Magnetoresistance in Mn Pyrochlore: Electrical Transport in a Low Carrier Density Ferromagnet

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We discuss magnetotransport in a low density electron gas coupled to spin fluctuations near and above a ferromagnetic transition. Provided the density is low enough [$n \lesssim 1/\xi^3(T)$, with $\xi(T)$ the ferromagnetic correlation length], spin polarons form in an intermediate temperature regime above T_c. Both in the spin polaron regime and in the itinerant regime nearer T_c, the magnetoresistance is large. We propose that this provides a good model for "colossal" magnetoresistance in the pyrochlore $Tl_{2-x}Sc_xMn_2O_7$, fundamentally different from the mechanism in the perovskite manganites such as $La_{1-x}Sr_xMnO_3$. [S0031-9007(98)06808-2]

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In recent years "colossal magnetoresistance" (CMR), particularly in the perovskite manganite $La_{1-x}Sr_xMnO_3$ and its variants, has emerged as a rich and extremely active area of experimental study [1,2]. The phenomena of magnetic transition and the simultaneous insulator-metal transition, as the temperature is lowered, is qualitatively understood as arising out of a combination of Mn^{3+}-Mn^{4+} double exchange and transport via Jahn-Teller polarons [3,4]. The magnetic exchange arises from electron hopping, itself dependent on the spin order, while Jahn-Teller distortions and the atomic size mismatch between Mn^{3+} and Mn^{4+} trap electrons in small polaronic states. The magnetic transition involves the cooperative effect of both the charge and spin degrees of freedom; spin ordering promotes electron hopping, increases the effective exchange, anneals out the lattice distortions, and, in a bootstrap effect, leads to the magnetic and insulator-metal transition.

The pyrochlore $Tl_2Mn_2O_7$ offers a surprising contrast, and demonstrates that neither double-exchange nor lattice polarons are *essential* for obtaining CMR. From recent experiments [5–8] the following picture has emerged. As in the perovskites, the large MR accompanies a paramagnet to ferromagnet transition, with T_c around 140 K. However, the carrier density estimated from the Hall effect is low [5] ($\sim$0.001–0.005 per formula unit, f.u.), and the ferromagnetic transition is driven by superexchange between the Mn sites, close to their nominal valence of Mn^{4+} [7]. The thermopower [8] in $Tl_2Mn_2O_7$ is almost 2 orders of magnitude larger than in good metals, attesting to a low Fermi energy. Electrical transport is provided by carriers on the Tl sites, in the tail of a broad Tl-O hybridized band that may overlap the topmost Mn d band [9]. *There is thus neither double exchange inducing the magnetism nor a driving mechanism for lattice polarons or Jahn-Teller distortions.*

Nevertheless, the MR is very large above T_c even though the resistance is "metallic" ($d\rho/dT > 0$) in the paramagnetic phase for $T \gtrsim 1.5T_c$. In terms of the rough scaling relation $[\rho(0) - \rho(H)]/\rho(0) \approx C(m/m_s)^2$ above T_c (m and m_s are the magnetization and saturation magnetization, respectively), the coefficient $C \approx 15$ is even larger than observed [10] in the metallic perovskite manganites. With substitution by In [6] or Sc [8] on the Tl site, the magnetic properties are weakly affected, while the transport is dramatically modified. The resistivity increases by orders of magnitude [8] and becomes activated in the paramagnetic phase, and the MR increases further.

This paper argues that the data provoke a simple model of a low density electron gas interacting with a spin background that orders ferromagnetically, *independently* from the conduction electrons. Although the density is low enough that the average magnetic properties (e.g., T_c) are hardly affected by the carriers, at low enough density, and sufficiently large electron-core spin coupling, carriers will self-trap into well defined, nonoverlapping, magnetic polarons. The core size of the magnetic polaron increases with decreasing temperature remaining finite at T_c, but the "interface" width, over which the local magnetization decays, is the magnetic correlation length, $\xi(T)$, which diverges as $T \to T_c$. When the density $n \approx \xi^{-3}$ (see Fig. 1), the polarons overlap and the carriers delocalize. In both the itinerant and the self-trapped regime we find the MR to be large.

