable at temperatures below approximately 50 K where most of the mobile holes have become trapped. The resistance of these two samples was greater than $10^6 \Omega$ below 50 K, which makes the open-circuit-like noise greater than the signal.

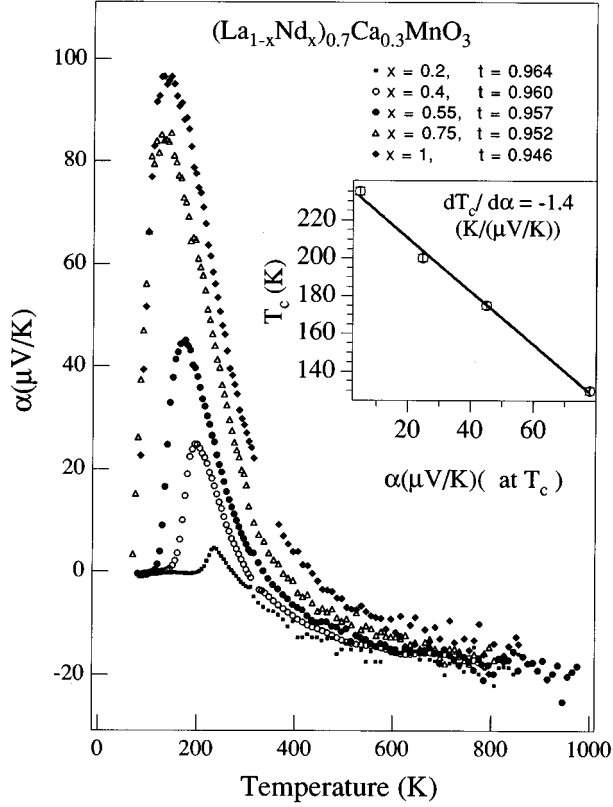


FIG. 2. Ambient-pressure thermopower α vs temperature T for nominal $(\text{La}_{1-x}\text{Nd}_x)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ for five values of x . *Inset*: Curie temperature T_C , taken as maximum in $\alpha(T)$, vs $\alpha(T_C)$.

Moreover, the maximum thermopower $\alpha(T_C)$ increases with decreasing t , i.e., with decreasing W_σ . In addition, T_C varies linearly with $\alpha(T_C)$ as $dT_C/d\alpha(T_C) = -1.4 \text{ K}/(\mu\text{V}/\text{K})$. The thermal hysteresis at $T_i = T_C$ found in the $\rho(T)$ curve of Fig. 3 is similar to that reported by Ref. 4; the relatively high value of ρ at $T < T_C$ suggests that only the untrapped holes occupy extended- σ^* states.

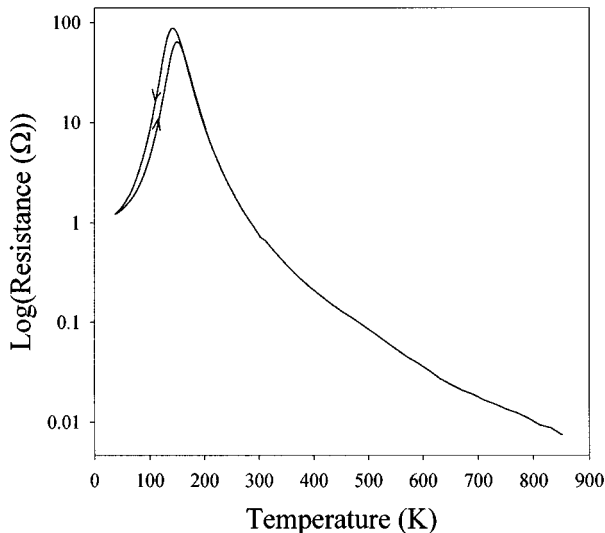


FIG. 3. $\text{Log}(\text{Resistance})$ vs T for $(\text{La}_{0.45}\text{Nd}_{0.55})_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ showing the thermal hysteresis near $T_C \approx 150 \text{ K}$ and activated behavior above T_C .

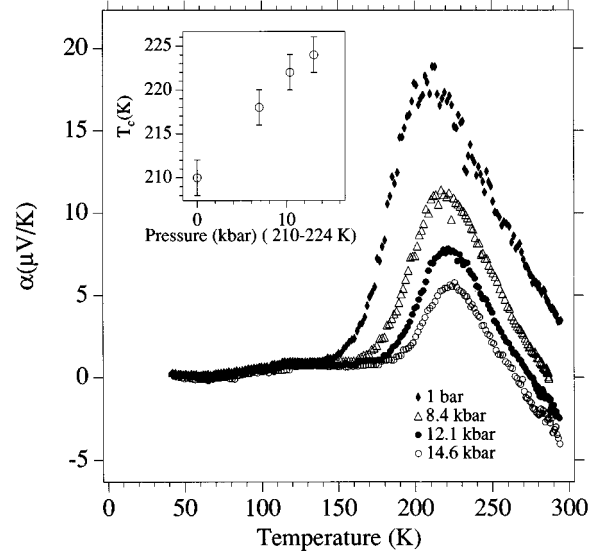


FIG. 4. Thermopower α vs temperature T for nominal $(\text{La}_{0.6}\text{Nd}_{0.4})_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ taken at several pressures. *Inset*: Curie temperature T_C , taken as maximum in $\alpha(T)$, vs pressure.

