Carrier Density Collapse and Colossal Magnetoresistance in Doped Manganites

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(Received 28 May 1998)

A novel ferromagnetic transition, accompanied by carrier density collapse, is found in doped charge-transfer insulators with strong electron-phonon coupling. The transition is driven by an exchange interaction of polaronic carriers with localized spins; the strength of the interaction determines whether the transition is first or second order. A giant drop in the number of current carriers during the transition, which is a consequence of bound pair formation in the paramagnetic phase close to the transition, is extremely sensitive to an external magnetic field. This carrier density collapse describes the resistivity peak and the colossal magnetoresistance of doped manganites. [S0031-9007(98)08141-1]

PACS numbers: 71.30.+h, 71.38.+i, 72.20.Jv, 75.50.Pp

The interplay of the electron-phonon and exchange interactions [1–3] is thought to be responsible for many exotic properties of oxides ranging from high-T_c superconductivity in cuprates [4] to colossal magnetoresistance (CMR) and ferromagnetism in doped manganites [5–9]. A huge negative magnetoresistance was observed in doped perovskite manganites $La_{1-x}D_xMnO_3$ (D = Ca, Sr, Ba) close to the ferromagnetic transition in a certain range of doping $x \approx 0.15$–0.4 [6–9], and this raised a question of possible applications.

The metal-insulator transition in lanthanum manganites has long been thought to be the consequence of a double exchange (DEX), which results in a varying bandwidth of holes doped into the Mn^{3+} d shell [10], as function of the doping concentration and temperature. Recently it has been realized [11], however, that the effective carrier-spin interaction in DEX model is too weak to lead to a significant reduction of the electron bandwidth and, therefore, cannot account for the observed scattering rate [12] (see also Ref. [13]) or for localization induced by slowly fluctuating spin configurations [14]. In view of this problem, it has been suggested [11] that the essential physics of perovskite manganites lies in the strong coupling of carriers to Jahn-Teller lattice distortions. The argument [11] was that in the high-temperature state the electron-phonon coupling constant λ is large (so that the carriers are polarons) while the growing ferromagnetic order increases the bandwidth and thus decreases λ sufficiently for metallic behavior to set in below the Curie temperature T_c. A giant isotope effect [15], the sign anomaly of the Hall effect, and the Arrhenius behavior of the drift and Hall mobilities [16] over a temperature range from $2T_c$ to $4T_c$ unambiguously confirmed the polaronic nature of carriers in manganites.

However, an early established unusual relation between magnetization and transport below T_c have led to a conclusion that the polaronic hopping is the prevalent conduction mechanism also below T_c [17]. Low-temperature optical [18–20], electron-energy-loss (EELS) [21], and photoemission spectroscopies [22] showed that the idea [11,14] of a "metallization" of manganites below T_c is not tenable. A broad incoherent spectral feature [18–20,22] and a pseudogap in the excitation spectrum [22,23] were observed while the coherent Drude weight appeared to be *2 orders* of magnitude smaller [19] than is expected for a metal. EELS [21] confirmed that manganites are charge-transfer-type doped insulators having p holes as the current carriers rather than d (Mn^{3+}) electrons. The photoemission and O $1s$ x-ray absorption spectroscopy of $La_{1-x}Sr_xMnO_3$ showed that the itinerant holes doped into $LaMnO_3$ are indeed of oxygen p character, and their coupling with d^4 local moments on Mn^{3+} ions aligns the moments ferromagnetically [24]. Moreover, measurements of the mobility [9,25] do not show any field dependence. The calculated resistivity is in poor agreement with the data and the characteristic theoretical field ($\sim$15 T) for CMR is too high compared with the experimental one ($\sim$4 T) [11]. As a result, self-trapping above T_c and the idea of metallization below T_c do not explain CMR either. Carriers retain their polaronic character well below T_c, as manifested also in the measurements of resistivity and thermoelectric power under pressure [26].

In the present paper, we propose a theory of the ferromagnetic/paramagnetic phase transition in doped charge-transfer magnetic insulators accompanied by a current carrier density collapse (CCDC) and CMR. Taking into account a tendency of polarons to form bound pairs and the (competing with binding) exchange interaction of p polaronic holes with d electrons, we find a novel ferromagnetic transition driven by nondegenerate polarons. As a result, we describe the magnetization and temperature/field dependence of the resistivity of $La_{1-x}Ca_xMnO_3$ close to T_c in a region $0.15 < x < 0.4$.

