Dynamic Jahn-Teller Effect and Colossal Magnetoresistance in

\( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \)

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Abstract

A model for \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \) which incorporates the physics of dynamic Jahn-Teller and double-exchange effects is presented and solved via a dynamical mean field approximation. In an intermediate coupling regime the interplay of these two effects is found to reproduce the behavior of the resistivity and magnetic transition temperature observed in \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \).
In this note we present and analyse a model which captures the important physics of the “colossal magnetoresistance” materials $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ (here A is a divalent element such as Sr or Ca). In the interesting doping range $0.2 \lesssim x \lesssim 0.4$, $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ is a ferromagnetic metal at low temperature, T, and a poorly conducting paramagnet at high T; the ferromagnetic-paramagnetic transition occurs at an x dependent transition temperature $T_c(x) \sim 300K$ 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].

Some aspects of the physics of $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ are well established [1]. 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 3 electrons go into tightly bound $d_{xy}$, $d_{yz}$, $d_{xz}$ 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 $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals [3]. The outer shell electrons are aligned to the core states by a Hund’s Rule coupling $J_H$ which is believed to be large [1].

The large value of $J_H$ 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 minimum when they are antiparallel. This phenomenon, called “double exchange” [4], has been widely regarded [3,5] 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 $T_c$. We suggested that the necessary extra physics is a strong electron-phonon coupling due at least in part to a Jahn-Teller splitting of the Mn d$^4$ state in a cubic environment. 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 $(\pi, \pi, \pi)$ [9]. We proposed that for $x > 0.2$ and $T > T_c(x)$, slowly fluctuating local Jahn-Teller distortions localize the conduction band electrons as polarons. The interesting physics issue is then how the polaron effect is “turned off” as T is decreased through $T_c$, permitting the formation of
a metallic state. Our picture is as follows. The competition between electron itineracy and self-trapping is controlled by the dimensionless ratio of the Jahn-Teller self-trapping energy $E_{J-T}$ and an electron itineracy energy which may be parametrized by an effective hopping matrix element $t_{\text{eff}}$. When $E_{J-T}/t_{\text{eff}}$ exceeds a critical value we expect a crossover from a Fermi liquid to a polaron regime. In models with both double exchange and a large $E_{J-T}$, an interesting interplay may occur because $t_{\text{eff}}$ is affected by the degree of magnetic order and conversely. As $T$ is increased from zero, the spins begin to disorder. This reduces $t_{\text{eff}}$ which increases $E_{J-T}/t_{\text{eff}}$ so phonon effects become stronger, further localizing the electrons and reducing $t_{\text{eff}}$ and thereby the effective ferromagnetic coupling.

To investigate this quantitatively we consider the model Hamiltonian $H_{\text{eff}} = H_{\text{el}} + H_{J-T}$ with

$$H_{\text{el}} = -\sum_{ij\sigma} t_{ij}^a d_{ia\sigma}^\dagger d_{j\sigma} + J_H \sum_{i,a,\alpha} \vec{S}_i \cdot \sigma_{ia\alpha} \vec{d}_{ia\alpha} + \vec{h} \cdot \vec{S}_c / S_c \quad (1)$$

and

$$H_{J-T} = g \sum_{ja\sigma} d_{ja\sigma}^\dagger Q_{ab}(j)d_{jb\sigma} + k \sum_j Q_{2}(j). \quad (2)$$

Here $d_{ia\sigma}^\dagger(i)$ creates an outer-shell d-electron of spin $\sigma$ in the $a$ orbital on site $i$. The local lattice distortions which cause the Jahn-Teller splitting transform as a two-fold degenerate representation of the cubic group which we parametrize by a magnitude $r$ and an angle $\phi$. They couple to the electron as a traceless symmetric matrix $Q = r(\cos(\phi)\tau_z + \sin(\phi)\tau_x)$. 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 $H_{\text{eff}}$ we have neglected intersite terms and also cubic and higher nonlinearities. In the electronic part of $H_{\text{eff}}$ we have neglected on-site Coulomb interaction effects; these will be important for higher energy properties of spectral functions but will only affect the low-energy properties we consider here by renormalizing parameters such as $t_{ij}^{ab}$.

To solve $H_{\text{eff}}$ 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 allow for magnetic order but assume that there is no long range order in the lattice degrees of freedom. To solve the electronic problem we use the ”dynamical mean field” approximation which becomes exact in a limit in which the spatial dimensionality $d \to \infty$ \cite{10}. Then, the free energy may be expressed in terms of a space-independent ”effective field” $G_{\text{eff}}(\omega)$ via

$$Z = \int r dr d\Omega \exp\left[-tr^2/2T + Tr\ln[tG_{\text{eff}}^{-1} + \lambda \vec{r} \cdot \vec{\sigma} + J_H \vec{S}_c \cdot \vec{\sigma} + \vec{h} \cdot \vec{\Omega}]\right]$$ (3)

