Phase separation in double exchange systems

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Ferromagnetic systems described by the double exchange model are investigated. At temperatures close to the Curie temperature, and for a wide range of doping levels, the system is unstable toward phase separation. The chemical potential decreases upon increasing doping, due to the significant dependence of the bandwidth on the number of carriers. The reduction of the electronic bandwidth by spin disorder leads to an enormously enhanced thermopower which peaks near $T_c$, with a sign opposite that predicted by a rigid band model.

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Doped manganese oxides exhibit many unusual features, most notably the eponymous phenomenon of colossal magnetoresistance (CMR) \cite{1–3}, and a phase transition from a high temperature paramagnetic insulator to a low temperature ferromagnetic metal. The Mn $3d$ states split into a lower $t_{2g}$ triplet, forming an $S = \frac{3}{2}$ core spin, and an upper $e_g$ doublet, the conduction band. This physics is described by the double exchange model \cite{4}: the conduction electrons which hop throughout the lattice are ferromagnetically coupled to the local core spins because of Hund’s rules. Typical values for the $e_g$ hybridization $t$ and intra-atomic exchange $J_H$ are $t \sim 0.1$ eV and $J_H \sim 1–3$ eV. Additionally, one may choose to incorporate other terms, most notably Heisenberg couplings between neighboring core spins (due to superexchange) and Jahn-Teller (JT) phonons which break the degeneracy of the $e_g$ level.

The simplest model, however, is one in which the degeneracy of the $e_g$ orbital is simply ignored (possibly due to a cooperative JT distortion), and $J_H$ is set to infinity. In this limit, the spin of each $e_g$ electron must agree with that of its $t_{2g}$ core, and we may write $c_{i\sigma} = c_{i\uparrow}^\dagger z_{i\sigma}$, where $z_{i\sigma}$ is the spinor describing the orientation of the core at site $i$: $z_{i\uparrow} = \cos(\frac{1}{2}\theta_i)$, $z_{i\downarrow} = \sin(\frac{1}{2}\theta_i)\exp(-i\phi_i)$. The Hamiltonian is then

$$H = -t \sum_{\langle ij\rangle,\sigma} \left[ z_{i\sigma} \bar{z}_{j\sigma} c_i^\dagger c_j + \text{H.c.} \right].$$

The hopping is maximized when neighboring core spins are parallel. The ferromagnetic interaction induced in this way describes qualitatively the physics of the manganites. The Curie temperature increases with the number of carriers, and, in the paramagnetic phase, the tendency towards localization is enhanced. On the other hand, it has been extensively argued that the double exchange model does not suffice to describe the insulating behavior at high temperatures \cite{5}. A disordered distribution of spin gives rise to off-diagonal disorder, which is in a sense weaker than the more conventional diagonal disorder, and most of the states in the band are delocalized \cite{6} (see, however, the comments of \cite{7}). The $e_g$ bandwidth remains finite and is unremarkable as one passes through the Curie temperature $T_c$ \cite{8}. Scattering by magnetic fluctuations near $T_c$ also is insufficient to explain the insulating regime \cite{9]. A variety of phenomena, including variable range hopping \cite{10}, formation of spin polarons \cite{11}, and the dynamic Jahn-Teller effect \cite{12} have been invoked in an attempt to understand the insulating paramagnetic phase.

Here we will show that the double exchange model \cite{13} is unstable toward charge segregation at low to moderate doping and temperatures near $T_c$. This phenomenon arises due to the coupling between magnetic fluctuations and the electronic chemical potential. Exchange interactions between core spins tend to suppress this effect, but do not completely eliminate it. The Coulomb interaction will suppress complete phase separation of charge carriers, resulting in microscopic domains of different charge density. This inhomogeneity in turn enhances localization of electrons. A small ferromagnetic region of high density, surrounded by a low density paramagnetic background, is indistinguishable from the spin polaron picture discussed in the literature.