To be specific, we consider the Hamiltonian

$$\hat{H} = \sum_{\vec{k},\sigma}(\epsilon_{\vec{k}} - \mu)c^{\dagger}_{\vec{k},\sigma}c_{\vec{k},\sigma} - J'\sum_i \vec{\sigma}_i \cdot \vec{S}_i - J\sum_{\langle i,j\rangle}\vec{S}_i \cdot \vec{S}_j - \sum_i \vec{h}\cdot\vec{S}_i\,. \tag{1}$$

Here S_i refer to the localized Mn core spin ($S = 3/2$), and J sets the scale for T_c (mean field $T_c \sim zJS^2$, and z is the Mn coordination). c, $c^{\dagger}$ refer to carriers in the Tl-O band [11], and $\vec{\sigma}_i = c^{\dagger}_{i,\alpha}\vec{\sigma}_{\alpha,\beta}c_{i,\beta}$ is the conduction electron spin operator. J' is the effective exchange coupling between a Mn spin and the conduction electron, and h is the external field.

For the Mn pyrochlores, we expect that $t \sim \mathcal{O}(0.1)$ eV [9], and J'/t may be of order unity [12]. The transition temperature $T_c \sim 140$ K. The carrier density in the nominally undoped compound is $\sim 10^{-2}$–10^{-3} f.u.$^{-1}$, while in

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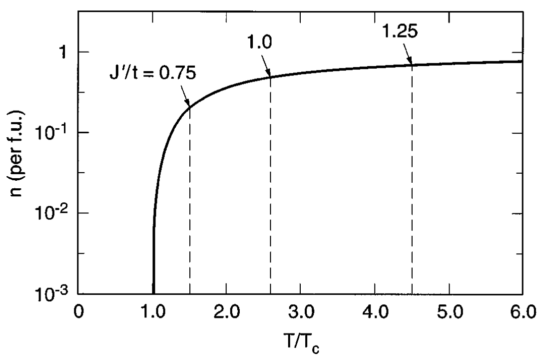

FIG. 1. Projection of the three dimensional density-temperature-J' space, at $t/T_c = 10$, indicating roughly the "critical scattering" and polaronic regimes. The solid line indicates polaron overlap, which we have taken to be $\xi \sim 1/n^{1/3}$. The regime above the solid line, with $\xi > n^{-1/3}$, should be described by scattering theory since single polarons are ill defined. In the regime below, isolated polarons can describe transport, up to a temperature $T_p(J')$ beyond which it becomes entropically unfavorable to bind the electron.

the Sc doped systems [8] the combined effect of disorder and lowered carrier density can be inferred from $\rho(T)$ as $T \rightarrow 0$.

Since our principal goal is to understand transport properties, and our assumption is that the spin correlations are *on average* unaffected by the carriers, we shall take the spin correlations to be given by the ferromagnetic Heisenberg model. In practice we shall use mean-field theory and Ginzburg-Landau (GL) or Ornstein-Zernicke (OZ) approximations for the correlation functions, since we are not concerned with details in the vicinity of T_c. We need to consider transport in the two regimes of Fig. 1, and begin with the itinerant regime.

Fluctuations near any critical point usually lead to large scattering, but the dominant $q \rightarrow 0$ fluctuations near a ferromagnetic transition usually have a negligible effect on transport because it is primarily modes near $q \sim 2k_F$ which are effective in backscattering. The obvious and interesting exception is a low electron density system, $k_F a \ll 1$ (a is the lattice constant), where the growth of magnetic fluctuations can be directly reflected in the resistivity. The standard theory for the "spin disorder" contribution to resistivity near a ferromagnetic transition was given by de Gennes and Friedel [13], subsequently criticized and modified by Fisher and Langer [14]. This Born scattering result for the transport relaxation rate τ^{-1}, normalized to its high temperature value $\tau_0^{-1} \sim (J'^2/t)S(S+1)k_F a$, is given by

$$\tau^{-1}/\tau_0^{-1} \sim \int_0^{\pi} \sigma(\theta)\,(1 - \cos\,\theta)\ \sin\,\theta\, d\theta\,,$$

where $\sigma(\theta)$ is the differential scattering cross section per magnetic spin, and θ is the scattering angle. The cross section, in turn, is given by

$$\sigma(\theta) \equiv \sigma(q = 2k_F\ \sin(\theta/2)) \sim \chi(q)\,,$$

where $\chi(q)$ is the static structure factor. Within the OZ approximation $\chi(q) \sim \xi^2/(1 + q^2\xi^2)$, where ξ is the magnetic correlation length. The form for τ^{-1} is easy to evaluate using $\chi(q)$ above but a fair amount of insight can be gained by simply using $\tau^{-1} \sim \chi(q \sim 2k_F)$. This is featureless for $k_F a \sim \mathcal{O}(1)$, but picks up significant temperature dependence for $k_F a \ll 1$, with $\tau^{-1}/\tau_0^{-1} \sim [k_F^2 a^2 + T/(T - T_c)]^{-1}$.

