Dynamic Jahn-Teller Effect and Colossal Magnetoresistance in $La_{1-x}Sr_xMnO_3$

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A model for the doped rare-earth manganites such as $La_{1-x}Sr_xMnO_3$ incorporating the physics of dynamic Jahn-Teller and double-exchange effects is presented and solved via a dynamical mean field approximation. The interplay of these two effects as the electron phonon coupling is varied reproduces the observed behavior of the resistivity and magnetic transition temperature. [S0031-9007(96)00502-9]

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In this Letter we show that the essential physics of the "colossal magnetoresistance" materials $Re_{1-x}A_xMnO_3$ (here Re is a rare earth such as La and A is a divalent element such as Sr or Ca) is the interplay between a strong electron-phonon coupling and the "double exchange" effect of spin alignment on electron kinetic energy.

In the interesting doping range $0.2 \lesssim x \lesssim 0.5$, $Re_{1-x}A_xMnO_3$ is a ferromagnetic metal at low temperature T and a poorly conducting paramagnet at high T; the paramagnetic-ferromagnetic transition occurs at an x dependent transition temperature $T_c(x) \sim 300$ K and is accompanied by a large drop in the resistivity [1]. The colossal magnetoresistance which has stimulated the recent interest in these materials is observed for temperatures near $T_c(x)$ [2]. The electronically active orbitals are the Mn d orbitals and the mean number of d electrons per Mn is $4 - x$. The cubic anisotropy and Hund's rule coupling are sufficiently large that three electrons go into tightly bound t_{2g} core states and make up an electrically inert core spin S_c of magnitude $3/2$; the remaining $(1 - x)$ electrons go into a band of width $\sim$2.5 eV made mostly of the outer-shell e_g orbitals [3]. The e_g electrons are aligned to the core states by a Hund's rule coupling J_H which is believed to be large [1].

The large J_H means that the hopping of an outer-shell electron between two Mn sites is affected by the relative alignment of the core spins, being maximal when the core spins are parallel and minimal when they are antiparallel. Also, electron hopping promotes ferromagnetic order. This phenomenon, called double exchange [4], has been widely regarded [5,6] as the only significant physics in the regime $0.2 \lesssim x \lesssim 0.5$. However, we have previously shown [7] that double exchange alone cannot account for the very large resistivity of the $T > T_c$ phase [8] or for the sharp drop in resistivity just below T_c, and have suggested that the necessary extra physics is a strong electron-phonon coupling due in part to a Jahn-Teller splitting of the Mn e_g states. The cubic-tetragonal phase transition observed for $0 \lesssim x \lesssim 0.2$ is known to be due to a frozen-in Jahn-Teller distortion with long-range order at the wave vector (π, π, π) [9].

We propose that for $x > 0.2$ and $T > T_c(x)$, the strong electron-phonon coupling localizes the conduction band electrons as polarons, but that the polaron effect is "turned off" as T is decreased through T_c, permitting the formation of a metallic state. This is possible because the competition between electron itineracy and self-trapping is controlled by the dimensionless ration λ_{eff} of the self-trapping energy $E_{\text{J,T}}$ to an electron itineracy energy which may be parametrized by an effective hopping matrix element t_{eff}. When λ_{eff} exceeds a critical value we expect a crossover from a Fermi liquid to a polaron regime. Double exchange leads to a temperature dependent λ_{eff} because as T is reduced through T_c, the spins become ordered, increasing t_{eff} and thereby reducing λ_{eff}.

To investigate this in more detail we study the model Hamiltonian $H_{\text{eff}} = H_{\text{el}} + H_{\text{JT}}$ with

$$H_{\text{el}} = -\sum_{ij\alpha} t_{ij}^{ab} d_{ia\alpha}^{\dagger} d_{jb\alpha} + J_H \sum_{i,a,\alpha} \vec{S}_c^{\,i} \cdot d_{ia\alpha}^{\dagger} \vec{\sigma} d_{ia\alpha} + \vec{h} \cdot \vec{S}_c / S_c \tag{1}$$

and

$$H_{\text{JT}} = g \sum_{ja\sigma} d_{ja\sigma}^{\dagger} \mathbf{Q}^{ab}(j) d_{jb\sigma} + \frac{k}{2} \sum_j \mathbf{Q}^2(j). \tag{2}$$

