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# Theory of colossal magnetoresistance in doped manganites

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**Abstract.** The exchange interaction of polaronic carriers with localized spins leads to a ferromagnetic/paramagnetic transition in doped charge-transfer insulators with strong electron–phonon coupling. The relative strength of the exchange and electron–phonon interactions 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 local bound-pair (bipolaron) formation in the paramagnetic phase, is extremely sensitive to an external magnetic field. Below the critical temperature of the transition,  $T_c$ , the binding of the polarons into immobile pairs competes with the ferromagnetic exchange between polarons and the localized spins on Mn ions, which tends to align the polaron moments and, therefore, breaks up those pairs. The number of carriers abruptly increases below  $T_c$  leading to a sudden drop in resistivity. We show that the carrier-density collapse explains the colossal magnetoresistance of doped manganites close to the transition. Below  $T_c$ , transport occurs by polaronic tunnelling, whereas at high temperatures the transport is by hopping processes. The transition is accompanied by a spike in the specific heat, as experimentally observed. The gap feature in tunnelling spectroscopy is related to the bipolaron binding energy, which depends on the ion mass. This dependence explains the giant isotope effect of the magnetization and resistivity upon substitution of  $^{18}\text{O}$  for  $^{16}\text{O}$ . It is shown also that the localization of polaronic carriers by disorder *cannot* explain the observed huge sensitivity of the transport properties to the magnetic field in doped manganites.

## 1. Introduction

The existence of a metal–insulator transition in lanthanum manganites was established in the early 1950s [1] and was extensively studied thereafter. The transition is associated with unusual transport properties, including large magnetoresistance in the vicinity of the transition, studied in a family of doped manganites with perovskite structure with the chemical formula  $\text{Re}_{1-x}\text{D}_x\text{MnO}_3$ , where Re is the rare earth (Re = La, Pr, Nd), and D is the divalent metal (D = Ca, Sr, Ba). It is worth mentioning the early studies of the transition in  $\text{La}_{1-x}\text{Pb}_x\text{MnO}_3$  [2], followed by the studies of  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  [3],  $\text{Nd}_{0.5}\text{Pb}_{0.5}\text{MnO}_3$  [4],  $\text{La}_{0.67}\text{Ba}_{0.33}\text{MnO}_3$  [5],  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$  [6], and  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  [7, 8] (see review [9]). The recent resurgence of interest in these systems is related to the demonstration of a very large negative magnetoresistance in thin films [5, 7] (sometimes termed colossal magnetoresistance (CMR)), which immediately raised the possibility of technological applications. The colossal magnetoresistance is not limited to doped perovskite manganites, but was also observed in pyrochlore manganites, chromium spinels [9], and some other systems, like europium compounds.

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The metal–insulator transition in lanthanum manganites [1, 7, 8] has been traditionally attributed to a ‘double-exchange’ mechanism, which results in a varying bandwidth of holes doped into the  $\text{Mn}^{3+}$  d shell as a function of the doping concentration and temperature [10]. Recently it has been realized [11], however, that the effective carrier–spin exchange interaction of the double-exchange 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 reference [13]) or for the localization induced by slowly fluctuating spin configurations [14]. In view of this severe shortcoming of the double-exchange model, it has been suggested [11] that the essential physics of perovskite manganites lies in the strong coupling of carriers to the Jahn–Teller lattice distortion. The argument [11] was that in the high-temperature state the electron–phonon coupling constant  $\lambda$  is large (so the carriers are polarons); as temperature decreases the growing ferromagnetic order increases the bandwidth and thus decreases  $\lambda$  sufficiently for metallic behaviour to occur below the Curie temperature  $T_c$ , in accordance with polaron theory [15]. A giant isotope effect [16], the sign anomaly of the Hall effect, and the Arrhenius behaviour of the drift and Hall mobilities [17] over a temperature range from  $2T_c$  to  $4T_c$  unambiguously confirmed the polaronic nature of the carriers in manganites. Polaron hopping transport accounts satisfactorily for the resistivity in the paramagnetic phase [17].

