Small Magnetic Polaron Picture of Colossal Magnetoresistance in Manganites

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We present a small-but-sizeable magnetic polaron picture where transport at high temperatures is activated while at low temperatures it is band-like. We show that both double exchange and finite bandwidth effects are important to understand colossal magnetoresistance as well as the coincidence of the metal-insulator and the ferromagnetic transitions in manganites. The magnetic transition is explained using band-like motion of the polarons.

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Studies on perovskite manganites of the form $A_{1-x}B_{x}MnO_3$ (A=La, Pr, Nd, etc.; B=Sr, Ca, Ba, etc.) have yielded a variety of rich phenomena as a function of doping $\delta \sim 0.2$. We use the polaron model of Eagles [8] to explain colossal magnetoresistance (CMR). Our starting total Hamiltonian is given by

$$H_T = H(t) + H_{sp} + H_{ph}$$

where

$$H(t) = t \sum_{\langle i,j \rangle,\sigma} c_{i,\sigma}^\dagger c_{j,\sigma},$$

$$H_{ph} = \sum_{q} \sum_{\sigma} \omega_q a_q^\dagger a_q + \sum_{j,\sigma} n_j^\sigma e^{i\vec{q}\cdot\vec{R}_j} M_\sigma (a_q + a_q^\dagger),$$

and

$$H_{sp} = \sum_{\langle ij \rangle} J_{ij} \vec{S}_i \cdot \vec{S}_j + K_H \sum_{\sigma} \vec{S}_i \cdot \vec{S}_i + U \sum_{j,\sigma} n_j^\sigma n_j^{-\sigma}.$$
In the above equations $c_{j\sigma}(aq)$ is the hole (phonon) destruction operator, $t$ is the hopping integral, $(ij)$ corresponds to nearest neighbors, $\omega_q$ is the optical phonon frequency ($\hbar = 1$), $M_q$ is the hole-phonon coupling, $J_{ij}$ is the strength of the spin coupling between neighboring localized ($S=3/2$) spins, $K_H$ gives the Hund's coupling between localized spins and itinerate hole ($\sigma = 1/2$) spin, $U$ is the strength of the same site repulsion, and $\omega_\sigma = c_{j\sigma}c_{i\sigma}$. Furthermore the $H_{ph}$ part corresponds to assuming a single orbital per site which on account of Jahn-Teller splitting may perhaps be justified.

To study transport we use double exchange modification and take the total Hamiltonian to be

$$H''_T = t_{DE} \sum_{(ij)} c_i^\dagger c_j + \sum_q \omega_q a_q^\dagger a_q + \sum_{j \neq j'} c_j^\dagger c_{j'} e^{iq\vec{R}_j} M_q(a_q + a_{-q}^\dagger),$$

where $t_{DE} = t\sqrt{(1 + M^2/M_S^2)/2}$, and $M_S$ is the saturated magnetization. Now the mobility is given by the Einstein relation $\mu = q_eD\beta$ where $q_e$ is the electronic charge, $D$ the diffusivity, and $\beta = 1/k_BT$. Including finite band width corrections, as done variationally by Gosar [9], to calculate the hopping-regime diffusivity $\kappa$ gives the finite band width corrections, as done variationally where

$$\theta = \frac{\omega_\sigma}{\omega_0}$$

for band conduction, it is obtained by extending Gosar’s work [9] and calculating the polaronic band energy [12].

The above expression is similar to the result due to Eagles [8]. Then the diffusivity for band conduction is given by

$$D_{band} = (|\vec{\nabla}E_k|^2/\tau) = 6\pi a_0^2 t^2 \left[1 + (M/M_S)^2 \right],$$

where $\tau = t \exp[-\theta \coth(\beta\omega_\sigma/2)]$. Then based on Friedman’s work [8] we take the total mobility ($\mu_T$) to be the sum of the band mobility and the hopping mobility and hence the total resistivity ($1/\rho = c_h q_e \mu_T$) to be given by

$$\frac{4\pi}{c_h q_e^2 a_0^2 \rho} = \beta \omega_0 \left[8\pi^2 t^2 \exp[-2\theta \coth(\beta \omega_\sigma/2)] + \left(1 + \frac{M^2}{M_S^2} \right) \exp[-2\theta \tan(\beta \omega_\sigma/4)] \right],$$

where $c_h$ is the density of holes. Here it should be mentioned that, even if $t$ and $K_H$ are of the same order of magnitude, we can have $\tilde{t} << K_H$ so that double exchange holds.