Here $d_{a\sigma}^{\dagger}(i)$ creates an outer-shell d electron of spin σ in the a orbital on site i. The local lattice distortions which cause the Jahn-Teller splitting transform as a twofold degenerate representation of the cubic group which we parametrize by a magnitude r and an angle ϕ. They couple to the electron as a traceless symmetric matrix $\mathbf{Q} = r[\cos(\phi)\tau_z + \sin(\phi)\tau_x]$. The electron-phonon coupling is g and the phonon stiffness is k. The external magnetic field is $\vec{h}$; for simplicity, we have coupled it to the core spin only. In the phonon part of H_{eff} we have neglected intersite and anharmonic terms, as well as other phonon modes, most notably the breathing mode which couples to on-site charge fluctuations. In the electronic part of H_{eff} we have neglected on-site Coulomb interaction effects which we believe will affect low-energy properties of primary interest here only by renormalizing parameters such as t_{ij}^{ab}.

To solve H_{eff} we introduce further simplifications. We take $J_H \to \infty$. Because we are interested in phenomena at temperatures of order room temperature, we assume

the phonons and the core spins are classical. We use the "dynamical mean field" approximation which becomes exact in a limit in which the spatial dimensionality $d \to \infty$ [10]. Then the free energy may be expressed in terms of a space-independent "effective field" $\mathbf{G}_{\rm eff}(\omega)$ via

$$Z = \int r dr d\phi d\Omega \, \exp[-\mathrm{tr}^2/2T + \mathrm{Tr}\,\ln(t\mathbf{G}_{\rm eff}^{-1} + \lambda\vec{r}\cdot\vec{\tau} + J_H\vec{S}_c\cdot\vec{\sigma}) + \vec{h}\cdot\vec{\Omega}]. \quad (3)$$

Here $\vec{\Omega}$ is the direction of $\vec{S}_c$ and $t = D/4$ (D is the full bandwidth, so from [3] one estimates $t \approx 0.6$ eV). The dimensionless electron-phonon coupling constant $\lambda = g/\sqrt{kt}$. $\mathbf{G}_{\rm eff}(\omega)$ is a tensor with orbital and spin indices; it obeys a self-consistency condition whose form depends upon the lattice whose $d \to \infty$ limit is taken. We have used the Bethe lattice equation, which corresponds to an underlying band structure with a semicircular density of states with $D = 2\sqrt{\mathrm{Tr}\mathbf{t}^2}$. The self-consistent equation is [10]

$$\mathbf{G}_{\rm eff}^{-1}(\omega) = \omega + \mu - \mathrm{Tr}[\mathbf{t}\mathbf{G}\mathbf{t}]/2 \quad (4)$$

where $\mathbf{G} = \partial\,\ln Z/\partial\mathbf{G}_{\rm eff}^{-1}$, the trace is over orbital indices and the chemical potential μ is related to the density n by $n = T\partial\,\ln Z/\partial\mu$. We assume no long-range Jahn-Teller order, so $\mathbf{G}_{\rm eff}$ is a scalar in orbital space, but allow for magnetic order. We have used two methods for treating the spin part of the problem. In the *direct integration* method, Eq. (4) is solved on the Matsubara axis by direct iteration starting with the $\lambda = 0$ solution, performing the integrals over angle and phonon coordinate numerically. From this solution Z is constructed and $\vec{m} = \langle\vec{S}_c^i\rangle/S_c$ and $\langle r\rangle$ are computed. The conductivity is calculated following [10]; the requisite $\mathbf{G}_{\rm eff}$ on the real axis is obtained by solving Eq. (4) for real frequencies, using the previously obtained Matsubara solution to define Z. In the *projection method,* one quantizes the electron spin on site i along an axis parallel to $\vec{S}_c^i$ and retains only the component parallel to $\vec{S}_c^i$. The J_H term then drops out but one must multiply t_{ij} by the double exchange factor $q_{ij} = \sqrt{(1 + \vec{S}_c^i\cdot\vec{S}_c^j)/2}$ [4,7]. Within mean field theory $q_{ij} \to q = \sqrt{(1+m^2)/2}$, with m determined self-consistently via $m = -T\partial/\partial h\{\coth\beta(Jm+h) - [\beta(Jm+h)]^{-1}\}$ and as shown previously [7], $J = (1/2\sqrt{2})\partial\,\ln Z/\partial t$ with Z evaluated at $q = \sqrt{(1+m^2)/2}$. The resulting $d = \infty$ involve a $G_{\rm eff}$ which is a scalar and a numerical integral over the phonon coordinate only. One solves the resulting mean field equations once at each T and λ to yield a $Z(T/t, \lambda^2/t)$; the q dependence and hence the magnetic properties are found by scaling $t \to qt$. The two approaches give very similar results for the magnetic phase boundary and the phonon contribution to the resistivity, but the direct integration approach gives also the spin disorder contribution to the resistivity. The main difference is that the projection method leads to a first order magnetic phase transition for $\lambda \approx 1$.