However, the known relation between magnetization and transport below  $T_c$  and the unusual magnetic ion dynamics have prompted the conclusion that polaronic hopping is also the prevalent conduction mechanism below  $T_c$  [18]. Low-temperature optical [19–21], electron energy-loss (EELS) [22], and photoemission spectroscopies [23] showed that the idea [11, 14] of a ‘metallization’ of manganites below  $T_c$  is not tenable. A broad incoherent spectral feature [19–21, 23] and a pseudogap in the excitation spectrum [23–25] were observed while the coherent Drude weight appeared to be *two orders* of magnitude smaller [20] than is expected for a metal, or even *zero* in the case of layered manganites [23]. EELS [22] confirmed that manganites are doped charge-transfer insulators having p holes as the current carriers rather than d ( $\text{Mn}^{3+}$ ) electrons. The photoemission and O 1s x-ray absorption spectroscopy of  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  showed that the itinerant holes doped into  $\text{LaMnO}_3$  are indeed of oxygen p character, and their coupling with the  $d^4$  local moments on  $\text{Mn}^{3+}$  ions aligns the moments ferromagnetically [26]. Moreover, measurements of the mobility [9, 27] do not show any field dependence and there are significant deviations from Arrhenius behaviour close to  $T_c$  [17, 28]. The resistivity calculated from the modified double-exchange theory 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 [29].

Therefore, the experimental evidence overwhelmingly suggests that the low-temperature phase of the doped manganites is not a metal, but a doped polaronic semiconductor. The double exchange and the presence of polaronic carriers are *insufficient* to explain the physics of colossal magnetoresistance. One can also add that there are known classes of CMR materials where it is guaranteed that double exchange is *non-existent*, like in pyrochlore manganites, chromium spinels [9], and other compounds.

In the present paper, we propose a new theory of the ferromagnetic/paramagnetic phase transition accompanied by a current-carrier-density collapse (CCDC) and CMR. Taking into account the tendency of polarons to form local bound pairs (bipolarons) as well as the exchange interaction of p polaronic holes with d electrons, we find a novel ferromagnetic transition driven by non-degenerate polarons in doped charge-transfer magnetic insulators. The crux of the matter is that in the paramagnetic state above the critical temperature a large fraction

of polarons is bound into immobile pairs (bipolarons). As the temperature decreases in the paramagnetic phase ( $T > T_c$ ), so does the density of mobile polarons, and the resistivity quickly increases with the decline of the number of carriers. With the onset of ferromagnetic order at  $T_c$ , the situation changes dramatically. As a result of the exchange interaction with the localized Mn spins, the energy of one of the polaron spin sub-bands sinks abruptly below the energy of the bound pairs. The pairs break up, the density of carriers (mobile polarons) jumps up, and the resistivity suddenly declines, as observed experimentally. The occurrence of the deep minimum in the carrier density close to the transition point, which we suggest calling a *current-carrier-density collapse*, allows us to explain the magnetization and temperature/field dependence of the resistivity of  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  close to  $T_c$  as well as the giant isotope effect, the unusual tunnelling gap, and the specific heat anomaly.

## 2. Ferromagnetic transition in doped manganites

The Hamiltonian containing the physics compatible with the experimental observations mentioned above is

$$\begin{aligned} \mathcal{H} = & \sum_{k,s} E_k h_{ks}^\dagger h_{ks} - \frac{J_{pd}}{2N} \sum_{k,j} m_k S_j^z + \mathcal{H}_{sf} + \mathcal{H}_{\text{Hund}} \\ & + (2N)^{-1/2} \sum_{k,q,s} \hbar\omega_q \gamma_q h_{k+qs}^\dagger h_{ks} (b_q - b_{-q}^\dagger) + \sum_q \hbar\omega_q (b_q^\dagger b_q + 1/2) \end{aligned} \quad (1)$$

where  $E_k$  is the local density approximation (LDA) energy dispersion [30],  $h_{ks}$  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  $\text{Mn}^{3+}$  ion at the site  $j$ ,  $m_k \equiv h_{k\uparrow}^\dagger h_{k\uparrow} - h_{k\downarrow}^\dagger h_{k\downarrow}$ ,  $S_j^z$  is the z-component of  $\text{Mn}^{3+}$  spin, which is  $S = 2$  due to the strong Hund coupling,  $\mathcal{H}_{\text{Hund}}$ , of the four d electrons on  $\text{Mn}^{3+}$  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 ( $\gamma_q = -\gamma_{-q}^*$  is the coupling constant [15]). The Hamiltonian also contains spin-flip processes,  $\mathcal{H}_{sf}$ , like  $S_j^+ h_{k'\downarrow}^\dagger h_{k\uparrow} + \text{h.c.}$ , and terms with non-diagonal components of the polaron magnetization operator  $m_{k'/k} = h_{k'\uparrow}^\dagger h_{k\uparrow} - h_{k'\downarrow}^\dagger h_{k\downarrow}$ , which are not essential for our discussion. If the holes were doped into the d shell instead of the p shell, the Hamiltonian would be similar to the Holstein  $t$ - $J$  model [31] with about the same physics of the CMR as proposed below.

