Phonon-Assisted Double Exchange in Perovskite Manganites

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Measurements of the temperature dependence of the thermoelectric power and the resistivity of $^{18}O/^{16}O$ isotope-exchanged $(La_{1-x}Nd_x)_{0.7}Ca_{0.3}MnO_3$ samples have confirmed the existence of vibronic electronic states below T_c in the narrow range of bandwidths where static, cooperative Jahn-Teller (J-T) deformations are suppressed and dynamic J-T deformations introduce vibrational modes into the interatomic spin-spin interactions. A giant isotope effect on T_c is related to a mass-enhanced change in both the density and mobility of the mobile charge carriers at T_c. [S0031-9007(98)05628-2]

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Conventional theories of interatomic spin-spin interactions in magnetic materials neglect atomic vibrations. The only exception was postulated [1] some years ago to account for the ferromagnetism found in the perovskite, single-valent system $LaMn_{1-x}Ga_xO_3$ on suppression by Ga of the *static*, cooperative Jahn-Teller (J-T) deformation of the high-spin Mn III ions found in $LaMnO_3$. It was pointed out that the cooperative oxygen vibrations of a *dynamic* J-T coupling would coordinate empty and half-filled Mn III σ-bonding orbitals alternating on opposite sides of an oxygen atom to give an isotropic ferromagnetic superexchange interaction. In 1951, Zener [2] had postulated that the observed [3] ferromagnetic order and metalliclike temperature dependence of the resistivity below T_c in the perovskite, mixed-valence system $La_{1-x}Ca_xMnO_3$ was due to a real charge transfer (a double-exchange mechanism) within Mn III-O-Mn IV pairs that preserved both the spin angular momentum and the intra-atomic Hund's field coupling between the localized spin of a t^3 configuration ($S = \frac{3}{2}$) and the spin of the e electron shared between the two Mn atoms of a pair. For global ferromagnetism to occur in Zener's model, pair diffusion without any activation energy is assumed implicitly to be rapid compared to a spin-relaxation time. Not understood at the time was how a motional enthalpy $\Delta H_m = 0$ might arise. On the other hand, in a double-exchange model that avoids the introduction of vibronic states, de Gennes [4] assumed that he mobile electrons occupy a narrow σ^* band of e-orbital parentage and that, if they are bound, they generate a local spin alignment.

The data reported for the perovskite manganites shows that the ferromagnetic transition at T_c is coupled to a drop in resistivity at a first-order phase change (see [5,6], for example). The unusual transport properties below T_c are suggestive of a vibronic state [7]. We have recently provided experimental evidence [8] for a transition from polaronic to metallic electronic behavior with increasing hydrostatic pressure in a temperature interval $T_{c0} < T < T_c$ in $La_{0.85}Sr_{0.15}MnO_3$, which exhibits charge ordering at temperatures $T < T_{c0}$ [9]. The unusual electronic behavior occurs in the compositional range where T_c increases sharply with increasing width of the σ^* band. Variations $60 < T_c < 360$ K have been found for the Curie temperatures of the $R_{0.7}A_{0.3}MnO_3$ perovskites (R = rare earth, A = alkaline-earth atoms) over a narrow range of bandwidths [5]. In this Letter, we compare thermoelectric-power measurements made at ambient pressure and resistivity data under different pressure on $^{18}O/^{16}O$ isotope-exchanged samples to show conclusively the mass dependence of the unusual electronic behavior below T_c in the O (orthorhombic) phase. This comparison also demonstrates that the giant isotope effect on T_c found for $La_{1-x}Ca_xMnO_3$ ferromagnets [10] is due to changes not only in the mobility of polaronic charge carriers, but also in their density above T_c, with changes in the oxygen mass M.

In the phase diagram of Fig. 1 for the perovskites $Ln_{0.7}Ca_{0.3}MnO_3$, the structure changes from O' [orthorhombic ($c/a < \sqrt{2}$)] to O [orthorhombic ($c/a > \sqrt{2}$)] with increasing room-temperature tolerance factor $t = (A\text{-O})/\sqrt{2}$ (Mn-O), where A-O and Mn-O are the equilibrium bond lengths. A larger thermal expansion of the A-O equilibrium bond length makes $t(T)$ increase

