Lattice Effects in the Colossal-Magnetoresistance Manganites

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We study the combined influence of spin double exchange and Jahn-Teller lattice coupling to holes in the $La_{1-x}A_xMnO_3$ perovskites (A = Ca, Sr, Ba). Using a mean-field approximation for the double exchange and a variational Lang-Firsov approximation for the lattice degrees of freedom, we show that the lattice effects decrease the magnetic transition temperature, and also cause the maximal value of the transition temperature as a function of dopant concentration x to depend on the Jahn-Teller coupling strength. We find a continuous rapid crossover from a large polaronic state to a quasi-self-trapped small polaron state accompanying the magnetic transition.

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The term "colossal magnetoresistance" (CMR) was introduced recently to describe the remarkable temperature and magnetic field dependence of the resistivity in the perovskite-based $La_{1-x}A_xMnO_3$ (A = Ca, Sr, Ba) compounds. For concentrations $x \approx \frac{1}{3}$ a sharp peak in the resistivity is observed around temperature $T_p = 100-400$ K, below which the resistivity behaves as in a dirty metal and above which it is activated as in an insulator. The attractive feature for technology is that the application of a magnetic field causes a dramatic decrease in resistivity especially close to the resistivity peak [1–4]. Connected with the resistivity peak is a ferromagnetic to paramagnetic transition at temperature $T_c^m \sim T_p$. To explain the ferromagnetism in this class of materials Zener [5] introduced a double-exchange (DE) mechanism, in which conduction occurs via a coherent hopping (strength t) of electrons (from Mn^{3+} ions) along Mn-O-Mn bonds. Strong Hund's rule coupling $J^H \gg t$ of the electronically active electrons to the localized electrons in Mn d_{xy}, d_{xz}, d_{yz} orbitals means the motion of electrons spin polarizes the localized Mn spins, leading to ferromagnetism. The DE model was refined and extended by Anderson and Hasegawa [6] and de Gennes [7]. Since in the La based CMR materials holes carry the charge, another version of the DE model was derived by Kubo and Ohata [8] from the Kondo lattice model.

Very recently, however, it was argued by Millis, Littlewood, and Shraiman [9] that a direct modeling of the electronic behavior using the Kondo-lattice Hamiltonian, or its large-coupling approximation, the DE model, is incompatible with many aspects of the resistivity data, and a coupling to lattice degrees of freedom was proposed as a necessary extension. A main part of the argument in [9] hinges on an estimate of T_c^m using the dopant concentration x as a measure for the carrier concentration, which results in a T_c^m that is more than an order of magnitude too large. If some of the charge carriers are trapped by a lattice distortion, T_c^m would decrease accordingly. This is in agreement with Hall effect measurements [10], which may indicate that only a small fraction of the dopant ions actually contribute charge carriers. A further argument for extending the DE model can be based on measurements of the dependence of T_c^m and the resistivity on external hydrostatic pressure [11]. In the DE model the resistivity depends only on the ratio of the hopping matrix element t to temperature T, i.e., $\rho = \rho(t/T)$. Since pressure primarily changes t, the resistivity as a function of T is only rescaled, and the DE model can therefore explain only the shift of the resistivity maximum, not its drastic decrease [12]. Direct experimental evidence for local Jahn-Teller (JT) distortions, especially around T_c^m, is also becoming available, e.g., by ion channeling techniques [13]. In addition, more recent x-ray fine structure experiments reveal uniform O-Mn bond length distortion and a striking change of this distortion across T_c^m at doping $x = \frac{1}{3}$ [14]. A theoretical analysis by Sarker [15] examined the effect of constraining the Hilbert space due to Hund's rule and emphasized the need to include incoherent scattering mechanisms, such as disorder and/or a coupling to lattice degrees of freedom.

Here we present the effect of including coupling to longitudinal optical phonons in the DE model, which arises from JT splitting of the doubly degenerate conduction electron levels. We treat the local spin dynamics in the mean-field theory of Kubo and Ohata [8] and neglect any correlation effects between holes. We will use single e_g orbitals for conduction electrons. We have shown elsewhere [16] that the JT effects (static and dynamic) will split the e_g double degeneracy, and hence a single orbital approximation is reasonable for doping $x < 0.4-0.5$. We will use a homogeneous mean-field approximation for the low-temperature metallic phase. As the temperature increases across above T_c^m, the spin-polaronic effect will enhance the self-trapping and localization of lattice polarons [17], the combination of DE and JT effects gives rise to qualitatively new inhomogeneous small polaron solutions. Rigorously, of course, self-trapping never happens in the pure Hamiltonian because of translational invariance. However, when the bandwidth of the polarons becomes extremely small, the polarons can be trapped by

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many types of physical perturbations, such as disorder and doping ions.