The essential results are readily obtained within the Hartree-Fock approach for the exchange interaction [32] and the Lang-Firsov polaron transformation [33] which removes terms of first order in the electron-phonon interaction in equation (1),  $\tilde{H} = e^U H e^{-U}$ , where

$$U = \sum_{jq} h_{js}^\dagger h_{js} u_{jq} (b_{-q}^\dagger + b_q) \quad (2)$$

Here,

$$h_{js} = N^{-1/2} \sum_k h_{ks} \exp(ik \cdot \mathbf{R}_j) \quad u_{jq} = (2N)^{-1/2} \gamma_q \exp(iq \cdot \mathbf{R}_j)$$

and  $\mathbf{R}_j$  is the lattice vector.

With the use of this transformation one finds spin-polarized p bands

$$\epsilon_{k\uparrow(\downarrow)} = \epsilon_k - (+) \frac{1}{2} J_{pd} S \sigma - (+) \mu_B H. \quad (3)$$

Here

$$\epsilon_k = \frac{1}{N} \sum_{i,j} t_{ij} e^{ik \cdot (\mathbf{R}_i - \mathbf{R}_j)} e^{-g_{ij}^2} \approx E_k e^{-g^2} \quad (4)$$

with

$$g_{ij}^2 = \frac{1}{2N} \sum_q |\gamma_q|^2 [1 - \cos \mathbf{q} \cdot (\mathbf{R}_i - \mathbf{R}_j)] \coth\left(\frac{\hbar\omega_q}{2k_B T}\right) \quad (5)$$

where  $g^2 \sim \gamma^2$  is the characteristic value of  $g_{ij}^2$  and  $\omega_q$  is the phonon frequency. Equation (5) describes the polaronic band narrowing [33] and the isotope effect [16]. The bare hopping integrals  $t_{ij}$  define the unrenormalized LDA (local density approximation) band dispersion in the initial Hamiltonian (1),

$$E_{\mathbf{k}} = \frac{1}{N} \sum_{i,j} t_{ij} \exp[i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)].$$

In equation (3),  $\sigma$  is the normalized thermal average of the Mn spin, found from the equations below;  $H$  is the external magnetic field, and  $\mu_B$  is the Bohr magneton. The p–d exchange interaction depends only on the total (average) magnetization because we assume that the system is homogeneous. In addition to band narrowing, the bands shift rigidly down; the value of this *polaron shift*  $E_p$  is

$$E_p = \frac{1}{2N} \sum_q \hbar\omega_q |\gamma_q|^2. \quad (6)$$

The ions  $\text{Mn}^{3+}$  are subject to a molecular field  $J_{pd}m/(2g_{\text{Mn}}\mu_B)$ , according to (1), and their magnetization  $\sigma \equiv \langle S_n^z \rangle / S$  is given by

$$\sigma = B_S \left( \frac{J_{pd}m + 2g_{\text{Mn}}\mu_B H}{2k_B T} \right) \quad (7)$$

with  $m$  the magnetization of holes determined as

$$m \equiv \frac{1}{N} \sum_k \langle m_k \rangle = \int d\epsilon N^{(p)}(\epsilon) [f_p(\epsilon_{k\uparrow}) - f_p(\epsilon_{k\downarrow})]. \quad (8)$$

Here

$$B_S(x) = [1 + 1/(2S)] \coth[(S + 1/2)x] - [1/(2S)] \coth(x/2)$$

is the Brillouin function,  $g_{\text{Mn}}$  the Landé  $g$ -factor for  $\text{Mn}^{3+}$  in a manganite,  $N^{(p)}(\epsilon)$  the density of states in the narrow polaron band, and  $f_p(\epsilon_{ks}) = [y^{-1} \exp(\epsilon_{ks}/k_B T) + 1]^{-1}$  the Fermi–Dirac distribution function with  $y = \exp(\mu/k_B T)$  determined by the chemical potential  $\mu$ . Note that for  $J_{pd} < 0$  (antiferromagnetic coupling) the main system of equations (16)–(18) remains the same after a substitution  $J_{pd} \rightarrow |J_{pd}|$ .