Figure 4 shows $\alpha(T)$ for $x=0.4$ under several hydrostatic pressures. Both $\alpha(T_C)$ and T_C vary linearly with pressure [$d\alpha(T_C)/dP = -0.85 \text{ } (\mu\text{V}/\text{K})/\text{kbar}$ and $dT_C/dP = 1.1 \text{ K}/\text{kbar}$] to give a calculated $dT_C/d\alpha(T_C) = -1.2 \text{ K}/(\mu\text{V}/\text{K})$ that is in close agreement with the $-1.4 \text{ K}/(\mu\text{V}/\text{K})$ obtained by varying x . Whether W_σ is varied chemically or by hydrostatic pressure at constant hole concentration, the relationship between T_C and $\alpha(T_C)$ remains the same. We note that Neumeier *et al.*⁹ obtained a $dT_C/dP = 1.57 \text{ K}/\text{kbar}$ for $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ from resistivity measurements, which is somewhat higher than the $1.1 \text{ K}/\text{kbar}$ in our $x=0.4$ sample.

The similarity of the curves in Figs. 1(a) and 1(b) shows that the tolerance factor t is a more important determinant of the long-range magnetic-ordering temperature than is the hole concentration.

Finally we show in Fig. 5 inverse magnetic-susceptibility data for three samples near t_c . A magnetic anomaly below room temperature, but above T_C , is clearly evident; it is suggestive of the formation of superparamagnetic clusters associated with holes trapped out in Ca^{2+} -rich regions.

DISCUSSION

We define four transition temperatures for our discussion: T_i is the transition temperature from an extended state to a small-polaron conductor obtained from transport data,

T_C is the Curie temperature for a metallic ferromagnetic phase,

T_C^* is the Curie temperature for a polaronic ferromagnetic phase,

T'_C is the Curie temperature for a superparamagnetic cluster.

The temperature-independent $\alpha(T)$ and activated conductivity above 600 K are typical of polaronic conduction, and the thermopower in the high-temperature limit should be described by the small-polaron formula

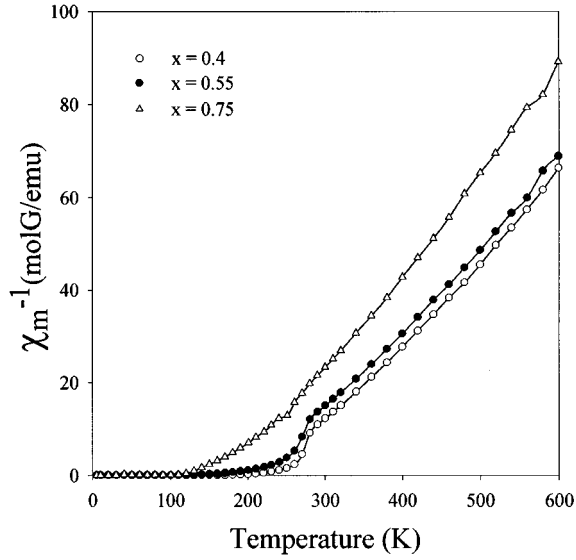


FIG. 5. Inverse magnetic susceptibility χ_m^{-1} vs temperature T for $x=0.4, 0.55, 0.75$ in nominal $(\text{La}_{1-x}\text{Nd}_x)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$.

$$\alpha = -\frac{k}{|e|} \ln[\beta(1-c)/c], \quad (6)$$

where c is the electron occupancy of the $\text{Mn}^{4+}/\text{Mn}^{3+}$ redox couple and the factor β represents the spin degeneracy. The mobile electrons hop from singly occupied e orbitals on a Mn^{3+} ion to the empty e orbitals of the Mn^{4+} ion, so they may hop for any orientation of the spin on the Mn^{4+} ion; the transferred electron has a twofold spin degeneracy ($\beta=2$) in the paramagnetic phase at high temperatures, but it has no spin degeneracy ($\beta=1$) in the ferromagnetic phase. The condition $\beta=1$ may be reached at T_C^* where there is no first-order transition, i.e., where T_C^* is the Curie temperature of the polaronic phase. Short-range ferromagnetic order may give a condition $1 < \beta < 2$ for the average value of β in the high-temperature phase at a first-order transition temperature $T_i = T_C > T_C^*$ where T_C is the measured Curie temperature.