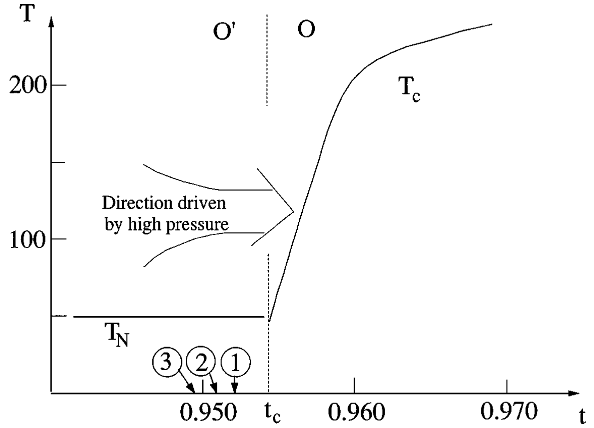

FIG. 1. The variation of T_c with room-temperature tolerance factor $t \equiv (A\text{-O})/\sqrt{2}$ (Mn-O), where the A-O and Mn-O equilibrium bond lengths are the sums of empirical ionic radii of an $AMnO_3$ perovskite; in this diagram, $A = R_{0.7}Ca_{0.3}$.

gradually with temperature T; an unusually high compressibility of the Mn-O bond makes hydrostatic pressure P move the O' to O transition at room temperature from t_c to a lower effective t [6]. In the O' phase, the e-orbital degeneracy of the high-spin Mn III: t^3e^1 configuration is removed by a cooperative, static J-T deformation that orders the occupied e orbital into the ***a-b*** plane; the charge carriers are localized at single Mn sites as Mn IV ions and move as small polarons in the Mn III matrix. In this phase, superexchange spin-spin interactions are dominant, and a canted-spin ferromagnetism is observed below the magnetic-ordering temperature T_N. In the O phase, the e-orbital degeneracy may be lifted by either dynamic, cooperative J-T deformations, or by transformation of the e electrons into itinerant σ^*-band electrons. An unusual electronic state has been found below the Curie temperature T_c in the O phase [7]; it would appear to be associated with a dynamic J-T lifting of the e-orbital degeneracy as a transitional state between the static J-T orbital ordering in the O' phase and the itinerant-electron state appearing at higher values of t. In order to probe this transitional state further, we use pressure to induce an O' to O transition; it is in the O phase near this transition that the peculiar properties of the unusual electronic state are maximized.

The composition $(La_{0.25}Nd_{0.75})_{0.7}Ca_{0.3}MnO_3$, which we have characterized elsewhere [6,7], lies at the position No. 1 in Fig. 1. Two additional samples with different t factors, marked No. 2 and No. 3 in Fig. 1, were prepared: $(La_{0.2}Nd_{0.8})_{0.7}Ca_{0.3}MnO_3$ and $(La_{0.15}Nd_{0.85})_{0.7}Ca_{0.3}MnO_3$. Isotope exchange of sample No. 1 was carried out in a furnace with two identical, parallel ceramic tubes passing ^{16}O and ^{18}O gas separately with identical gas flows. Two pieces cut from the same $(La_{0.25}Nd_{0.75})_{0.7}Ca_{0.3}MnO_3$ pellet were put in the same heating zone of the furnace. The two samples were first loaded at 950 °C for 72 h with ^{16}O or ^{18}O, furnace cooled over 24 h, and then weighed precisely. An exchange of samples between the two tubes was followed by the same annealing procedure; the isotope exchange, as determined by the weight change, was 79% ^{16}O to ^{18}O and 73% ^{18}O to ^{16}O. Each of the samples No. 1–No. 3 has a tolerance factor $t < t_c$. A four-probe method was used to measure the resistivity $\rho(T)$ under high pressure in a self-clamped pressure cell with silicone oil as the pressure-transfer medium. The thermoelectric power $\alpha(T)$ was measured in a home-built apparatus. We have taken T_c to be the temperature at which $d\rho/dT = 0$; the error in this reading of T_c has been shown to be within ± 0.5 K. In a test for thermal hysteresis of T_c, all samples were measured on cooling to 12 K before being measured on warming for each pressure applied. The connection between the T_c defined as above from the first-order transition and the Curie temperature from magnetic susceptibility has been well-established [5,6]. Therefore, we are able to monitor the ferromagnetic Curie temperature by measuring the transition in resistivity.