Along with the band-narrowing effect, the strong electron–phonon interaction binds two polarons into a local pair (bipolaron), as described in detail in reference [15]. These bipolarons are practically immobile in manganites because of the strong electron–phonon interaction, in contrast with the case for cuprates, where bipolarons are mobile and responsible for in-plane transport [34], owing to their geometry [35] and their moderate coupling with phonons [36].

If these bound pairs are extremely local objects, i.e. two holes on the same oxygen, then they will form a singlet. If, however, these holes are localized on different oxygens, then they may well have parallel spins and form a *triplet* state. The latter is separated from the singlet state by some exchange energy  $J_{st}$ , with some interesting consequences discussed below. Because of their zero spin, the only role of the singlet bipolarons in manganites is to determine the chemical potential  $\mu$ , which can be found with the use of the total doping density per cell  $x$  [34].

The interplay between the localization of p holes into bipolaron pairs and the exchange interaction with the  $\text{Mn}^{d^4}$  local moments is responsible for CMR. The density of these pairs

has a sharp peak at the ferromagnetic transition when the system is cooled down through the critical temperature  $T_c$ . As the system is cooled, but is still in a paramagnetic state above  $T_c$ , an increasing fraction of the polarons forms immobile pairs (bipolarons), and the resistivity of the system increases. Below  $T_c$ , the binding of polarons into immobile pairs competes with the ferromagnetic exchange, which tends to align the polaron moments and, therefore, breaks those pairs apart. The number of carriers abruptly increases below  $T_c$  leading to a sudden drop in resistivity. These competing interactions lead to the unusual behaviour of CMR materials and the extreme sensitivity of their transport to external fields.

To prove the point, we shall find the thermodynamic potential and solve for its extremal value to find the equation of state for the polarons. The thermodynamic potential  $\Omega$

$$\Omega = \Omega_p + \Omega_{bp} + \Omega_S + \frac{1}{2} J_{pd} S \sigma m \quad (9)$$

has contributions from polarons, bipolarons, localized  $Mn^{3+}$  spins, and the double-counting term, respectively. For the polarons

$$\Omega_p = -k_B T \sum_s \int d\epsilon N_s^{(p)}(\epsilon) \ln(1 + y e^{-\epsilon/k_B T}) \quad (10)$$

where  $N_s^{(p)}(\epsilon)$  is the density of spin-polarized states in the polaron band. We can easily estimate the integral, assuming that the critical temperature of the ferromagnetic transition is comparable with the polaron and bipolaron bandwidth [37]. Then (bi)polarons are not degenerate in the relevant temperature range,  $f_p \simeq y \exp(-\epsilon/k_B T)$  and  $f_{bp} \simeq y^2 \exp[(\Delta - \epsilon)/k_B T]$ , and we get

$$\Omega_p = -2\nu v k_B T \cosh \frac{J_{pd} S \sigma + g \mu_B H}{2k_B T} \quad (11)$$

where  $\nu$  ( $=3$ ) is the degeneracy of the polaron p band.

Polarons, bound in bipolarons with a binding energy  $\Delta$ , give a contribution

$$\Omega_{bp} = -k_B T \ln(1 + \nu^2 y^2 D e^{\Delta/k_B T}) \quad (12)$$

where  $D$  accounts for the presence of triplet bipolarons (see below, section 6). We shall consider here a simple case in which the separation of the triplets from the singlets,  $J_{st}$ , is much larger than the critical temperature. In this case  $D = 1$ .

Finally, for the localized spin contribution we will have

$$\Omega_S = -k_B T \ln \frac{\sinh(S + \frac{1}{2})\eta}{\sinh \frac{1}{2}\eta} \quad (13)$$

with  $\eta = (\frac{1}{2} J_{pd} m + g_{Mn} \mu_B H)/k_B T$ .