The change from $\beta=2$ to $\beta=1$ would enhance $\alpha(T)$ in the polaronic phase by no more than $58 \mu\text{V/K}$ on cooling from $T \gg T_C$ to T_C . Therefore an observed increase of over $100 \mu\text{V/K}$ in the $x=1$ sample requires, in addition to suppression of the spin degeneracy, some trapping out of mobile holes at lower temperatures if Eq. (6) is to be applicable. Moreover, a high-temperature $-20 < \alpha < -10 \mu\text{V/K}$ is a little low for a Mn^{4+}/Mn ratio of 0.3 and $\beta=2$; the Mn^{4+}/Mn ratio needs to be adjusted to 0.37 to give $c \approx 0.63$, corresponding to $-(k/|e|)\ln\beta - (k/|e|)\ln[(1-c)/c] \approx [-59 + 45] \mu\text{V/K}$ for $\beta=2$.

This latter discrepancy is readily rationalized since the orthomanganites are known to be oxygen rich if prepared in air; they become cation-deficient perovskites $A_{1-\delta}\text{Mn}_{1-\delta}\text{O}_3$, and a $\delta \approx 0.015$ would lower the high-temperature $\alpha(T)$ from $+13$ to $-20 \mu\text{V/K}$. The variation between samples in the high-temperature saturation value of $\alpha(T)$ thus appears to reflect variations in the oxygen excess; i.e., in δ .

The former discrepancy reflects a trapping of the mobile holes at Mn atoms neighboring Ca^{2+} ions. The magnetic data of Fig. 5 show a break in the inverse magnetic susceptibility

versus temperature that is indicative of the formation of superparamagnetic clusters; we believe they are stabilized by a local transition to itinerant (or molecular-orbital) σ^* electrons below a $T_C' > T_i$ within hole-rich Mn clusters.

The first-order transition at $T_C = T_i$ increases with t as if the extended-state σ^* electrons below T_i introduce a stronger double-exchange ferromagnetic coupling with decreasing concentration of trapped holes. Double exchange is responsible for $T_C \approx 350 \text{ K}$ at a tolerance factor $t \approx 0.98$ in Fig. 1(a) where there appear to be no trapped charge carriers. Saturation of $T_i = T_C$ at $t = 0.98$ reflects a smooth transition to the paramagnetic phase for $t > 0.98$. An apparent linear decrease in T_C with increasing $\alpha(T_C)$ in Fig. 2 for $0.2 \leq x \leq 0.75$ would also reflect the dependence of T_C on the mobile charge carriers and hence on the degree of hole trapping at T_C . The $x=1$ sample has a $t < t_c$ and an $\alpha(T_C^*)$ like the $\alpha(T_C)$ in the $x=0.75$ sample if allowance is made for the different oxygen stoichiometry made apparent by the high-temperature values of $\alpha(T)$.

Finally, both physical pressure and an increase in the tolerance factor t increase the transition temperature $T_i = T_C$ and change the other physical properties in a similar way, which shows that t increases with pressure. From the definition of t , Eq. (1), a $dt/dP > 0$ can only occur if the compressibility of the Mn-O bond is greater than that of the A-O bond. This anomalous situation is only found where there is a double-well potential associated with two equilibrium M-O bond lengths¹⁰ such as is found, for example, at the metal-insulator transition in NdNiO_3 ,¹¹ and in the copper-oxide superconductors.¹² A $dt/dP > 0$ thus implies the existence of a double-well potential for the equilibrium Mn-O bond length at a crossover from polaronic- e to extended- σ^* electronic conduction, a crossover that, from the Virial theorem of Eq. (5), we have argued should be first order. The conclusion of a first-order phase transition at T_i has also been made by Hwang *et al.*⁴ on the basis of an observed thermal hysteresis of their resistivity vs temperature curves at a T_ρ corresponding to our T_i .

In conclusion, the orthomanganites represent one more example of a double-well potential for the M-O bond length in a perovskite at a transition where the mean kinetic energy of the d electrons of a transition-metal atom M changes discontinuously. The data thus support our interpretation of the remarkable drop in T_C in the range $0.96 < t < 0.98$, Fig. 1, viz. that it reflects a first-order change from polaronic- e hopping and superexchange ferromagnetic coupling to extended- σ^* metallic conductivity and double-exchange ferromagnetic coupling at a transition temperature $T_i = T_C$. The ferromagnetic phase is stabilized by stronger Mn-O-Mn interactions and hence by both a larger t factor and by reduction of the spin-dependent resonance integral $t_{ij} = b_\sigma \cos(\theta_{ij}/2)$ in a ferromagnetically ordered state; θ_{ij} is the angle between spins on neighboring atoms. Therefore $T_i = T_C$ is raised by an applied magnetic field, by pressure, and by chemical substitutions that increase t ; it is relatively independent of the Mn^{4+}/Mn ratio. The relatively high resistivity of the $x=0.55$ sample below T_C , Fig. 3, indicates that as the strength of the Mn-O-Mn interactions decrease with decreasing t , more and more mobile holes become trapped out at low temperatures; the density of free holes is small and/or they have a low mobility even below T_C . The nature

of the extended σ^* states below $T_t = T_C$ needs to be explored further. We suggest the unusual trapping out of mobile holes above T_C is due to local, static Jahn-Teller deformations that increase the activation energy E_a of the small-polaron mobility.

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