The Hamiltonian containing the physics compatible with the experimental observations is

$$\mathcal{H} = \sum_{k,s} E_{\mathbf{k}} h^{\dagger}_{\mathbf{k}s} h_{\mathbf{k}s} - \frac{J_{pd}}{2N} \sum_{\mathbf{k},i} m_{\mathbf{k}} S^{z}_{i} + \mathcal{H}_{\mathrm{Hund}} + (2N)^{-1/2} \sum_{\mathbf{k},\mathbf{q},s} \hbar\omega_{\mathbf{q}} \gamma_{\mathbf{q}} h^{\dagger}_{\mathbf{k}+\mathbf{q}s} h_{\mathbf{k}s} (b_{\mathbf{q}} - b^{\dagger}_{-\mathbf{q}}) + \sum_{\mathbf{q}} \hbar\omega_{\mathbf{q}} (b^{\dagger}_{\mathbf{q}} b_{\mathbf{q}} + 1/2), \quad (1)$$

where $E_{\mathbf{k}}$ is the local density approximation energy dispersion [27], $h_{\mathbf{k}s}$ is the annihilation hole operator of a (degenerate) p oxygen band with spins $s = \uparrow$ and $\downarrow$, J_{pd} is the exchange interaction of p holes with four d electrons of the Mn^{3+} ion at the site i, $m_{\mathbf{k}} \equiv h^{\dagger}_{\mathbf{k}\uparrow} h_{\mathbf{k}\uparrow} - h^{\dagger}_{\mathbf{k}\downarrow} h_{\mathbf{k}\downarrow}$, S^{z}_{i} is the z component of Mn^{3+} spin, which is $S = 2$ due to the strong Hund coupling, $\mathcal{H}_{\mathrm{Hund}}$, of the four d electrons on Mn^{3+} sites, and N is the number of unit cells. The two last terms of the Hamiltonian describe the coupling of p holes with phonons and the phonon energy, respectively ($\omega_{\mathbf{q}}$ is the phonon frequency; $\gamma_{\mathbf{q}} = -\gamma^{*}_{-\mathbf{q}}$ is the coupling constant [1]). If the holes were doped into d shell instead of p shell, the Hamiltonian would be similar to the Holstein t-J model [3] with about the same physics of CMR as proposed below.

Essential results are readily obtained within the Hartree-Fock approach for the exchange interaction [28] and the Lang-Firsov polaron transformation, which eliminates terms linear in the electron-phonon interaction in Eq. (1) [1]. Thus, we find spin-polarized p bands

$$\epsilon_{\mathbf{k}\uparrow(\downarrow)} = \epsilon_{\mathbf{k}} - (+)\frac{1}{2} J_{pd} S\sigma - (+)\mu_B H, \quad (2)$$

where $\epsilon_{\mathbf{k}} = E_{\mathbf{k}} e^{-g^2}$, and $g^2 \sim \gamma^2$ describes the polaronic band narrowing [1] and the isotope effect [15], σ is the normalized thermal average of the Mn spin (3); H is the external magnetic field, and μ_B is the Bohr magneton. The p-d exchange interaction depends only on total (average) magnetization because we assume that the system is homogeneous. The magnetization of Mn^{3+} ions is given by

$$\sigma \equiv \langle S^{z}_{i} \rangle / S = B_S\left(\frac{J_{pd} m + 2 g_{\mathrm{Mn}} \mu_B H}{2 k_B T}\right), \quad (3)$$

where m is the absolute value of the magnetization of holes determined as

$$m \equiv \frac{1}{N} \sum_{\mathbf{k}} \langle m_{\mathbf{k}} \rangle = \int d\epsilon N_{\mathrm{p}}(\epsilon) \left[f_{\mathrm{p}}(\epsilon_{\mathbf{k}\uparrow}) - f_{\mathrm{p}}(\epsilon_{\mathbf{k}\downarrow}) \right]. \quad (4)$$