The density of polarons  $n = -(\partial \Omega_p / \partial \mu)_T$  is found from the condition that the total number of carriers is given by the doping concentration  $x$  [34]:

$$x = -(\partial \Omega / \partial \mu)_T \quad (14)$$

whereas one can find equations for the magnetization and the normalized spin  $\sigma$  from the following conditions:

$$(\partial \Omega / \partial \sigma)_T = (\partial \Omega / \partial m)_T = 0. \quad (15)$$

Thus, we obtain the following main system of mean-field equations, assuming for a moment that the contribution from triplet bipolarons is small ( $D = 1$ ):

$$n = 2\nu y \cosh[(\sigma + h)/t] \quad (16)$$

$$m = n \tanh[(\sigma + h)/t] \quad (17)$$

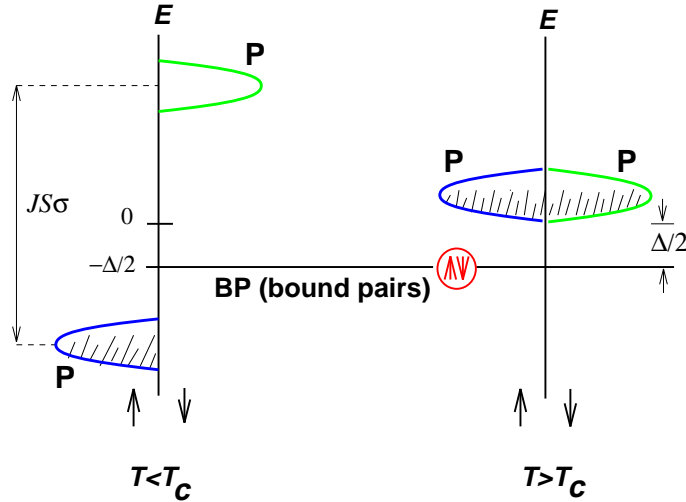
$$\sigma = B_2[(m + 4h)/(2t)] \quad (18)$$

and

$$y^2 = \frac{x-n}{2v^2} \exp(-2\delta/t) \quad (19)$$

which follows from (14). When triplet bipolarons become important, one should replace equation (19) by the more accurate equation (28). 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 bipolaron binding energy  $\delta \equiv \Delta / (J_{pd} S)$ , and  $v (=3)$  is defined after equation (11).

The polaron density  $n$  is determined by equations (16), (19) 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 with temperature and saturates at  $n = (1 + 2x)^{1/2} - 1$  at large temperatures. This is reminiscent of ordinary semiconductor behaviour.



**Figure 1.** A schematic diagram of free-polaron (P) and polaron bound-pair (BP) densities of states at temperatures below and above  $T_c$  for up-spin ( $\uparrow$ ) and down-spin ( $\downarrow$ ) moments. The pairs (BP) break below  $T_c$  if the exchange  $J_{pd} S$  between p-hole polarons and Mn  $d^4$  local spins exceeds the pair binding energy  $\Delta$ , as in the case shown. The exchange interaction of polarons with the localized spins sets in below  $T_c$ ; the spin-up polaron sub-band sinks abruptly below the bipolaron band, causing the break-up of the immobile bipolarons (left-hand panel). A sudden drop (collapse) of the density of the current carriers (polarons) in the vicinity of the ferromagnetic transition is the cause of a large peak in resistivity and colossal magnetoresistance.

### 3. Competing interactions and carrier-density collapse

The remarkable observation is that there is a sharp increase of the polaron density (and the conductivity) at temperatures below  $T_c$ . The polaron density approaches the total density  $x$  at  $T \rightarrow 0$  if  $\delta \equiv \Delta / J_{pd} S < 1$ , as one can see from equation (16) with a saturated magnetization  $\sigma = 1$ . 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 Mn  $d$  electrons. The spin-polarized polaron band falls below the bipolaron band, so all carriers are unpaired at  $T = 0$  if  $J_{pd} S \geq \Delta$ . The evolution of the Hartree–Fock bands with temperature, which corresponds to this behaviour, is illustrated in figure 1. Note that at all  $T > T_c$  the position of the polaron bands is fixed at  $\Delta/2$  above the bipolaron band, since there

$\sigma = m = 0$  (equation (3)). Their population depends on temperature via the chemical potential. The exchange interaction of polarons with the localized spins sets in at  $T_c$ , and in the low-temperature ferromagnetic phase one of the polaron spin sub-bands sinks abruptly below the bipolaron band, causing the break-up of the immobile bipolarons. This interesting feedback mechanism can result in either a continuous or discontinuous ferromagnetic transition, as follows from a simple analysis below.