Here $\vec{\Omega}$ is the direction of $\vec{S}_c$ and $t = D/4$ (D is the full bandwidth, so from \cite{3} one estimates $t \approx 0.6$eV). The dimensionless electron-phonon coupling constant $\lambda = g/\sqrt{kt}$. $G_{\text{eff}}(\omega)$ 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 \cite{10}. We have used the Bethe lattice equation, which corresponds to an underlying band structure with a semicircular density of states with $D = 2Trt^2$. The self consistent equation is \cite{10}

$$G_{\text{eff}}^{-1}(\omega) = \omega - \mu - Tr[tGt]/2$$ (4)

where $G = \partial \ln Z/\partial G_{\text{eff}}^{-1}$. Because we assume there is no long range order in the lattice degrees of freedom, we take $G_{\text{eff}}$ to be the unit matrix in orbital space. We have used two methods for treating the spin part of the problem. In the direct integration method, one solves Eq. (4) by performing the integrals over the angle and phonon coordinates numerically. In the projection method, one quantizes the electron spin on site $i$ along an axis parallel to $\vec{S}_c$ and retains only the component parallel to $\vec{S}_c$. The $J_H$ term then drops out of the Hamiltonian but as shown previously \cite{4,7}, one must multiply $t_{ij}$ by the double exchange factor $q_{ij} = \cos(\theta_{ij}/2) = \sqrt{(1 + \vec{S}_c \cdot \vec{S}_c)/2}$. Within mean field theory one may replace $q_{ij}$ by $q = (1 + m^2/2)/\sqrt{2}$, where $\vec{m} = \langle \vec{S}_c \rangle / S_c$ is determined self consistently via $m = -T\partial/\partial h[\coth(\beta(Jm + h) - (\beta(Jm + h))^{-1})$ and as shown previously \cite{4}, $J = (1/2\sqrt{2})\partial \ln Z/\partial t$ with $Z$ evaluated at $q = \sqrt{(1 + m^2)/2}$. The resulting $d = \infty$ equations involve a $G_{\text{eff}}$ which is a scalar and a numerical integral over the phonon coordinate only. Because $t$ enters the mean field equations only as an energy scale, it is necessary only to solve the resulting mean
field equations once at each $T$ and $\lambda$ to yield a $Z(T/t, \lambda^2/t)$; the $q$ dependence and hence the magnetic properties may be 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 between the two calculations is that projection method leads to a first order magnetic phase transition for $\lambda \approx 1$.

We now discuss the solutions. Several soluble limits exist. At $\lambda = 0$ there is a second order ferromagnetic transition at a $T_c(x)$ which is maximal for the half filled band ($T_c(0) = 0.17t$) and decreases as the band filling is decreased. For $T > T_c$ there is spin disorder scattering which (in the mean field approximation used here) is temperature independent and of small magnitude. This scattering decreases below $T_c$ as discussed previously [5–7].

In the limit $T \to 0$, ground state is a fully polarized ferromagnet for all $\lambda$. The phonon probability distribution $P(r) = \int d\phi d\Omega e^{-tr^2/2T+Tr\ln[tG_{\text{eff}}^{-1}+\lambda r^2]}$ is sharply peaked about the most probable value $r = r^\ast$. For $\lambda < \lambda_c(x)$, $r^\ast = 0$ and the ground state is a conducting Fermi liquid. For $\lambda_{\text{eff}} > \lambda_c$, $r^\ast > 0$, implying a frozen-in lattice distortion and, if $r^\ast$ is large enough, a gap in the electronic spectrum. For $x = 0$, $\lambda_c = 1.08^{...}$ and the transition is second order, with $r^\ast$ linear in $\sqrt{\lambda - \lambda_c}$ but very rapidly growing, reaching the point $r^\ast = 1$ at $\lambda = 1.15$. For $r^\ast > 1$, $r^\ast$ becomes linear in $\lambda$ and a gap appears in the spectral function. For $x > 0$ the transition is first order, involves a jump to a nonzero $r^\ast$, and occurs at a $\lambda_c > 1.08$. A detailed discussion of the spectral functions and transitions will be presented elsewhere [12].

The increase of $\lambda_c$ with $x$ is due to the increased kinetic energy per electron. Note that the double exchange effect means that the kinetic energy is maximal in the fully polarized ferromagnetic state. For uncorrelated spins, the kinetic energy is smaller by a factor of $\sqrt{2}$ and $\lambda_c$ smaller by a factor of $2^{1/4}$. 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 $T > T_c(x)$.

Another analytically solvable limit is $\lambda \gg 1$. In this limit an expansion in $1/\lambda$ may be constructed for arbitrary $1/\lambda T$, and in the leading order one may evaluate the $r$ integral by
steepest descents. Here we find a second order phase transition at \( T_c = t/12\lambda^2 \) separating two insulating phases with slightly different gaps.

We turn now to numerical results, limiting ourselves to \( x=0 \) for simplicity.

The \( J_H \to \infty \) limit means that the d-bands arising from the outer-shell orbitals are half filled, so the chemical potential \( \mu = 0 \). Eq (4) is solved on the Matsubara axis by direct iteration starting with the \( \lambda = 0 \) solution. From this solution \( Z \) is constructed and \( \langle m \rangle \) and \( \langle r \rangle \) are computed. The conductivity is calculated following [10]; the requisite \( G_{\text{eff}} \) on the real axis is obtained by solving Eq. 4 for real frequencies, using the previously obtained Matsubara solution to define \( Z \).