To proceed further one needs to obtain the magnetization as a function of temperature. To this end we consider the following thermally averaged Hamiltonian

$$H_{mag} = H(t) + H_{sp}.$$

Next we note that $|J_{ij}| << K_H$ and that $U >> t (k_BT)$ and hence completely project out double occupation (see Ref. [14] for details). From the above Hamiltonian $H_{mag}$ it follows that, within a mean-field treatment, the magnetization in the presence of a magnetic field $H$ is

$$S \frac{M}{M_S} = \frac{\sum \varepsilon_{\sigma} - \sum \varepsilon_{\sigma} H_S \beta_{\sigma}}{\sum \varepsilon_{\sigma} - \sum \varepsilon_{\sigma} H_S \beta_{\sigma}},$$

where $\Phi \equiv K_H \left( n^\dagger f(n^\dagger) - n^\dagger f(n^\dagger) \right)$, $f(n^\dagger) \equiv 1/(1 - n^\dagger)$, and $n^\dagger$ is the probability of occupation of a site by spin $\sigma$ hole and is given by

$$n^\dagger = \frac{1}{N} \sum_k n^\dagger_k \left[ \epsilon_k \Psi - \Psi \sigma - \mu \right] \approx \frac{1}{\exp[-\beta (\Psi \sigma + \mu)] + 1},$$

where $\Psi \equiv (K_HS/M_S + g\mu_B H)f(n^\dagger), \sigma = 1/2/(-1/2)$ for spin $\alpha = \uparrow/\downarrow$ holes and

$$\epsilon_k^\dagger = 2\hbar \delta f(n^\dagger) \sum l \cos(k^\dagger a) \ll k_BT_C.$$

In the above equation $\hbar(\delta) = 1 - \delta$ and $T_C$ is the ferromagnetic transition temperature whose value, by treating $M$ and $\Delta n \equiv n^\dagger - n^\dagger$ as small parameters in Eq. (2), is obtained to be

$$k_B T_C = \sqrt{2(1-\delta)^2 \frac{(9/2)^2}{K_H S |\sigma|}.}$$

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$$\epsilon_k^\dagger = 2\hbar \delta f(n^\dagger) \sum l \cos(k^\dagger a) \ll k_BT_C.$$
We see that $T_C$ increases with increasing $\delta$ for $0 < \delta < 2/3$ and that it is independent of both $t$ and $J_{ij}$. Furthermore because of Eq. (13), the values of $M$, $n^c$, and $T_C$ are all independent of dimensions [see Eq. (12)]. Here it must also be mentioned that when double occupancy is allowed $h(\delta) = f(n^{(t)}) = 1$.

Using the constraint that $n \uparrow + n \downarrow = \delta$, we can obtain $\Delta n$ and $M$ by solving Eq. (13). In Fig. 2 we have plotted the magnetization ratio $M/M_S$ as a function of the reduced temperature $T/T_C$ for $\delta = 0.3$ and $0.4$, $g = 2$, and magnetic fields $H = 0T$ and $15T$. We have assumed a smaller value for the Hund’s coupling ($K_H \approx 0.0858\text{eV}$) than what seems to be its value based on experiments ($\sim 1\text{eV}$) because we wanted to set $T_C = 300K$ at $\delta = 0.3$. Alternately one can also get lower $T_C$ by assuming, as suggested in Ref. [15], that only a small fraction of the dopants yield mobile holes. The values of the magnetization for $H = 15T$ at $T_C$ are sizeable because of the tendency of the system towards a ferromagnetic phase. Here it should also be mentioned that $\Delta n$ attains saturation values much faster than $M$. We have also calculated the magnetization curves with double occupation of a site being allowed and find that the $M/M_S$ values for with and without double occupation being allowed are close to each other both in zero field and at $15T$ [15]. Although our magnetization curves are qualitatively similar to the experimental curves of Urushibara et al. [10], the experimental $M/M_S$ values rise faster as $T$ lowered.