To see why phase separation should occur in \cite{13}, let us reexamine de Gennes’ mean field approach \cite{14}. The quantity $\bar{W} \equiv \sqrt{\langle |z_{i\sigma} \bar{z}_{j\sigma}|^2 \rangle} = \langle \cos^2(\frac{1}{2}\theta_{ij}) \rangle^{1/2}$ is a “spin reduction factor” which multiplies the fermion hopping $t$, compressing the bare ($\bar{W} = 1$) dispersion $E$ to $\bar{W}E$.

At zero temperature, states with $E < E_F$ are filled, and $\mu = \bar{W}E_F$. The density of states $D(E)$ and doping $x \equiv \frac{\mu}{\bar{W}}$ determine $\delta$ via $\delta = \int_0^{E_F} dE D(E)$. Thus,

$$\frac{\partial \mu}{\partial \delta} = \frac{\bar{W}}{D(\mu/\bar{W})} + \frac{\mu}{\bar{W}} \frac{\partial \bar{W}}{\partial \delta}. \quad (2)$$

When $\partial \mu/\partial \delta < 0$, the system can lower its energy
through phase separation. Now at zero temperature we should expect perfect order in the spins, hence $W = 1$ and the compressibility is positive. At finite temperature, however, we expect $\mu \partial \ln W / \partial \delta < 0$ since increased carrier density $|\delta|$ enhances the fermion kinetic energy, which serves as an exchange coupling for the spins (this is true whether the carriers are electrons or holes). If we assume the fermions to be degenerate, the condition for negative compressibility is $\mu D(\mu/W) \partial W / \partial \delta < -W$. To satisfy this relation requires both finite $T$ and low to intermediate $|\delta|$ (note $\mu \approx 0$ for $\delta \approx 0$, assuming a symmetric band). As we shall see, this behavior may persist above the Curie temperature as well. At sufficiently large $T$, however, the fermions are nondegenerate and the chemical potential dominates the bandwidth, giving $\delta = \frac{1}{2} \tanh(\mu/2k_B T)$ and $\partial \mu / \partial \delta = 4k_B T/(1 - 4\delta^2) > 0$.

This picture also leads to an anomalous thermopower [18]. At low temperatures the variation of the chemical potential with $T$ arises from two sources: the Fermi distribution (e.g. the Sommerfeld expansion) and the band narrowing $W$. Thus one obtains

$$\frac{\partial \mu}{\partial T} = \mu_0 \frac{\partial W}{\partial T} - \frac{\pi^2}{3} \frac{D(\mu_0)}{D(\mu)} k_B^2 T + \ldots \quad (3)$$

For models where $D'(E)/E > 0$, such as the elliptical density of states, the first term, arising from the band narrowing, opposes the second. As we shall see for all but the lowest and highest temperatures it is the first term which dominates, and the critical behavior of $W$ in the vicinity of $T_c$ leads to a peak in the thermopower which is several orders of magnitude larger than that usually encountered in metals.

Adding purely ferromagnetic superexchange between the core spins reduces the dependence of $W$ on $\delta$ and thereby opposes phase separation. In La$_{1-x}$A$_x$MnO$_3$, however, the interplane superexchange is antiferromagnetic for small $x$, and its competition with double exchange leads to a canted structure [14]. The bandwidth then depends on the canting angle and increases with increasing number of carriers. This property leads to phase separation even at $T = 0$ [14].

There is a subtlety in the mean field theory surrounding which density of states $D(E)$ one should use. Integrating out the fermions from (6) gives a free energy

$$F = \sum_{p=1}^{\infty} \frac{(-1)^p}{p!} I^{(p)}(-\mu) \frac{\partial}{\partial \mu} \langle \Omega_i \rangle - TS[\Omega_i] \quad (4)$$

where $I(\varepsilon) = -k_B T \ln(1 + e^{-\varepsilon/k_B T})$ and $H_{ij} = z_i z_j$. $T_{ij}$ with $T_{ij} = t$ if $i$ and $j$ are nearest neighbors and 0 otherwise. The entropy $S[\Omega_i] = -k_B \ln \Omega_i$ and the trace in (6) are computed from a trial density matrix $\Omega_i$ for the spins. Assuming an uncorrelated $\Omega = \prod_i P(\Omega_i)$ with $P(\Omega_i) \propto \exp(Q\Omega_i)$, we have that $\exp(i\phi_i) = 0$, hence in the locator expansion of $\langle \exp(i\phi_i) \rangle = 0$, hence in the locator expansion of $\langle \Omega_i \rangle H^p$, many of the $2^p$ terms associated with a given length $p$ path average to zero. These cancellations are avoided for paths which retrace themselves, for which each $z_i z_j$ term has a $\bar{z}_i z_j$ mate. Thus, in the vicinity of $T_c$ where magnetic fluctuations are significant, it is better to use the retraced path approximation [15],