Fig 1. shows the phase diagram in the \( T - \lambda \) plane. The solid line is a second order transition separating ferromagnetic (F) and paramagnetic (P) regions obtained via the direct solution method. The light dashed 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 \( \lambda \) decreases \( T_c \); the variation is particularly rapid in the crossover region \( \lambda \sim 1 \), consistent with the very rapid dependence of \( r_* \) on \( \lambda \) mentioned above. Here also the magnetic transition calculated via direct integration becomes more nearly first order. 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 approximations of the model. Other physics, not included here, will also tend to drive the transition first order. We mention in particular anharmonicity in the elastic theory, which will couple the Jahn-Teller distortions to the uniform strain, and also the conduction electron contribution to the binding energy of the crystal, which produces the observed volume change at \( T_c \) [14].

The inset to fig 1 shows the average of the square of the lattice displacement. This would be measurable in a scattering experiment sensitive to \( \text{rms} \) oxygen displacements. In
the classical model used here, $r^2 \to r_*^2 + T$ as $T \to 0$. One sees that for intermediate couplings the high temperature state has a non-zero extrapolation to $T = 0$ while the low $T$ state has a vanishing extrapolation, while for larger couplings both sides of the transition have non-zero but different extrapolations.

Fig 2 shows the temperature dependence of the calculated resistivity for several different values of $\lambda$. At small $\lambda$ and $T > T_c$, $\rho$ 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 in fig 2), due to electron-phonon scattering. As $T$ is decreased through $T_c$, $\rho$ drops as the spin scattering is frozen out and the phonon contribution changes slightly. For larger $\lambda$ a gap opens in the electron spectral function at $T > T_c$ and the resistivity rises as $T$ is lowered to $T_c$ and then drops sharply below $T_c$, 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 $\rho$ at $T_c$.

Fig 3 shows the magnetic field dependence of $\rho$ for $\lambda = 1.12$, 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 $T_c$), but is very small in comparison to the microscopic scales of the theory.

The series of resistivity curves presented in fig 2 bears a striking resemblance to measured resistivities on the series La$_{1-x}$A$_x$MnO$_3$. We have already noted that the calculation, which neglects long range order, gives the generic behavior at any carrier concentration. We identify the experimental doping $x$ with the relative strength of the electron phonon interaction, $\lambda$ because increasing $x$ increases the kinetic energy per electron. With this identification the results are consistent with the observed variation of $T_c$ and $\rho$ with $x$, and also with the opening of a gap observed [13] in the optical conductivity. Note also that as $T$ moves through $T_c$, the effective ferromagnetic $J$ should drop by about 10 percent, producing a perhaps observable shift in the position of the zone boundary magnon.

The present theory is consistent with a recent study of a La(Pr, Y)Ca$_3$MnO$_3$ series of compounds [14]. The substitution of Pr, Y for La decreases the effective d-d overlap,
decreasing \( t \) and increasing \( \lambda \). 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.

In summary, we have presented a solution of a model describing the Jahn-Teller and double exchange physics, and have shown that it 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. In obtaining this behavior the interplay of polaron and double exchange physics is essential. We have solved the \( d = \infty \) equation appropriate to Eq. 3 with \( J_H = 0 \) and found metallic behavior (with \( \rho \) and \( r^2 \) linear in \( T \)) at temperatures greater than the \( T = 0 \) gap and insulating behavior at temperatures less than the \( T = 0 \) gap. A more detailed exploration of the MF theory allowing uniform or staggered ordering of the lattice distortions and varying carrier concentration will be needed to study the structural transition at low \( x \) and the "charge ordered" phase \([11,15]\) at \( x \approx .5 \). These calculations however must also include the intersite phonon coupling.

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Figure Captions

Fig. 1: Phase diagram. Solid line: ferromagnetic $T_c$ as a function of electron-phonon coupling, $\lambda$, calculated by direct integration method. The area enclosed by the solid line and the heavy dashed line is the region of metastability found in one formulation of mean field theory. Light dotted lines: metal-insulator crossover obtained from calculated resistivities. Regions labelled 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 $\lambda = 0.71$ (lowest), 0.9, 1.05, 1.12, 1.2.

Fig. 2: Resistivity calculated by direct integration method plotted versus temperature for different couplings $\lambda$. Heavy solid curve (top) $\lambda = 1.2$, heavy dotted curve, $\lambda = 1.12$, heavy dot-dash curve $\lambda = 1.05$, light solid curve $\lambda = 0.95$, light dashed curve $\lambda = 0.85$, light dot-dashed curve (bottom) $\lambda = 0.71$.

Fig 3. Magnetic field dependence of resistivity calculated by direct integration method for $\lambda = 1.12$ and magnetic field $h$ as shown. Note $h=0.01t$ corresponds to 15 Tesla if $t = 0.6eV$ and $S_c = 3/2$. 
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