The complete answer for the scattering rate, within the OZ approximation, is

$$\tau^{-1}/\tau_0^{-1} \sim \frac{1}{k_F^2 a^2}\left[4 - \frac{1}{k_F^2\xi^2}\ \log(1 + 4k_F^2\xi^2)\right]. \quad (2)$$

This result should be modified close to T_c, where non-mean-field effects are important, and also when $\xi(T) \gtrsim l(T)$, the mean-free path [14]. These effects remove the cusplike T dependence at T_c, but the important density dependence remains unchanged. Notice that since $\chi(0) \sim \xi^2$ within the OZ theory, Eq. (2) implies a direct relation between the scattering rate and the susceptibility. For $k_F\xi(T) \ll 1$ it is easy to see that $\tau^{-1} \sim \xi^2 \sim \chi$ over a wide temperature range emphasizing that $d\rho/dT < 0$ is possible in the paramagnetic *metallic* state.

We calculate the magnetoresistance arising from the field suppression of magnetic fluctuations, i.e., the reduction in correlation length; $\xi^2 \Rightarrow \xi^2(m,T)$ which, within the GL theory, can be shown to be $\sim \partial m/\partial h|_m$, where $m(h,T)$ is the magnetization due to an applied field. We may calculate the MR from the equation above but to make the qualitative point, $\delta\rho/\rho(0) \sim [\tau^{-1}(m,T) - \tau^{-1}(0,T)]/\tau^{-1}(0,T)$ which is approximately $[\chi(2k_F,m,T) - \chi(2k_F,0,T)]/\chi(2k_F,0,T)$. Using the finite field version of $\chi(q)$ from GL, one can easily show that $C \sim 1/k_F^2 a^2$ for $k_F\xi \gg 1$ [15]. C involves a numerical constant ~ 1, and temperature dependence arising out of $\xi(T)$, but we want to emphasize only the density dependence. Obviously lower densities can greatly enhance C consistent with the observations in [5], *without involving an insulator-metal transition.* This perturbative framework, however, cannot be continued to arbitrarily low density or to $J'/t \gtrsim 1$ where, if the spin background were treated as "quenched disorder," one would expect electron localization [16]. However, for $J'/t \gtrsim 1$, and low carrier density, the electrons actually self-trap into magnetic polarons, as we discuss next.

The issue of magnetic polarons was raised long ago [17], but apart from certain limiting cases studied by Kasuya *et al.* [18] we know of no systematic calculation [19] on the size and energy of the bound state. Our calculation consists of the following: (i) a variational ansatz for the electron wave function $\psi(r)$ (with spin $\uparrow$, say); (ii) calculation of the polarization and free energy of the spin background due to the effective "field" $J'\langle\sigma_z(r)\rangle$; and (iii) minimization of the total free energy; electron kinetic energy + magnetic free energy, with respect to the variational parameter. While our numerical results are shown for $S = 1/2$, for simplicity, we provide an analysis which generalizes the answers to arbitrary S.

The simplest ansatz is that of an electron isotropically delocalized over a region of radius L_p (measured in terms of a), involving $\sim L_p^3$ sites. This leads to a field $h_p \sim J'/L_p^3$ acting on the spins, which lead to polarization and gain in magnetic free energy. The magnetization of the polarized region can be estimated from mean-field theory, $m = \tanh \beta(T_c m + h_p)$ and the mean-field magnetic free energy is

$$\Delta F_m \sim L_p^3\{\tfrac{1}{2}T_c m^2 - T \ \ln[\cosh \ \beta(T_c m + h_p)]\}.$$

The total free energy $\Delta F = \Delta F_m + t/L_p^2$ is minimized with respect to L_p. Temperature dependence enters through the magnetization equation, which encodes the diverging susceptibility, while external fields add to the polaronic field and require a straightforward generalization. Our result for the binding energy, $\Delta_p = \min[\Delta F(L_p)]$, as a function of temperature and external field is shown in Fig. 2.