Figure 2 compares the $\alpha(T)$ curves for the two oxygen isotopes of sample No. 1. We have shown elsewhere [6] that the increase in $\alpha(T)$ with decreasing temperature $T > T_c$ is due to a trapping out of mobile charge carriers (polarons), and that for samples with $t > t_c$ the Curie temperature T_c increases sensitively with the concentration of mobile polarons just above T_c as t increases. The polaronic character above T_c has been confirmed by neutron diffraction [11,12] and other spectroscopic techniques [13,14]. The increase in the maximum value of $\alpha(T)$ on replacing ^{16}O by ^{18}O means a reduction in the concentration of mobile polarons just above T_c and is equivalent to a reduction in t. We have found a similar isotope effect on $\alpha(T)$ in samples with $t > t_c$ but it diminishes with increasing $t > t_c$. It follows that at least part of the giant isotope effect on T_c previously reported [10] is due to an increased trapping energy of the polarons above T_c with increased oxygen mass M. However, any mass dependence of the ferromagnetic coupling below T_c remains to be demonstrated.

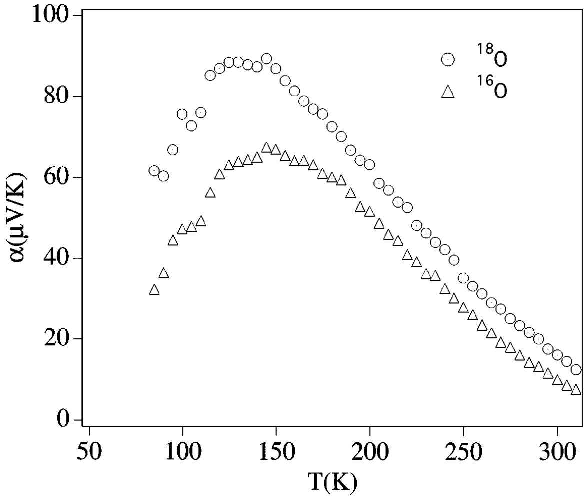

FIG. 2. Temperature dependence of the thermoelectric power for the two isotopes of sample No. 1.

In order to identify any additional mass dependence of the interatomic ferromagnetic exchange below T_c, we turned to measurements of $\rho(T)$ under pressure, Figs. 3 and 4. We used enough pressure to make t of all our samples cross t_c, where a maximum of the mass dependence is expected. We summarize in Fig. 5 the measured values of T_c. The transition at $d\rho/dT = 0$ found for pressures $P < P_c$ in the range $40 < T < 50$ K appears to be second order as it shows no hysteresis.

With increasing pressure P, a first-order phase change occurs a little below 2 kbar in the ^{16}O sample No. 1 and a little below 11 kbar in the ^{18}O sample No. 1; the dramatic onset of a thermal hysteresis at T_c is taken to mark a $t(P) \approx t_c$ at $P = P_c$. It follows that the ^{18}O sample No. 1, which has a larger P_c, is equivalent to the ^{16}O sample No. 1, but with a lower effective tolerance factor t as was also deduced from the $\alpha(T)$ data. At a pressure $P = 11$ kbar $> P_c$, a giant isotope coefficient $d\ln T_c/d\ln M = 4.9$ has been obtained; it is about 6 times

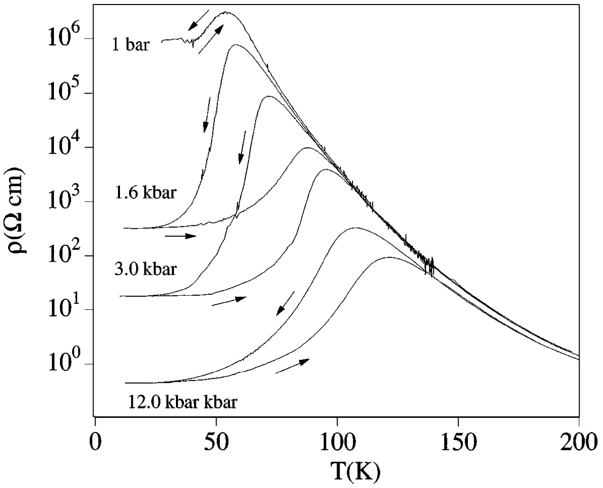

FIG. 3. The resistivity versus temperature for ^{16}O sample No. 1 under different pressures; the pressure labeled is taken from the value at T_c. A high noise level made measurement of the resistivity below 30 K not meaningful in the phases without a first-order transition.