$$D(\gamma) = \frac{2}{\pi} \frac{\sqrt{1-\gamma^2}}{1-\frac{4}{3} \gamma^2} \quad (5)$$

where $z$ is the lattice coordination number, in one’s mean field calculations. $D(\gamma)$, given above with $\gamma = -E/B$ in units of the bare half-bandwidth $B = 2(\varepsilon - 1)^{1/2}t$, interpolates between the exact one-dimensional tight binding density of states at $z = 2$ to a semi-elliptic form at $z = \infty$. The hopping is then modulated by $W$, the root-mean-square average of $z_i z_j$.

The mean field equations of de Gennes’ model are

$$\delta = \frac{1}{2} \int_{-1}^{1} d\gamma \frac{D(\gamma)}{2} \tanh \left( \frac{\alpha + W\gamma}{2\Theta} \right) \quad (6)$$

$$\frac{2\Theta WQ}{M} = \frac{1}{2} \int_{-1}^{1} d\gamma \frac{D(\gamma)}{2} \tanh \left( \frac{\alpha + W\gamma}{2\Theta} \right) \quad (7)$$

where $M = \tanh(Q) - Q^{-1}$ is the magnetization, and $W = \sqrt{\frac{1}{2}(1 + M^2)}$. The temperature and chemical potential are scaled by $\alpha = \mu/B$ and $\Theta = k_B T/B$.

The mean field solution exhibits a Curie temperature $\Theta_c(\delta)$. With $t \approx 100$ meV [14], the cubic lattice model has $B = 2\sqrt{5}t \approx 5200$ K. We find a maximum $\Theta_c = \ldots$
0.0545 at \( \delta = 0 \), corresponding to a Curie temperature of \( T_c = 280 \text{K} \), very much consistent with experimental values. \( M \) vanishes at \( \Theta_c \), and for \( \Theta > \Theta_c \) the bandwidth is finite, reduced by the spin factor \( \frac{1}{\sqrt{2}} \). The compressibility \( \kappa^{-1} \equiv \partial n / \partial \delta \) and thermopower \( S = \partial n / \partial \Theta \) are discontinuous at the transition. \( S \) peaks near \( T_c \) with an anomalously large value; we shall return to this point below. For the \( z = \infty \) case, we find a crescent region of phase separation \( \Theta \in [\Theta_c(\delta), \Theta_c(\delta)] \) extending from \( \delta = 0.382 \) to \( \delta = \frac{1}{4} \), in qualitative agreement with our earlier discussion. In Fig. 1(a) we plot the mean field phase diagram for the limiting case \( z = \infty \). (As one approaches the one-dimensional limit \( z = 2 \), the region of phase separation is enlarged.) For \( z > 2 \) we find \( \Theta_c \propto \bar{\tau} \) and \( \Theta_k \propto \bar{\tau}^{-1/3} \) as \( \bar{\tau} = \frac{1}{4} - \delta \to 0 \). (The model is of course invariant under \( x \leftrightarrow \bar{\tau} \).

An unphysical aspect of the preceding mean field analysis is that \( \bar{W} \), which should be determined by local spin correlations, is tied to the magnetization \( M \). Initially \( \bar{W} \) decreases linearly with \( \Theta_c \), leading to artifactual behavior in the low temperature magnetization and thermopower. The root of the problem is the classical treatment of the core spins. At temperatures \( \Theta < \mathcal{O}(1/S) \), one must treat the spins quantum mechanically. We should then expect, from spin wave, theory, that \( \bar{W} = 1 - \mathcal{O}(\Theta^{5/2}) \).