We now discuss the solutions. In the limit $T \to 0$, ground state is a fully polarized ferromagnet for all λ. The phonon probability distribution $P(r) = \int d\phi d\Omega \times \exp[-\mathrm{tr}^2/2T + \mathrm{Tr}\,\ln(t\mathbf{G}_{\rm eff}^{-1} + \lambda\vec{\tau}\cdot\vec{r})]$ is a delta function at the most probable value $r = r^*$. For $\lambda < \lambda_c(x)$, $r^* = 0$. The ground state is a metal with $\rho(T=0) = 0$; the momentum-integrated spectral function $A(\omega) = \int[d^dp/(2\pi)^d]\mathrm{Im}G(p,\omega)/\pi$ takes the noninteracting form $A(\omega) = \sqrt{4t^2 - (\omega+\mu)^2}/2\pi t^2$. For $\lambda_{\rm eff} > \lambda_c$, $r^* > 0$, implying a frozen-in lattice distortion and a $\rho(T=0) > 0$. For $r^* < r_c$ ($r_c = 1$ at $n = 1$), A is distorted from its noninteracting form but the density of states at the Fermi level ($\omega = 0$ in present conventions) remains nonzero so $0 < \rho(T=0) < \infty$. If $r^* > r_c$, A has three separated peaks, two of weight n centered at $\pm\lambda r^* - \mu$ corresponding to full and empty orbitals on occupied sites and one of weight $2(1-n)$ centered at $-\mu$ corresponding to the unsplit orbitals on empty sites. The Fermi level is in a gap between the peaks and $\rho(T=0) = \infty$.

Figure 1 shows the numerically calculated phase diagram in the $T - \lambda$ plane. Consider first the $n = 1$ results. The solid line, obtained via the direct integration method, is a second order transition separating ferromagnetic (F) and paramagnetic (P) regions. The light dash-dotted lines separate regions of weak electron-phonon coupling in which $d\rho/dT > 0$ from regions of strong electron-phonon coupling in which $d\rho/dT < 0$. We identify these regions as metal (M) and insulator (I), respectively. The T dependence of the $d\rho/dT$ line below T_c is due mostly to the temperature dependence of the magnetization. Increasing λ decreases T_c; the variation is particularly rapid in the crossover region $\lambda \sim 1$. The projection method leads to a region of two-phase coexistence for $0.92 < \lambda < 1.1$. This is shown on Fig. 1 as the area between the heavy dotted line and the solid line. The different behavior of the two models suggests that in the crossover region the order of the transition is sensitive to the approximation of the model. $T_c(\lambda)$ for $n = 0.75$ and $n = 0.5$ are also shown as lighter dashed lines. $T_c(\lambda = 0)$ decreases with n because the total kinetic energy decreases. The crossings occur because at lower n the kinetic energy per electron is greater, so the effective electron-phonon coupling is weaker.