larger than that reported [10] for $La_{0.8}Ca_{0.2}MnO_3$. However, this giant coefficient may reflect only the change in the density of mobile charge carriers in the paramagnetic state; the $\alpha(T)$ data have shown an important mass dependence of the mobile polaron density above T_c. To probe the mass dependence of the electronic state below T_c, we note that for $t > t_c$ both the hysteresis width $\Delta T_c = T_c$(warming)-T_c(cooling) and the coefficient dT_c/dP are mass dependent. The maximum $\Delta T_c \approx 27$ K for ^{16}O and 19 K for ^{18}O occurs at $P = P_c$; at a $P > P_c$, ΔT_c and dT_c/dP are reduced significantly on going from ^{16}O to ^{18}O, Fig. 5(a). To clarify whether this reduction is due to a pressure dependence or a mass dependence of ΔT_c and dT_c/dP, we did pressure experiments on samples No. 2 and No. 3. According to Fig. 1, a higher P_c is to be expected for these samples with smaller tolerance factor t than for the ^{16}O sample No. 1. As shown in Fig. 5(b), a P_c(No. 3) > P_c(No. 2) > P_c(No. 1) is observed, and the maximum $\Delta T_c \approx 27$ K of all ^{16}O samples is nearly pressure independent. Moreover, the coefficients dT_c/dP, which are labeled in Fig. 5, are reduced under pressure, but they remain higher than that of the ^{18}O sample No. 1. Comparison of these parameters for ^{18}O sample No. 1 and ^{16}O sample No. 3 is particularly significant as P_c is nearly the same in the two samples. This comparison rules out any pressure dependence on ΔT_c and dT_c/dP. We have thus demonstrated that both the thermal hysteresis width ΔT_c and dT_c/dP found in the ferromagnetic perovskite manganites are mass dependent.

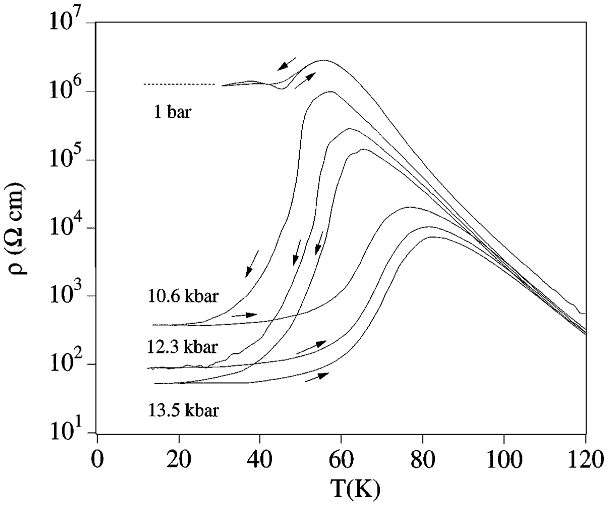

FIG. 4. The resistivity versus temperature for ^{18}O sample No. 1 under different pressures as in Fig. 3.

To interpret the mass dependence of ΔT_c and dT_c/dP, we refer to the virial theorem and the observation [6] that the compressibility of the Mn-O bond is greater than that of the A-O bond, where $A = (La_{1-x}Nd_x)_{0.7}Ca_{0.3}$ in our samples. For a central-force r^{-1} potential energy, the virial theorem states that $2\langle T\rangle + \langle V\rangle = 0$, where $\langle T\rangle$ and $\langle V\rangle$ are the mean kinetic and potential energies of the system. We have argued that the anomalously large compressibility of the Mn-O bond reflects a double-well potential of the equilibrium Mn-O bond length that can be expected to occur where there is a discontinuous change in the mean kinetic energy of the electronic system. Although a discontinuous change in the kinetic energy of the electronic system may be expected on passing from polaronic to itinerant electronic behavior on lowering T

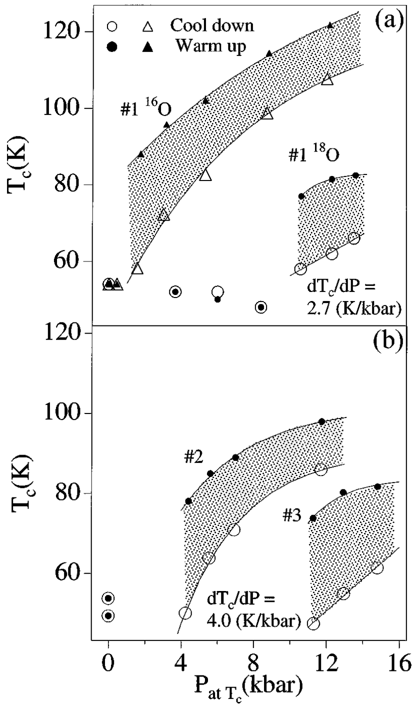

FIG. 5. The pressure dependencies of T_c (warming) and T_c (cooling) taken from $d\rho/dT = 0$ and fit to an exponential function: (a) for ^{16}O and ^{18}O sample No. 1 from Figs. 3 and 4; (b) for samples No. 2 and No. 3. The labeled dT_c/dP values were taken from T_c (cooling) and fit to a linear curve at $P = P_c$ for ^{18}O sample No. 1 and sample No. 3.