A somewhat more sophisticated mean field theory can be implemented using the Schwinger boson method. A nondynamical field \( \lambda_j \) enforces the constraint \( z_{ij} z_{ij} \equiv 1 \) at every site. The core spins are quantized according to \( [z_{ij} , z_{ji}^\dagger] = \delta_{ij} \delta_{\sigma \sigma'}/2S \). The mean field Hamiltonian is obtained through a Hartree decoupling of the bosonic \( z_{ij} z_{ij} \) and fermionic \( c_j^\dagger c_j \) hopping terms:

\[
H_{\text{MF}} = N(ztW K - \lambda) - \mu \sum_i c_i^\dagger c_i + \lambda \sum_{i, \sigma} (\bar{z}_{ij} z_{ij} - \bar{z}_{ij}^\dagger z_{ij}^\dagger)
\]

(8)

\[-tW \sum_{(ij)} (c_i^\dagger c_j + c_j^\dagger c_i) - tK \sum_{(ij)} (\bar{z}_{ij} z_{ij} + \bar{z}_{ij}^\dagger z_{ij}^\dagger),\]

where \( K = \langle c_i^\dagger c_j \rangle \) and \( W = \langle z_{ij} z_{ij}^\dagger \rangle \). Such a model was introduced by Sarker [20], who identified a Curie transition and found that the \( c \) fermion band becomes incoherent above \( T_c \). For our purposes we are interested in phase separation. Counting for the possibility of condensation of Schwinger bosons, we write \( \Psi_{k\sigma} \equiv \langle z_{k\sigma} \rangle \). Assuming condensation only at \( k = 0 \), we define \( \rho \equiv |\Psi_{k=0,\sigma}|^2 \).

The mean field equations are then

\[
1 + \frac{1}{2S} = \rho + \frac{1}{2S} \int_1^1 d\gamma D(\gamma) \tanh \left( \frac{\Lambda - K \gamma}{4S\Theta} \right)
\]

\[
W = \rho + \frac{1}{2S} \int_1^1 d\gamma D(\gamma) \tanh \left( \frac{\Lambda - K \gamma}{4S\Theta} \right)
\]

\[
\delta = \frac{1}{2} \int_1^1 d\gamma D(\gamma) \tanh \left( \frac{\alpha + W \gamma}{2\Theta} \right)
\]

\[
K = \frac{1}{2} \int_1^1 d\gamma D(\gamma) \tanh \left( \frac{\alpha + W \gamma}{2\Theta} \right),
\]

(9)

where \( \Lambda = \lambda/zt, \Theta = k_\text{B} T/zt, \) and \( \alpha = \mu/zt (B = zt) \).

We have solved the mean field equations for a semi-elliptic density of states. Several features of the solution are noteworthy. Again as expected there is a Curie transition at \( \Theta_c(\delta) \). In the absence of an external magnetic field, the magnetization \( M \) is equal to the condensate fraction \( \rho \) and vanishes for \( \Theta > \Theta_c(\delta) \). Second, the quantity \( W \), which is directly proportional to the fermion bandwidth, is unremarkable through \( T_c \). It decreases monotonically and eventually vanishes at a temperature \( \Theta_c(\delta) = (1 + S^{-1})^{1/2} / \sqrt{T - 3\delta^2/2\sqrt{2}} \). The dimensionless electronic kinetic energy \( K \), which is proportional to the boson bandwidth, also vanishes at this point. The vanishing of \( K \) and \( W \) at \( \Theta \) is likely a spurious artifact of the mean field theory; it was noted in [17,18]. However, in a range \( \Theta_c < \Theta < \Theta_c \) above the Curie transition this theory describes a state with vanishing magnetization yet finite and \( \Theta \)-dependent fermion bandwidth. The mean field parameters are shown versus \( \Theta \) in Fig. 3.