The inset to Fig. 1 shows the average of the square of the lattice displacement for $n = 1$. This is measurable in a scattering experiment sensitive to rms oxygen displacements. In the classical model used here, $r^2 \to r^{*2} + T$ as

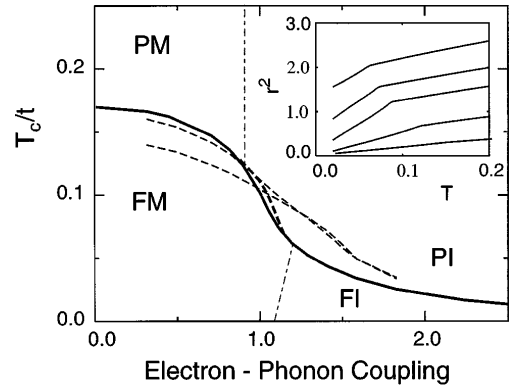

FIG. 1. Phase diagram. Solid heavy line: ferromagnetic $T_c(\lambda)$, calculated by direct integration method for $n = 1$. The area enclosed by the solid line and the heavy dashed line is the region of metastability found from the projection method. Lighted dashed lines: $T_c(\lambda)$ for $n = 0.75$ and $n = 0.5$. Light dotted lines: metal-insulator crossover obtained from calculated resistivities for $n = 1$. Regions labeled as PM (paramagnetic metal), FM (ferromagnetic metal), PI (paramagnetic insulator), and FI (ferromagnetic metal) according to the value of the magnetization and $d\rho/dT$. Inset: square of average lattice distortion plotted vs temperature for $n = 1$ and $\lambda = 0.71$ (lowest), 0.9, 1.05, 1.12, 1.2.

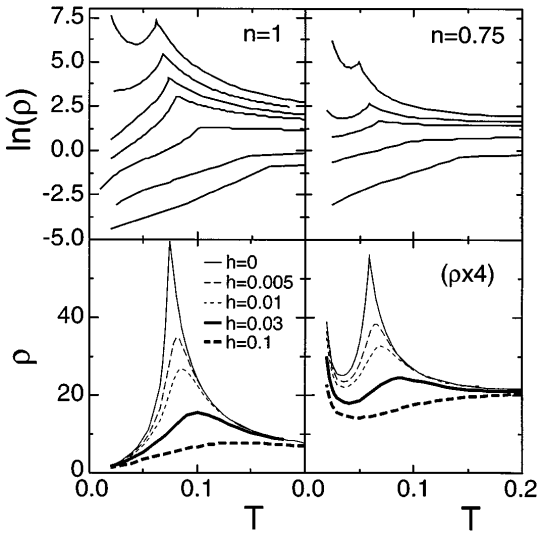

FIG. 2. Upper left: Resistivity calculated by the direct integration for $n = 1$ plotted vs temperature for different couplings $\lambda = 1.2$ (top), 1.12, 1.05, 0.95, 0.85, 0.71 (bottom). Lower left: Magnetic field dependence of resistivity calculated by the direct integration method for $n = 1$ and $\lambda = 1.12$ and magnetic field h as shown. Note $h = 0.01t$ corresponds to 15 Tesla if $t = 0.6$ eV and $S_c = 3/2$. Upper right: Resistivity calculated by the direct integration method for $n = 0.75$ and $\lambda = 0.71$ (lowest), 1.12, 1.41, 1.49, 1.58 (highest). Lower right: Magnetic field dependence of resistivity for $n = 0.75$ and $\lambda = 1.49$. In this panel the resistivity has been multiplied by a factor of 4.

$T \to 0$. One sees that for intermediate couplings the high temperature state extrapolates to $r^* > r_c = 1$ at $T = 0$ while the low T state has a $r^* < r_c$. In other words, there is a regime of parameters in which the electron-phonon interaction is insufficient to localize the electrons at $T = 0$ but sufficient to localize them at $T > T_c(x)$. This behavior is also seen in the resistivity.