through T_c, which is the conventional interpretation of this transition, alternative transitions are also possible. For example, a polaron gas in equilibrium with regions of trapped polarons may transform to a vibronic phase in which the trapped polarons form extended Mn IV-rich domains as in a mobile charge-density wave within which larger polarons are organized. In order to distinguish between these possibilities, we consider the significance of ΔT_c. At T_c, the Gibbs free energy ΔG is identical for both the ferromagnetic and paramagnetic phases and the hysteresis ΔT_c is due to an interface strain energy associated with the nucleation of the second phase as a result of the volume change ΔV occurring at a first-order transition. Neutron-diffraction data [12,15] have corroborated the volume change $\Delta V < 0$ on lowering the temperature at T_c in the O (orthorhombic) phase. Therefore, ΔT_c can be used as an indicator of the relative magnitude of the volume change. The larger ΔV, the larger ΔT_c; therefore, the larger ΔT_c for ^{16}O compared to ^{18}O samples indicates a $\Delta V(^{16}\mathrm{O}) > \Delta V(^{18}\mathrm{O})$. This conclusion is also verified by the greater pressure sensitivity dT_c/dP for the ^{16}O compared to the ^{18}O sample.

If the electrons are itinerant, the tight-binding bandwidth W_0 is mass independent. However, the Mott bandwidth for polaronic conduction [16] varies as $W \sim W_0\ \exp(-\gamma\varepsilon_b/\hbar\omega_0)$, where ε_b is the polaron binding energy by a lattice optical mode of frequency ω_0 and γ is a constant; the polaron bandwidth is clearly mass dependent through ω_0. The mean kinetic energy $\langle T\rangle$ increases with the bandwidth; therefore, the mean kinetic energy of itinerant electrons should be independent of the oxygen mass M_0, whereas that of polarons decreases with decreasing $\omega_0 \sim \sqrt{M_0}$. It follows from the virial theorem that the volume of the ferromagnetic state below T_c is mass dependent if the electrons are polaronic, but is mass independent if they are itinerant. If, as is generally assumed, a polaronic to itinerant electronic transition occurs on cooling through T_c, then the mass dependence of ΔT_c is due to the mass dependence of the paramagnetic-state volume since there would be no mass dependence of the volume of an itinerant-electron state. But from the virial theorem, the lower polaron kinetic energy of the ^{18}O paramagnetic state would make $\Delta V(^{18}\mathrm{O}) > \Delta V(^{16}\mathrm{O})$ for itinerant electrons below T_c, which is opposite to what is observed in our samples. We are, therefore, forced to conclude that the volume of the ferromagnetic state below T_c is more mass dependent than that of the paramagnetic state, the higher mobility of the charge carriers in the ^{16}O ferromagnetic phase resulting in a smaller volume than is found in the ^{18}O ferromagnetic phase. This conclusion requires retention of some form of polaronic phase below T_c at the crossover from static to dynamic Jahn-Teller site deformations. This requirement is consistent with the stabilization of a vibronic state below T_c in a small interval Δt above t_c.

In conclusion, the thermoelectric power measurements on $^{16}\mathrm{O}/^{18}\mathrm{O}$ isotope samples confirm that the isotope shift of T_c is partially due to a mass-dependent trapping out of mobile polarons in the paramagnetic state. Trapping out of mobile charge carriers indicates a segregation into hole-rich clusters within a hole-poor matrix in the paramagnetic state. Moreover, the pressure dependence of the resistivity shows a sharp transition from a second-order to a first-order transition at T_c on passing from the O' to the O phase. In addition, the observations of a mass dependence in both the thermal hysteresis width ΔT_c and the coefficient dT_c/P indicate that lattice vibrations are involved in the transport properties of the ferromagnetic state in the O phase. This mass-dependent ferromagnetic state is understandable with a polaronic picture below T_c. With twofold-degenerate σ-bonding atomic orbitals occupied by one or less localized electron per atom, dynamic J-T deformations would introduce vibronic processes. Where vibronic processes among σ^*-band electrons occur in the presence of localized spins in π-bonding orbitals, the interatomic spin-spin exchange interactions are not independent of the oxygen-atom vibrational dynamics. These vibronic processes introduce a double-exchange component to the global ferromagnetic coupling above T_c that increases not only with the polaron density, but also with the polaron mobility, and hence, inversely with the root of the oxygen mass.

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