We will now discuss the resistivity given by Eq. (10). The conduction goes from a hopping type at high temperatures to a band type at low temperatures. In Fig. 2 we have shown the dependence of resistivity $\rho$ on temperature at various magnetic fields. The general trend of the resistivity including the drop at the MI transition at $H = 0T$ is similar to the experimental results [10]. On introducing a magnetic field the system gets magnetized at temperatures higher than $T_C$ and thus the value of $\theta$ is smaller (see Eq. (10)). Consequently the resistivity is smaller and $T_{\rho\text{max}}$ (the temperature at which resistivity becomes maximum) increases [14].

For $T \geq T_C$, when $D_{\text{band}}/D_{\text{hop}} >> 1$ the magnetoresistance $\Delta \rho/\rho(0) \equiv (\rho(H) - \rho(0))/\rho(0)$ is given by (see Eq. (10))

$$\Delta \rho/\rho(0) \approx \exp \left[-\frac{(z+1)^2 M^2}{2\gamma^2 \omega_0^2} \text{csch}\left(\frac{\beta \omega_0}{2}\right)\right] - 1,$$

and when $D_{\text{band}}/D_{\text{hop}} << 1$ it is given by

$$\Delta \rho/\rho(0) \approx \exp \left[-\frac{(z+1)^2 M^2}{2\gamma^2 \omega_0^2} \tanh\left(\frac{\beta \omega_0}{2}\right)\right] - 1.$$  

For a fixed value of the reduced temperature $T/T_C$, an increase in the ratio $\mu_BH/K_H$ increases $M/M_S$ and consequently the magnetoresistance also increases.

Actually $T_{\rho\text{max}}$ (the temperature at which the resistivity given by Eq. (10), after taking $M = 0$, attains a maximum) need not be equal to the ferromagnetic transition temperature $T_C$. If $T_{\rho\text{max}} < T_C$, by decreasing $\gamma^2$ or increasing $\frac{\omega}{\omega_0}$ activation energy $(\theta \omega_0)/2$ decreases and $T_{\rho\text{max}}$ can be increased [11] to be made equal to $T_C$ and this also increases the magnetoresistance (see Eqs. (11), (13), and (14)). For $T_{\rho\text{max}} < T_C$, the MI transition can still occur at $T_C$ if $(\frac{z+1)^2}{2\gamma^2 \omega_0^2}$ is sufficiently large [14] while if $(\frac{z+1)^2}{2\gamma^2 \omega_0^2}$ is very small the MI transition occurs below $T_{\rho\text{max}}$ as can be seen from Eq. (10). The other case, where $T_{\rho\text{max}} > T_C$, corresponds to MI transition occurring at a higher temperature than $T_C$ and is in any case not experimentally observed [17].

In Table 1 we report the calculated values of magnetoresistance $-\Delta \rho/\rho(0)$ at $T_C$ and the optimum values of $\gamma^2$ (obtained when $T_{\rho\text{max}} = T_C$) for doping $\delta$ equal to 0.3 and 0.4, Debye temperature $T_D = 500K$, and for various values of the dimensionless hopping integral $t/\omega_0$. We find that the magnetoresistance increases with increasing values of $t/\omega_0$ thus showing the importance of bandwidth. Also $\gamma_{\text{opt}}^2$ values increase with increasing $t/\omega_0$ because $T_{\rho\text{max}} = T_C$. Furthermore, it is mainly due to the larger values of $(M/M_S)^2$ for $\delta = 0.4$ compared to those of $\delta = 0.3$ that the values of $-\Delta \rho/\rho(0)$ are larger for $\delta = 0.4$. It appears that our model can give magnetoresistance values comparable to the experimental ones [10]. In fact one can get a larger magnetoresistance by taking a smaller $T_C$ value but keeping $\omega_0/(K_BT_C)$ fixed [14].