Our Hamiltonian consists of the DE part $\mathcal{H}^{\mathrm{DE}}$ and $\mathcal{H}^{\mathrm{JT}}$ from the coupling to the lattice. $\mathcal{H}^{\mathrm{DE}}$ can be derived from the Kondo-lattice Hamiltonian in the limit where the coupling to localized spins $J_H \gg t$ [8]:

$$H^{\mathrm{DE}} = -t \sum_{\langle i,j\rangle,\sigma} \sigma_{ij}(c_{i\sigma}^{\dagger} c_{j\sigma} + \mathrm{H.c.}), \quad \sigma_{ij} = \frac{\langle s_0^{ij} + \frac{1}{2}\rangle}{2S+1}, \tag{1}$$

where s_0^{ij} is the total spin of the subsystem consisting of the two localized spins on sites i and j and the electron. The operators $c_{i\sigma}$ ($c_{i\sigma}^{\dagger}$) annihilate (create) a hole with spin σ at site i. At this point we neglect the fact that holes cannot doubly occupy sites by approximating $c_{i\sigma}^{\dagger}(1 - n_{i,-\sigma})$ by $c_{i\sigma}^{\dagger}$. $\langle \cdots \rangle$ denotes a thermal average. In the DE model the hopping matrix element in (1) is calculated in a virtual crystal approximation by letting the hole hop between sites i and j in the average field created by all the other spins.

In the single e_g orbital approximation, the two JT phonon modes can be approximated by one effective JT phonon mode, and the JT coupling Hamiltonian can be written as

$$\mathcal{H}^{\mathrm{JT}} = -\lambda^{\mathrm{JT}} \sum_i q_i n_i + (K/2) \sum_i q_i^2, \tag{2}$$

where q_i is the lattice deviation from equilibrium, n_i is the number of holes on site i, and K is the spring constant. (We use $K = 6t$.) Quantizing $\mathcal{H}^{\mathrm{JT}}$, we obtain $\mathcal{H} = -\sqrt{\epsilon_p \hbar\omega} \sum_i n_i(b_i^{\dagger} + b_i) + \hbar\omega \sum_i (b_i^{\dagger} b_i + \frac{1}{2})$, where the electron-phonon coupling strength is $\epsilon_p = (\lambda^{\mathrm{JT}})^2/2K$ and $\hbar\omega$ is the phonon frequency. We treat the dynamical phonons within the inhomogeneously modified variational Lang-Firsov approximation [18] using a canonical transformation $\tilde{\mathcal{H}} = \mathcal{U}^{\dagger}\mathcal{H}\mathcal{U}$, $\mathcal{U} = e^{-S_1(\{\Delta_i\})} e^{-S_2(\gamma)}$, where $S_1 = 1/2\sqrt{\epsilon_p \hbar\omega} \sum_i \Delta_i (b_i^{\dagger} - b_i)$ is designed to describe static lattice distortions through the introduction of a set of static site-dependent displacement fields Δ_i. The formation of polarons is controlled by $S_2 = -\sqrt{\epsilon_p/\hbar\omega} \sum_i \gamma n_i (b_i^{\dagger} - b_i)$, with γ measuring the degree of the polaron effect, which is most pronounced in the antiadiabatic ($\hbar\omega \to \infty$) limit, where $\gamma \to 1$. Averaging $\tilde{\mathcal{H}}$ over the phonon vacuum and adding $\mathcal{H}^{\mathrm{DE}}$ yields (apart from constants)

$$\begin{aligned} \tilde{\mathcal{H}} = & -t\xi(\gamma) \sum_{\langle i,j\rangle,\sigma} \sigma_{ij}(c_{i\sigma}^{\dagger} c_{j\sigma} + \mathrm{H.c.}) \\ & + (1-\gamma) \sum_i n_i \Delta_i + \frac{1}{4\epsilon_p} \sum_i \Delta_i^2 \\ & - \epsilon_p (2\gamma - \gamma^2) \sum_i n_i, \end{aligned} \tag{3}$$

where the polaronic band narrowing is given by $\xi(\gamma) = \exp(-\epsilon_p \gamma^2/\hbar\omega)$. Note that $\tilde{\mathcal{H}}$ also contains the static Hamiltonian (2) in the adiabatic limit ($\hbar\omega \to 0, \gamma \to 0$).