Here, $B_S(x) = (1 + 1/2S)\coth[(S + 1/2)x] - (1/2S)\coth(x/2)$ is the Brillouin function, g_{Mn} is the Lande g factor for Mn^{3+} in a manganite, $N_{\mathrm{p}}(E)$ is the density of states in the narrow polaron band, and $f_{\mathrm{p}}(E) = [\, y^{-1} \exp(E/k_B T) + 1]^{-1}$ is the Fermi-Dirac distribution function with $y = \exp(\mu/k_B T)$ determined by the chemical potential μ. Note that for $J_{pd} < 0$ (antiferromagnetic coupling) the main system of Eqs. (5)–(7) remains the same after a substitution $J_{pd} \to |J_{pd}|$.

Along with the band narrowing effect, the strong electron-phonon interaction binds two holes into a pair (bipolaron) [1]. The bipolarons are practically immobile in cubic manganites because the electron-phonon interaction is too strong in contrast with cuprates, where bipolarons are mobile owing to their geometry and a moderate coupling with phonons [29].

If these bound pairs are extremely local objects, two holes on the same oxygen, then they will form singlet. If, however, these holes are localized on different oxygens, then they may well form a triplet state. Because of their zero spin, the only role of singlet bipolarons in manganites is to determine the chemical potential μ, which can be found with the use of the total carrier density per cell x as $2\int dE N_{\mathrm{bp}}(E) f_{\mathrm{bp}}(E) = x - n$, where $N_{\mathrm{bp}}(E)$ is the density of bipolaronic states, $f_{\mathrm{bp}}(E) = \{y^{-2} \exp[(E - \Delta)/k_B T] - 1\}^{-1}$ is the bipolaron distribution function, Δ is the bipolaron binding energy, n is the density of single (unbound) hole polarons, which are the only current carriers in manganites, and x is the doping concentration.

It is the localization of p holes into immobile bound pairs combined with their exchange interaction with the Mn d^4 local moments that are responsible for CMR. The density of these pairs has a sharp peak at a ferromagnetic transition when the system is cooled down through the critical temperature T_c. Below T_c, the binding of polarons into pairs competes with the ferromagnetic exchange which tends to align the polaron moments and, therefore, breaks those pairs apart. These competing interactions lead to unusual behavior of CMR materials and a huge sensitivity of their transport to the external field.

To illustrate the point, we assume that T_c is comparable with the polaron, W, and bipolaron bandwidths [30]. Then (bi)polarons are not degenerate in the relevant temperature range, $f_{\mathrm{p}} \simeq y \exp(-E/k_B T)$ and $f_{\mathrm{bp}} \simeq y^2 \exp[(\Delta - E)/k_B T]$, and we can evaluate integrals reducing the system of mean field equations to

$$n = 2\nu y \cosh[(\sigma + h)/t], \quad (5)$$

$$m = n \tanh[(\sigma + h)/t], \quad (6)$$

$$\sigma = B_2[(m + 4h)/2t], \quad (7)$$

and

$$y^2 = \frac{x - n}{2\nu^2} \exp(-2\delta/t). \quad (8)$$

Here, we use the dimensionless temperature $t = 2k_B T/J_{pd} S$, magnetic field $h = 2\mu_B H/J_{pd} S$, and the binding energy $\delta \equiv \Delta/J_{pd} S$, while $\nu(= 3)$ is the degeneracy of the p band.

The polaron density n is determined by Eq. (5) with $\sigma = 0$ above T_c. At the critical temperature, the polaron density has a minimal value $n_c \simeq (2x)^{1/2} \exp(-\delta/t_c)$; it then grows exponentially with temperature and saturates at $n = (1 + 2x)^{1/2} - 1$. The remarkable observation is

that there is a sharp increase of the polaron density at temperatures below T_c. The physical origin of the unusual minimum of the current carrier density at T_c lies in the instability of bipolarons below T_c due to the exchange interaction of polarons with d electrons. The spin-polarized polaron band falls below the bipolaron band with decreasing temperature, so that all carriers are unpaired at $T = 0$ if $J_{pd}S \geq \Delta$.