From Eq. (10) (or Eqs. (13) and (16)) we see that for small values of $M/M_S$ the magnetoresistance (for $T \geq T_C$) is of the form $-\Delta \rho/\rho(0) = C(M/M_S)^2$ where $C$ is a constant of proportionality. We found, for the cases considered in Table 1, that the optimum values of $\gamma^2$ that make $T_{\rho\text{max}} = T_C$ are such that $D_{\text{band}}/D_{\text{hop}} < 1$ so that the magnetoresistance can be qualitatively given by Eq. (11). In Eq. (11), close to $T_C$, $\tanh(\beta \omega_0/4) \approx \omega_0/4$. From Eq. (14) we see that $T_C$ increases with the doping $\delta$ and hence the constant of proportionality $C \propto \sqrt{(1-\delta)}$ decreases with increasing $\delta$ which agrees with the findings of Ref. [17]. Furthermore the coefficient also increases with increasing values of $(\frac{z+1)^2}{2\gamma^2 \omega_0^2}$. We have calculated values of $C$ by treating $M/M_S$ as a small parameter in the exact expression for $-\Delta \rho/\rho(0)$ at $T = T_C$. When $t/\omega_0 = 4(8)$ and $\gamma^2 = 9.5(15.0)$, for $\delta = 0.3$ we get $C \approx 3.8(8.5)$ while for $\delta = 0.4$ we obtain $C \approx 3.1(6.4)$. Our calculated values of $C$ are larger than those reported in Ref. [14]. Past attention [17,18] has focused at dependence of $C$ on the ratio $K_H/t$ in Kondo lattice type models that ignored electron-phonon coupling. While Inoue and Maekawa [17] for $K_H \rightarrow \infty$ obtained $C = 7/4$, Furukawa [18] found that the value of $C$ increased with
increasing values of $K_H/t$ and that at larger values of $K_H/t$ the value of $C$ decreases with increasing doping.

In conclusion we say that both double exchange and finite band-width corrections are important to understand CMR. In our picture, adiabatic small-but-sizeable magnetic polarons are involved in activated transport at high temperatures and metal-like conduction at low temperatures. At the MI transition, the band-like motion of the carriers also produces a paramagnetic-ferromagnetic transition due to strong Hund’s coupling between itinerant and localized spins. Studying the transport behavior at low temperatures, including a Fermi liquid analysis, is left for future. The effect of including both $d_{xz}$, $d_{yz}$ and $d_{x^2−y^2}$ orbitals also needs to be investigated for our model. Lastly we note that as the system’s temperature is lowered below $T_C$ the magnetization increases and consequently the activation energy $(θω_0/2)$ decreases and the polarons tend towards large polaronic behavior.

FIG. 1. Plot of the magnetization ratio $M/M_S$ versus the reduced temperature $T/T_C$ when no double occupation is allowed, doping $δ = 0.3$ (and 0.4), Hund’s coupling $K_H ≈ 0.0858eV$, and magnetic fields $H = 0T$ and $H = 15T$.

FIG. 2. Plot of the resistivity $ρ$ in units of $4π/(c_0q_0^2a^2)$ versus temperature $T$ in 3 dimensions when no double occupation is allowed, $δ = 0.3$, $K_H ≈ 0.0858eV$, dimensionless hopping integral $t/ω_0 = 6$, optimum $γ^2 = 12.2$, Debye temperature $T_D = 500K$, and for the following magnetic fields: (i) $H = 0T$; (ii) $H = 15T$; (iii) $H = 30T$; and (iv) $H = 45T$.

TABLE I. Calculated values of the magnetoresistance $−Δρ/ρ(0)$ at $T_C$ and the optimum $γ^2$ for various values of $t/ω_0$, $T_D = 500K$, $δ = 0.3$ and 0.4, magnetic field $H = 15T$, $K_H ≈ 0.0858eV$, and $T_{ρ_{max}}/T_C = 0.8$.

| $t/ω_0$ | $γ^2_{opt}$ | $ρ/ρ(0)$ | $γ^2_{opt}$ | $ρ/ρ(0)$ |
|---------|-------------|-----------|-------------|-----------|
| 4       | 9.5         | 35%       | 8.4         | 42%       |
| 5       | 10.8        | 44%       | 9.8         | 50%       |
| 6       | 12.2        | 51%       | 11.2        | 58%       |
| 7       | 13.6        | 58%       | 12.5        | 68%       |
| 8       | 15.0        | 64%       | 13.9        | 74%       |

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