In the low-T metallic phase we expect homogeneity and therefore replace the site-dependent variational parameters by their averages: $\Delta_i \to \Delta, N^{-1}\sum_i n_i \to x$ (hole concentration), and $\sigma_{ij} \to \sigma$. Introducing the concentration dependence of the band energy via $e_B(x) = -t\sum_{\langle i,j\rangle,\sigma}(c_{i\sigma}^{\dagger} c_{j\sigma} + \mathrm{H.c.}) = N^{-1}\sum_{k<k_F(x)} n_k \epsilon_k$, we obtain for the energy per site

$$\begin{aligned} h^{\mathrm{homo}}(\gamma, \Delta, \sigma) = & \, \xi(\gamma)\sigma(\lambda) e_B(x) + (1-\gamma)\Delta x \\ & + \frac{1}{4\epsilon_p}\Delta^2 - \epsilon_p(2\gamma - \gamma^2)x. \end{aligned} \tag{4}$$

We now need an expression for the reduction of the hopping due to DE (through σ). We follow Kubo and Ohata [8] and introduce an effective magnetic field h^{eff}. Then $\sigma = \sigma(\lambda = h^{\mathrm{eff}}/T)$, and adding an entropy term to (4) we obtain a variational free energy (per site)

$$f(\lambda, \gamma, \Delta) = h^{\mathrm{homo}}(\gamma, \Delta, \sigma(\lambda)) + k_B T(\lambda m_S - \log \nu_S), \tag{5}$$

with the magnetization of the localized spins given by $m_S = \nu_S^{-1} \sum_{l=-S}^{S} l/S \exp(\lambda l/S)$ and $\nu_S = \sum_{l=-S}^{S} \exp(\lambda l/S)$. Taking the derivative of f with respect to λ, γ, Δ yields a set of two coupled equations, which must be solved self-consistently:

$$\lambda = \frac{\partial_\lambda \sigma}{\partial_\lambda m_S} \frac{[-e_B(x)]\xi(\gamma)}{k_B T} \tag{6}$$

and

$$\gamma = \left[1 + \frac{1}{\hbar\tilde{\omega}} \exp\left(-\frac{\tilde{\epsilon_p}}{\hbar\tilde{\omega}}\gamma^2\right)\right]^{-1}. \tag{7}$$

Here the phonon frequency $\hbar\omega$ and electron phonon coupling ϵ_p are both rescaled by the factor $r(x) = (x^2 + x)/[-e_B(x)\sigma(\lambda)]$ to yield $\hbar\tilde{\omega}$ and $\tilde{\epsilon_p}$. The homogeneous distortion Δ is given by $\Delta = 2\epsilon_p(1-\gamma)x$: $\Delta(x=0) = 0$, where $\bar{q} = 0$. To obtain T_c^m we expand (6) around $\lambda = 0$ and use $S = 2$:

$$T_c^m(x) = \frac{9}{50}[-e_B(x)]\xi(\gamma). \tag{8}$$

We numerically solved Eqs. (6) and (7) with $\sigma(\lambda = 0) = \frac{3}{5}$. In Fig. 1 we show the variation of T_c^m with the strength of the electron-phonon coupling. For zero coupling one simply obtains the doping dependence given by $e_B(x)$, since $\xi(\gamma) = 1$. Hence the curve is symmetric around half filling. For finite JT coupling one indeed observes the desired effect of a reduction of T_c^m due to polaronic band narrowing controlled by $\xi(\gamma)$. However, since γ