Linearizing (5)–(7), we find the critical temperature in zero magnetic field is $t_c = (n_c/2)^{1/2}$, where the polaron density at the transition n_c is determined by

$$n_c^{1/2} \ln \frac{2(x - n_c)}{n_c^2} = 2^{3/2}\delta . \qquad (9)$$

This equation has solutions only for δ below some critical value $\delta_c(x)$ [Fig. 1(b), inset]. The numerical solution of the system Eqs. (5)–(8) shows that for $\delta > \delta_c(x)$ the ferromagnetic phase transition is first order with jumps of the polaron density and the magnetization, as observed [31] [Fig. 1(a)]. The transition is continuous when $\delta < \delta_c(x)$ [Fig. 1(b)]. A relatively weak magnetic field has a drastic effect on the inverse carrier density, $1/n$, near the first order transition, as shown in Fig. 2. As a result, the resistivity $\rho = 1/en\mu_p$ has a sharp maximum, which is extremely sensitive to the magnetic field in the vicinity of T_c.

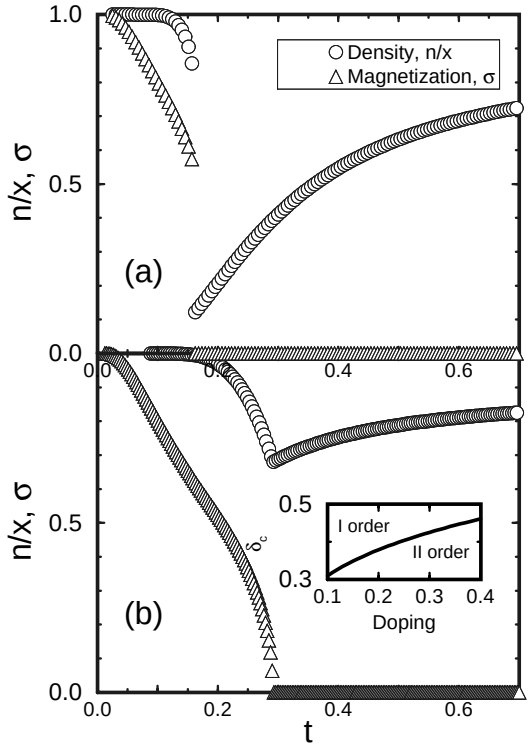

FIG. 1. Polaron density n/x and magnetization as a function of temperature $t = 2k_BT/J_{pd}S$ in a doped charge-transfer insulator near (a) the first order, $\delta \equiv \Delta/J_{pd}S = 0.5$, and (b) second order, $\delta = 0.25$, phase transitions (doping $x = 0.25$). Inset: The critical value of the relative binding energy of polaron pairs δ separating the regions of the first and second order phase transitions.

It is assumed, as is usually the case, that the triplet states always lie higher in energy than the singlet state. If the singlet-triplet separation becomes smaller than the gap, $J_{st} \lesssim \Delta$, then, because of a higher number of the triplet states, their thermal population leads to a deeper minimum in the density of polarons. We make an essential assumption that the exchange between spins on Mn and triplet bipolarons is suppressed because the bipolarons are strongly localized. Otherwise, the triplet bound pairs, if they were formed in the paramagnetic phase, can survive in the ferromagnetic phase thus reducing the carrier density collapse. One can draw an analogy of this situation with singlet magnetism, e.g., in Pr compounds [32].

In fact, our theory, Eqs. (5)–(8), describes all of the major features of the temperature/field dependence of $\rho(T)$ [7], with a temperature and field independent polaron drift mobility μ_p [33] in the experimental range of the magnetic field [Fig. 3]. That suggests that CCDC is the origin of CMR. In general, one has to take into account the temperature dependence of the polaron mobility to extend our theory for temperatures far away from the transition.

We have also compared this scenario with the localization of p holes due to a random field with a gap $\Delta/2$ between localized impurity levels and the conduction band [34]. We have found the same features of the phase transition in zero field. However, Zeeman splitting of the impurity states, and a different behavior of y with density, makes the transition *far less sensitive to the magnetic field*. As a result, *no* quantitative description of the experimental CMR has been found in this case.