The upper left panel of Fig. 2 shows the temperature dependence of the calculated resistivity for $n = 1$ and different λ. At small λ and $T > T_c$, ρ is small and has a T-independent piece due to the spin disorder and a T-linear piece (difficult to perceive on the logarithmic scale used) due to electron-phonon scattering. As T is decreased through T_c, ρ drops as the spin scattering is frozen out and the phonon contribution changes slightly. For larger λ a gap opens in the electron spectral function at $T > T_c$ and ρ rises as T is lowered to T_c. Below T_c, ρ drops sharply as the gap closes and metallic behavior is restored. Finally, at still stronger coupling, insulating behavior occurs on both sides of the transition, although there is still a pronounced drop in ρ at T_c. The lower left panel shows the magnetic field dependence of ρ for $\lambda = 1.12$ and $n = 1$, demonstrating that in this region of the phase diagram the colossal magnetoresistance phenomenon occurs. The magnetic field scale is too large relative to experiment (as is the calculated $T_c \approx 800$ K if $t = 0.6$ eV), but is very small in comparison to the microscopic scales of the theory. The upper right panel of Fig. 2 shows the resistivity for $n = 0.75$. One sees that rather strong couplings are required to obtain "insulating" $d\rho/dT < 0$ behavior. Also the upturn in ρ, when it exists, is less pronounced than for $n = 1$. The lower right panel of Fig. 2 shows the magnetoresistance for $n = 0.75$ and $\lambda = 1.13$. Note that the resistivity in this panel has been multiplied by 4. We have found it is not possible to get a large magnetoresistance in combination with metallic low T behavior at $n = 0.75$.

The resistivity and magnetoresistance calculated for $n = 1$ bear a striking resemblance to data on $Re_{1-x}A_xMnO_3$. The variation of the amplitude of the Jahn-Teller distortion shown in the inset to Fig. 1 may also have been observed [11,12]. The calculated doping dependence of the T_c at intermediate couplings is also in qualitative accord with data. The calculations are also consistent with a recent study of a La(Pr, Y)$Ca_{0.3}MnO_3$ series of compounds [13]. The substitution of Pr, Y for La decreases the effective d-d overlap, decreasing t and increasing λ. Experimentally, it results in a shift of T_c to lower temperatures and an increasing resistivity anomaly, as found in the calculation. The observed first order transition also occurs in one of the mean field theories we have considered.

For these reasons we think it very likely that our model contains the essential physics of the colossal magnetoresistance phenomenon. However, the resistivity calculated for $n \neq 1$ is in poor agreement with data. This disagreement is due to the previously mentioned midgap states which are a consequence of the particular Jahn-Teller coupling we have assumed. Figure 3 shows $A(\omega)$ for $n = 1$

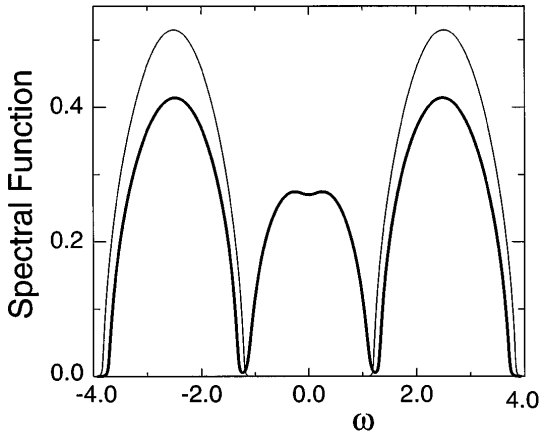

FIG. 3. Spectral functions for $\lambda = 1.58$, $T = 0.025$ and $n = 1$ (light line), $n = 0.75$ (heavy line). Note $n = 0.75$ curve is shifted by $\mu = -1.29$.

and $n = 0.75$ numerically calculated for $\lambda = 1.58$ and $T = 0.025$. At $n = 1$ the gap is large and well formed, but at $n = 0.75$ although the Jahn-Teller splitting (given by the separation between the outer peaks) is similar the activation gap controlling low-T physics is evidently much smaller, because of the midgap states, and so also is the temperature below which the $T \to 0$ behavior is displayed. A modification of the model which pushes the midgap states to higher energy will cause the behavior at $n = 0.75$ to more closely resemble that calculated for $n = 1$. The breathing distortion of an oxygen octahedron couples to charge fluctuations on an Mn site and will have precisely this effect. A complete theory of the doping dependence must also involve the on-site Coulomb interaction, which will lead as usual to an x dependence of the kinetic energy [14], and hence of T_c and λ_{eff}. Another open problem is to extend the mean field theory to allow for uniform and staggered ordering of the lattice distortions in order to study the low-x structural transitions and the $x > 0.5$ charge ordering transitions [15].

Detailed calculations including these effects will be left for future work. The results for $n = 1$ show that the interplay of electron-phonon coupling and double exchange accounts naturally for the existence of a high-T insulating phase, the dramatic changes of resistivity at T_c, and the extreme sensitivity to magnetic field.

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