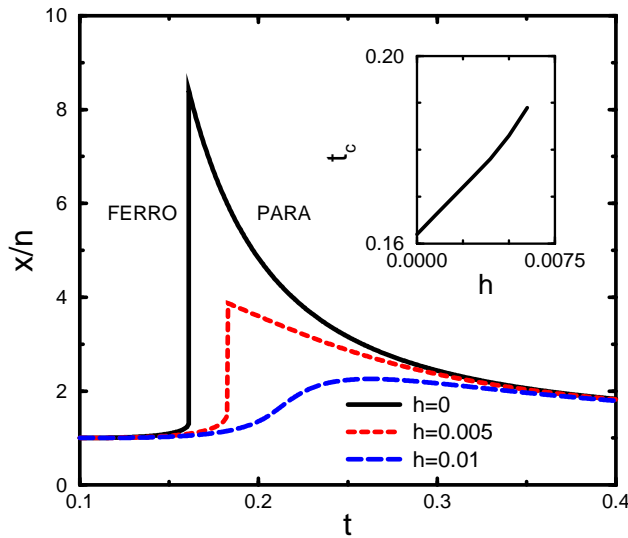
Linearizing equations (16)–(18) with respect to  $\sigma$  and  $m$  near  $T_c$ , we find the critical temperature in zero magnetic field

$$t_c = (n_c/2)^{1/2} \quad (20)$$

where the polaron density at the transition  $n_c$  is determined by

$$n_c^{1/2} \ln \frac{2(x - n_c)}{n_c^2} = 2^{3/2} \delta. \quad (21)$$

It is easy to see that this transcendental equation has solutions only for  $\delta$  below some critical value  $\delta_c(x)$ . This means that for  $\delta > \delta_c(x)$  the ferromagnetic phase transition is first order with jumps of the polaron density and the magnetization [38], as has been observed [39]. The transition is continuous when  $\delta < \delta_c(x)$ . The numerical solution of the system of equations (16)–(19) defines the crossover between first- and second-order phase transitions [38].



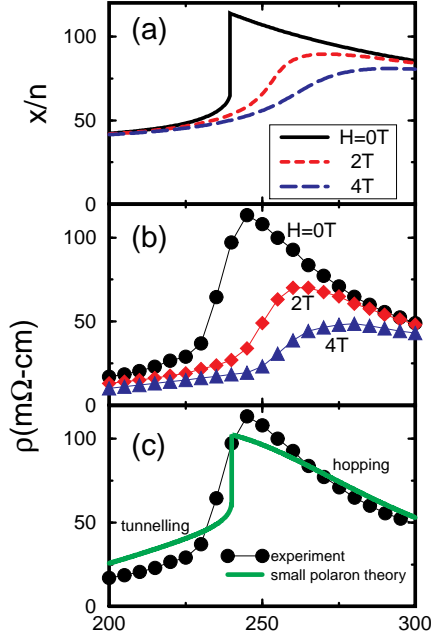
**Figure 2.** Inverse polaron density  $x/n$  in a doped charge-transfer insulator for different magnetic fields  $h \equiv g\mu_B H/J_{pd}S$ ,  $\Delta/J_{pd}S = 0.5$ , doping  $x = 0.25$ .  $\Delta$  is the pair binding energy;  $J_{pd}S$  is the exchange energy of the O p hole polarons with Mn d localized spins. For other notation see the text. Note that the transition is strong first order, and then becomes continuous when the external magnetic field exceeds some critical value. Inset: the temperature of the phase transition as a function of the external magnetic field.

A relatively weak magnetic field has a drastic effect on the inverse carrier density,  $1/n$ , near the first-order phase transition, or second-order phase transition close to first order, since an order parameter abruptly changes close to  $T_c$ . A field equal to only  $0.005 J_{pd}S/(2\mu_B)$  reduces the carrier-density collapse by more than a factor of two, and a field of  $0.01 J_{pd}S/(2\mu_B)$  changes the transition into the continuous one; see figure 2. This behaviour directly relates to



the colossal magnetoresistance found in doped manganites, as we shall discuss in the following section.