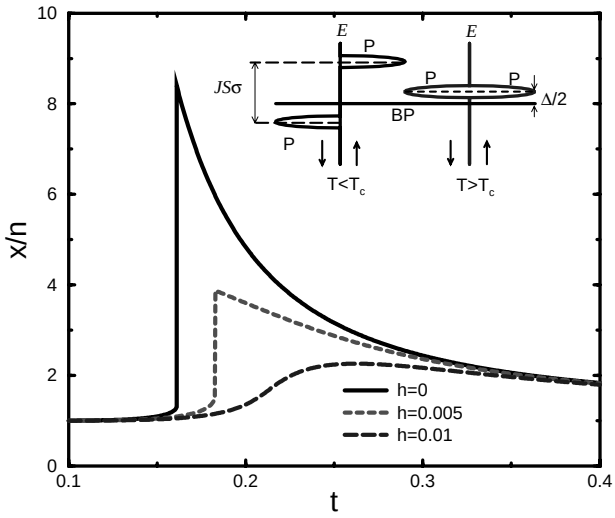

FIG. 2. Inverse polaron density for different magnetic fields, $\Delta/J_{pd}S = 0.5$, doping $x = 0.25$. Note that the transition is a strong first order, and becomes continuous only when the external magnetic field exceeds some critical value. Inset: Schematic of polaron (P) and bipolaron (BP) densities of states at temperatures below and above T_c for up (↑) and down (↓) spin moments. The pairs (BP) break below T_c if exchange $J_{pd}S$ exceeds the pair binding energy Δ.

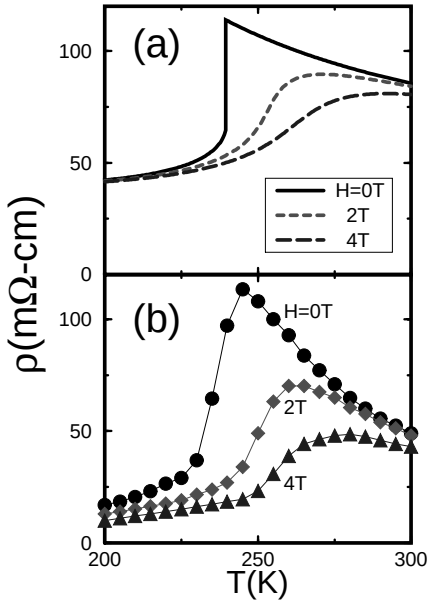

FIG. 3. Resistivity of $La_{0.75}Ca_{0.25}MnO_3$ calculated within the present theory for the pair binding energy $\Delta = 900$ K, and polaron exchange with the localized Mn^{3+} spins $J_{pd}S = 2250$ K (a), compared with experiment [7] on panel (b). Note an extreme sensitivity of the theoretical resistivity to external magnetic field (a), observed experimentally (b) for the doped manganite.

In conclusion, we have found that a few nondegenerate polarons in the p band polarize localized d electrons because of a huge density of states in the narrow polaronic band. For a sufficiently large p-d exchange $J_{pd}S > \Delta$, we have obtained current carrier density collapse at the transition owing to the formation of immobile bipolarons in the paramagnetic phase with the binding energy Δ [1]. Competition between the binding energy of polarons, which promotes a formation of local pairs, and their exchange interaction with d electrons, which breaks them at lower temperatures, results in a huge negative magnetoresistance close to the ferromagnetic transition.

We have explained the resistivity peak and the colossal magnetoresistance of doped perovskite manganites [Fig. 3] as a result of the current carrier density collapse. Depending on the ratio $\Delta/J_{pd}S$, the transition is first or second order [Fig. 1]. It is not clear at present whether the main idea underlying this picture, the assumption of singlet bound states of charge carriers, is true for manganites. The available experimental data, e.g., the tunneling spectroscopy [23], suggests that it is. Our goal is to stimulate a wider discussion and new experiments in this direction. We expect that the present theory is general enough to also account for the giant magnetoresistance observed in pyrochlore manganites [8].

We acknowledge useful discussions with A. R. Bishop, G. A. D. Briggs, D. M. Edwards, M. F. Hundley, P. B. Littlewood, S. von Molnar, V. G. Orlov, W. E. Pickett, D. J. Singh, S. A. Trugman, and R. S. Williams. We thank G. Aeppli, D. S. Dessau, H. T. Kim, A. P. Ramirez, and G.-m. Zhao for the information on their data and helpful discussions.

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