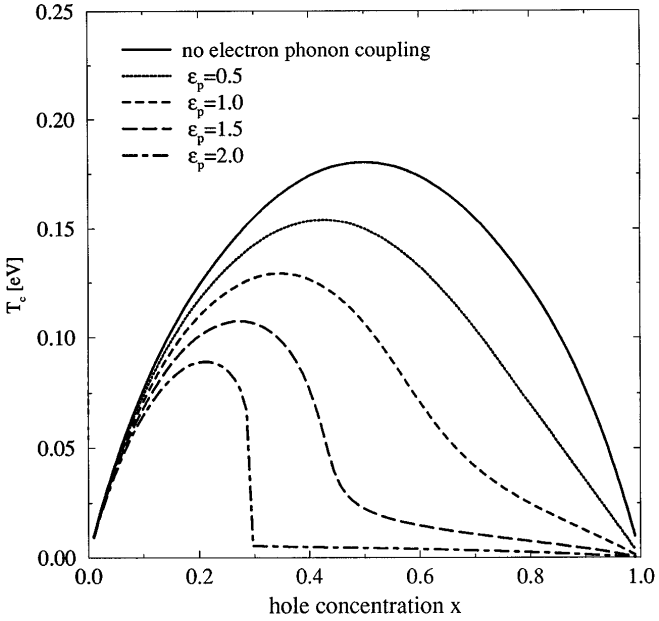

FIG. 1. The variation of T_c^m with ϵ_p for $\hbar\omega = 0.5$.

is strongly concentration dependent [the rescaling factor $r(x)$ diverges as $x \to 1$ for a simple $e_B(x) \approx x(x-1)$] the maximum in T_c^m monotonically moves to smaller hole concentrations as ϵ_p increases. As x increases the renormalized $\hbar\tilde{\omega}$ increases and the system is increasingly driven into the antiadiabatic limit characterized by a value of γ close to 1. This results in a strong Lang-Firsov band narrowing, since $\epsilon_p/\hbar\omega$ is not too small. For small x, γ becomes small and the polaronic band narrowing $\xi(\gamma)$ is much smaller than for large x, resulting in a larger T_c^m. The drastic doping dependence of the band narrowing effect is due to the self-amplifying coupling of both DE and JT effects: The polaronic band narrowing $\xi(\gamma)$ multiplies the double exchange reduction $\sigma(\lambda)$; see Eq. (4). For larger $\epsilon_p/\hbar\omega$ the concentration at which T_c^m is reduced dramatically due to the polaron effect decreases; see Fig. 1. Changing the concentration therefore leads to a change in the *effective* strength of the electron-phonon coupling, although the parameters remain fixed. Similar effects are found in the behavior of the resistivity [16]. For qualitative trends, we show the x dependence for our model for all $x \in [0,1]$, however, we note that this model is only directly applicable for CMR perovskite for $x < 0.4-0.5$.

Above T_c^m or in the case of extreme electron-phonon interactions close to the adiabatic limit one obtains a quasi-self-trapped state, and the assumption of spatially homogeneous parameters breaks down. We therefore need to allow for inhomogeneous distributions of σ_{ij} and inhomogeneous charge distributions $n_i \neq n_j$. To simplify the calculation we consider here the case of a single hole in the adiabatic limit. In order to calculate the T dependence of σ_{ij} we again treat the spin subsystem in mean field theory with the (spin) Hamiltonian $H^{\mathrm{mf}} = -\sum_i h_i^{\mathrm{eff}} S_i$, where the spatially dependent local fields contain a contribution from an externally applied field $h_i^{\mathrm{eff}} = h_i^{\mathrm{local}} + h^{\mathrm{ext}}$. This again results in a variational free energy

$$F(\{h_i\},\{q_i\}) = -\sum_i (h_i - h^{\mathrm{ext}}) m_i + E_0^{\mathrm{el}}(\{h_i\},\{q_i\}) + (\beta)^{-1} \sum_i \ln\Big[\cosh(\tfrac{1}{2}\beta h_i)\cosh(\beta h_i)\Big], \tag{9}$$

where m_i is the magnetization on site i, and the h_i must be chosen such that the free energy is minimal. E_0^{el} is the electronic ground state energy calculated for a given set of distortions q_i and reduced hopping amplitudes σ_{ij}. The free energy (9) must be minimized with respect to the $2L^3$ variational parameters $\{h_i\},\{q_i\}$, where L is the linear dimension of the system. To limit finite size effects we use $L = 30$ and minimize (9) with respect to 54 000 parameters using a conjugate-gradient algorithm. For $T = 0$ our model reduces to the three-dimensional Holstein model. One thus expects a transition from a large to small lattice polaron at $\lambda \approx 6t$. In Fig. 2 we show the average kinetic energy t_{eff} as a function of T and h^{ext}. Notice that t_{eff} decreases abruptly to a small value above $\lambda_c^{\mathrm{JT}} \approx 6.8$, indicating that the electron becomes "self-trapped" by the lattice distortion, and the composite particle appears as a localized lattice distortion with a spin polarization around the position of the hole. λ_c^{JT} increases with T and decreases with h^{ext}. The shape of the self-trapped state is depicted in Fig. 3. Whereas the