Postponing a complete discussion of the polaron calculation to a separate communication [20] we remark on the essential results here. (a) As in [18] we find that for a given set of parameters $\{t, J', T_c\}$, the spin polaron becomes favored only *below a certain temperature,* T_p, say. Assuming a saturated core this is approximately given by $T_p \ \ln(2S + 1)/t \sim (zJS^2/t) + (J'S/t)^{5/2}$. Thus the "window" above T_c where the polaron exists increases with J'/t. Figure 1 indicates the variation in T_p with J'/t, deduced from the numerics, roughly consistent with the above result. At high temperature, the polaron is confined to a few sites, and the local magnetization is saturated. In fact, for $J'/t \gtrsim 1$, $m \gtrsim 0.9$ down to T_c. (b) With reducing temperature both the polaron size $\bar{L}_p$ and Δ_p increase. Since the numerical minimization reveals that $m \simeq 1$, a simple analysis is possible. Close to saturation the magnetization equation yields $m \sim 1 - 2e^{-2\beta(T_c + h_p)}$. Using this, to leading order, the free energy function $\Delta F \sim L_p^3(T \ \ln 2 - T_c/2) - J' + t/L_p^2$ where the terms can be readily interpreted as the magnetic free energy of $\mathcal{O}(L_p^3)$ saturated spins, the $\mathcal{O}(1)$ exchange energy J' of the electron, and the kinetic energy. Minimizing this yields $\bar{L}_p^5 \sim (2t/3)/(T \ \ln 2 - T_c/2)$. The "formation" temperature is given by $\Delta F[\bar{L}_p(T_p)] = 0$ and the binding energy $\Delta_p/t \sim \frac{5}{3}[\frac{3}{2t}(T \ln 2 - T_c/2)]^{2/5} - J'/t$. This almost completely describes the numerically obtained zero field curve in Fig. 2. (c) In the presence of an external field the binding energy is the *difference* between the energy of the polaron and that of the delocalized electron in the applied field. This is principally $\sim J'(m - m_{\rm ext})$, where m and $m_{\rm ext}$ are, respectively, the core magnetization and the external magnetization, which diminishes as the field magnetizes the spin background. For fields large enough to "saturate" the spin background the magnetic energy of the carrier is $-J'$ irrespective of whether it is in a localized or extended state, and the energy gain $\Delta_p \rightarrow 0$. Conversely, for $T \rightarrow T_c$, when the susceptibility is largest, the reduction in binding energy is most pronounced (Fig. 2).

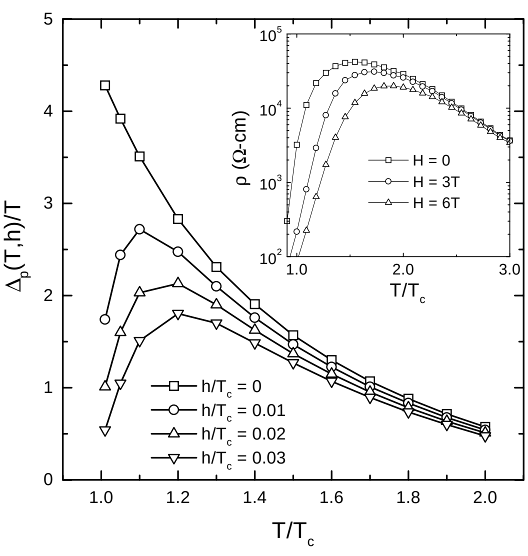

FIG. 2. Binding energy Δ_p/T for $t/T_c = 10$, $J'/t = 1$, and varying h/T_c. Inset: log ρ for Sc doped sample, $x = 0.3$, replotted from [8].

In the regime, $J'/t \sim \mathcal{O}(1)$, that we are interested in, the above analysis readily generalizes to arbitrary S, and we have $\Delta_p/t \sim \frac{5}{3}[\frac{3}{2t}(T \ \ln(2S + 1) - T_c/2)]^{2/5} - J'S/t$. So, for a system with $S > 1/2$, e.g., the pyrochlores, the result in Fig. 2 needs only to be scaled by appropriate factors of S.

There is no accepted single theory of transport via spin polarons. For a "small" spin polaron, the principal mode of conduction would be polaron "hopping" over a barrier or "ionization" of the trapped carrier. Since both these processes are activated, with energies $\sim\Delta_p$, one expects $\ln \ \rho \sim \Delta_p/T$ (see Fig. 2). The large MR follows from the magnetic field dependence of Δ_p. Using our results for $\Delta_p(T, h)$ we estimate the MR that can arise from an activated transport process in Fig. 3.

We now discuss the regime of validity of the results. (a) The boundary between the polarized and unpolarized regions is not sharp, in fact, scaling as $\xi(T)$ which diverges as $T \rightarrow T_c$. A description in terms of isolated polarons will break down when $n\xi^3 \approx 1$, which for the parameters used here is in the range $T/T_c \lesssim 1.05-1.1$. In that regime transport would be described by itinerant scattering, also leading to large MR (see Fig. 3). (b) The calculation of the bound state wave function and the magnetic polarization should be self-consistent, and a sharp boundary leads to an overestimate of the binding energy for $T \rightarrow T_c, \xi \gg \bar{L}_p$. This regime, where the electron "delocalizes" over a length scale $\sim\mathcal{O}(\xi)$, is important for $T/T_c \lesssim 1.05$.