Third, we find that \( \kappa^{-1}(\Theta) \) has a discontinuity in slope at \( \Theta_c \) and a jump discontinuity at \( \Theta_a \). The locus of points where \( \kappa^{-1}(\delta, \Theta) = 0 \) marks the boundary of the region of phase separation. This is shown in Fig. 3(b). Again corroborating our initial discussion, we find that phase separation occurs for \( |\delta| > \delta_0 \approx 0.289 \), and for a range of temperatures \( \Theta \in [\Theta_a(\delta), \Theta_c(\delta)] \) surrounding \( \Theta_c \). The upper boundary is \( \Theta_c(\delta) \) itself; this is likely an artifact of the mean field theory. We expect that \( W \) should continue to decrease as \( \Theta \) increases, tending to a finite asymptotic value that this mean field approach cannot describe. At any rate, for large \( \Theta \) the third of the mean field equations gives \( \alpha \approx \Theta \ln[(1+2\delta)/(1-2\delta)] \) and \( \kappa^{-1} \approx 4\Theta/(1-4\delta^2) \). Thus, \( \kappa > 0 \) for sufficiently large \( \Theta \) and there is a finite area of phase separation.

The thermopower \( S \) is anomalous, owing to the dependence of bandwidth on temperature through \( W(\Theta) \). It peaks at \( \Theta_c \) with a \( \delta \)-dependent value \( S_{\text{max}}(\delta) \) which is enormous by standards of metal physics (the dimensions of \( \partial n / \partial T \) in Fig. 3 are restored by multiplying \( \partial n / \partial T \) by \( k_\text{B}/e = 86.2 \text{mV/K} \). The order of magnitude of \( S \) and the existence of a peak near \( T_c \) agree with experiments [21]. The sign of \( S \) is opposite to that predicted by a rigid band model (for either carrier type). At temperatures well above \( \Theta_c \), the temperature dependence of the bandwidth vanishes, and the usual sign is restored. Finally, at very low temperatures the thermopower also changes sign – the \( T^{5/2} \) dependence of \( 1 - W \) is eventually overwhelmed by the \( T^2 \) dependence of \( \mu \) coming from the Sommerfeld expansion. Within our model this happens at a very low value of \( T \) (e.g. \( T/B = 1.5 \times 10^{-5} \) for \( \delta = 0.2 \)).

We have ignored so far all interactions except the double exchange mechanism. Electrostatic effects will inhibit the full phase separation described here. The standard RPA result \( \chi^{-1}(q) = X_0^{-1}(q) - V(q) \), where \( X_0(q) \) is the bare charge susceptibility and \( V(q) = 4\pi e^2/q^2 \), predicts an instability at finite wavevector \( q \), whenever \( \lim_{q \to 0} X_0(q) = -\nu^{-1}(q) \).
FIG. 2. Solution to the model (8,9) using an elliptical density of states and $S = \frac{3}{2}$ at $\delta = 0.33$. The bottom panel shows thermopower (dashed; units of $k_B$) and inverse compressibility (solid), which is negative over a band of temperatures.

With volume, with

$$q_* = \sqrt{-\frac{4\pi e^2}{\mathcal{V}} \frac{\partial x}{\partial \mu}}.$$  \hspace{1cm} (10)

At low dopings, $q_*^2 \sim x$, while at higher fillings, $q_*$ is proportional to the Thomas-Fermi wavevector $q_{TF}$. Thus, we expect that electrostatic effects will give rise to a domain structure, at a length scale of order $q_*^{-1}$.

In the CMR manganites, the $e_g$ orbitals are doubly degenerate in the absence of JT distortions. While we expect intraatomic Coulomb effects to preclude multiple occupancy of the $e_g$ levels, orbital ordering could significantly alter the picture discussed here (for example, the sign of the thermopower could reverse). We have also ignored interactions with the lattice. Our results suggest that the tendency towards phase separation gives rise to domains with a very low concentration of holes. In these domains, JT deformations will be favored. In general, the enhancement of charge fluctuations near $T_c$ should induce significant lattice deformations, because of the different sizes of the Mn$^{3+}$ and Mn$^{4+}$ ions. A structure with domains of different electronic density and bandwidth enhances the tendency towards localization. Standard models for the influence of critical spin fluctuations are not applicable if, in addition, there are strong charge fluctuations. A domain with extra charge and stronger ferromagnetic order is akin to the spin polarons proposed in the literature. In our case, however, such a structure arises from magnetic effects alone.

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