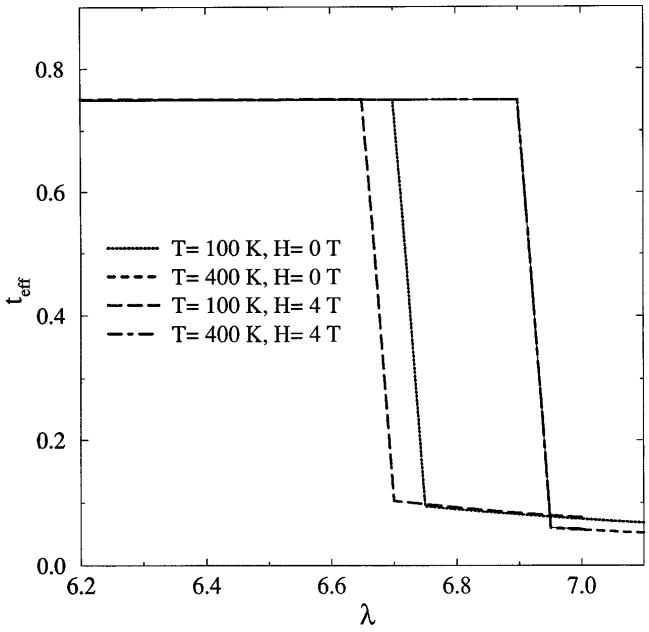

FIG. 2. The effective kinetic energy t_{eff} as a function of λ^{JT} for various temperatures and magnetic fields.

charge distribution is nearly T independent, we see that the magnetization distribution changes noticeably. At low T the magnetization induced by the localized electron saturates on the central site and its six neighbors. At higher T entropic effects become more important, and the gain in entropy further localizes the "magnetopolaron," causing a reduction in the magnetization on neighboring sites.

In conclusion, following a recent proposal [9] we have studied the inclusion of a JT coupling in the DE model of mixed-valence perovskite manganites. Using a mean-field theory for the spin degrees of freedom and neglecting electronic correlation effects we found that the lattice coupling indeed has the effect of decreasing T_c^m, the magnetic transition temperature. Interestingly, the JT coupling can also explain the doping dependence of T_c^m. We also studied the nature of a small magnetopolaron in the insulating regime above T_c^m in the dilute limit, and found that it comprises a localized charge surrounded by a spin cloud on nearest neighbors. Close to T_c^m the approximation of dilute and noninteracting polarons breaks down, and one needs to include many-particle effects to study the polaron-polaron interactions and polaron ordering. In addition, close to T_c^m effects of short-range ferromagnetic order may become important. Notwithstanding these possible extensions of this work, it appears that the *combined* effect of lattice degrees of freedom and DE is essential to understand both the metallic and insulating properties of CMR materials, as well as the systematic variation of T_c^m with doping.

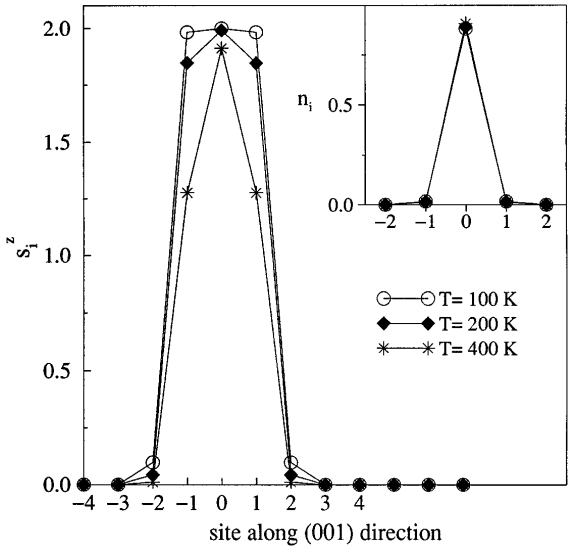

FIG. 3. The magnetization distribution of the self-trapped magnetopolaron for $\lambda = 7.0$. The charge distribution is shown in the inset. The lines are guides to the eye.

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