A quantitative comparison of our results with the data on $Tl_{2-x}Sc_xMn_2O_7$ is difficult because the carrier concentration is not accurately known and disorder is not controlled. There is substantial variation between the results of different groups on nominally the same material, even as to the sign of $d\rho/dT$. However, the end member in this series, $Sc_2Mn_2O_7$, is a ferromagnetic insulator

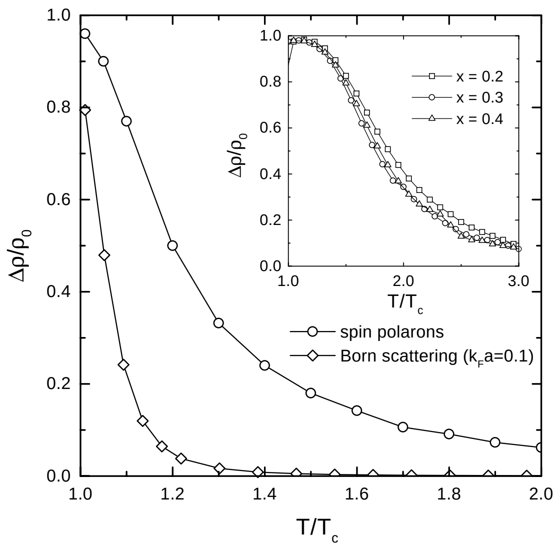

FIG. 3. MR for $h/T_c = 0.02$, from the two scenarios. The Born scattering result [Eq. (2)] corresponds to $n \sim (k_F a)^3 \sim 10^{-3}$. Inset: "universal" MR data in $Tl_{2-x}Sc_xMn_2O_7$ at 6 T for $x = 0.2, 0.3, 0.4$ (replotted from [8]).

so there is definitely a reduction in carrier density with increasing x. (a) The $T \rightarrow 0$ phase at $x = 0$ is metallic, albeit with rather large resistivity, while for $x \gtrsim 0.2$, $\rho(T)$ as $T \rightarrow 0$ shows an upturn, indicating the onset of Anderson localization, arising out of a combination of decreasing n and increasing disorder. The resistivity at this low-temperature metal insulator transition is compatible with the usual Ioffe-Regel criterion. (b) The resistivity in the paramagnetic phase at $x = 0$ shows $d\rho/dT$ weakly negative for $T \gtrsim T_c$. This, and the large MR coefficient [5], is consistent with magnetic scattering in a low density metal. (For $T > 1.5T_c$, $d\rho/dT > 0$ probably due to nonmagnetic sources of scattering.) (c) For $x \gtrsim 0.2$ the resistivity for $T > T_c$ is much too large to be described as a strongly scattered metal (one would have $k_F l \ll 1$). Furthermore $d\rho/dT < 0$ up to $T \sim 350$ K, and if fitted to an activated form the activation energy is on the order of 0.1 eV. Despite the very different absolute scales for the resistivity at $x = 0.2$, 0.3, and 0.4, the temperature dependence is almost identical as a normalized plot based on the data in [8] reveals. This is a regime we believe should be described by polaronic transport. To compare with the data we reproduce the measured $\rho(T)$ at $x = 0.3$ in the inset of Fig. 2. The measured magnetoresistance for $x = 0.2, 0.3$, and 0.4 are almost identical, and we reproduce this as an inset of Fig. 3 to compare with the "MR" derived within our polaron calculation. The correspondence between experimental and theoretical field scales is approximately 1 T $\equiv 0.01T_c$.

In conclusion, we have argued that a simple model scattering of carriers by ordering moments can yield large MR when the carrier density is low. At ultralow densities, the carriers will self-trap as magnetic polarons and $Tl_2Mn_2O_7$ appears to be close to this regime, especially upon Sc substitution. Direct evidence of spin polarons could be best sought with NMR and ESR measurements, as well as the appearance of an ionization gap in the optical conductivity.

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[12] We estimate that $J' \sim t_{sd}^2(\frac{1}{\Delta_{cf}-\epsilon_s-J_H} - \frac{1}{\Delta_{cf}-\epsilon_s+J_H})$ where t_{sd} is the effective hopping between the Mn e_g level and the Tl 6s, $\Delta_{cf} - \epsilon_s$ is their energy separation, and J_H the Hund's rule coupling of the e_g level to the core t_{2g} spin S. J' is a coupling between Tl and Mn sites, not "on site" as we have written, but that does not modify our conclusions.
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