One can draw an analogy of this situation with singlet magnetism, e.g. in Pr compounds [40]. In this case the ground state of magnetic ions is a singlet. Depending on the ratio between the exchange constant and the singlet–triplet (doublet) energy gap produced by crystal-field splitting, there exist first- or second-order phase transitions into a ferromagnetic state. In our case the triplet states become important when  $J_{st} \lesssim \Delta$ ; the larger statistical weight of triplet bipolarons leads to a deeper minimum in the density of polarons at the critical temperature, and, therefore, to a larger jump in resistivity. The effect of polaron binding in a triplet state will be discussed below.



**Figure 3.** The resistivity of  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$  calculated within the present theory for  $\Delta = 900$  K,  $J_{pd}S = 2250$  K for a temperature-independent mobility (a). The experimental results [8] are shown in panel (b). Note the extreme sensitivity of the theoretical resistivity to the external magnetic field (a), also observed experimentally for the doped manganite (b) (the thin solid curve is a guide to the eye). Panel (c): the resistivity calculated with a temperature-dependent mobility according to equation (26) with  $\omega_0 = 50$  meV and  $E_a = 300$  meV, and the temperature-dependent polaron density from panel (a) compared with the experimental results. Note the crossover of the transport mechanism from low-temperature tunnelling to high-temperature hopping at about the transition temperature. For the notation see the caption to figure 2.

#### 4. Colossal magnetoresistance

As a result of the carrier-density collapse, the resistivity  $\rho = 1/(en\mu_p)$  has a sharp maximum, which is extremely sensitive to the magnetic field in the vicinity of  $T_c$ . In fact, our theory, equations (16)–(19), describes all of the major features of the temperature/field dependence of  $\rho(T)$  [8], with a temperature and the field-independent polaron drift mobility  $\mu_p$  in the experimental range of the magnetic field; see figures 3(a), 3(b). It gives the correct magnitude of the effect on resistivity and explains the extreme sensitivity to external magnetic fields. This

suggests that *current-carrier-density collapse* 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. At high temperatures, the mobility  $\mu_p$  of polarons is dominated by hopping events since the polaron band-narrowing factor  $g^2$  grows linearly with  $T$ , making tunnelling in a narrow polaron band virtually impossible at  $k_B T > \hbar\omega_0/2$ , where  $\omega_0$  is the characteristic phonon frequency [33]. A simple estimate for the so-called adiabatic hopping conductivity together with the Einstein relation between the diffusion constant and mobility immediately yields

$$\mu_p^{(\text{hop})} \sim \frac{\mu_0}{2\pi} \frac{\hbar\omega_0}{k_B T} \exp(-E_a/k_B T) \quad (22)$$

where  $\mu_0 = ea^2/\hbar$  is the characteristic mobility (one can estimate  $a$  as the O–O distance in manganites), and  $E_a$  is the activation energy for the hopping. The tunnelling mobility is given by

$$\mu_p^{(\text{tun})} = \mu_0 \frac{\bar{t}^2 e^{-2g^2}}{\hbar k_B T} \tau \quad (23)$$

with the relaxation time  $\tau$  estimated by Lang and Firsov [33]:

$$\tau \approx (E_a/\bar{t})^4 [\Delta\omega/\omega_0^2] \sinh^2(\hbar\omega_0/2k_B T) \quad (24)$$

where  $\bar{t}$  is the characteristic bare hopping integral  $t_{ij}$ , and  $\Delta\omega$  is the phonon dispersion. The resistivity is then given by

$$\rho = 1/\sigma \quad \sigma = ne(\mu^{(\text{tun})} + \mu^{(\text{hop})}). \quad (25)$$

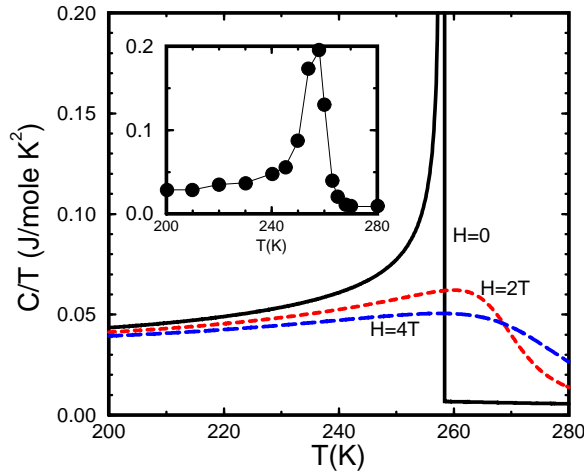
With our low polaron density at the transition, the polaron mobility is  $\mu_p = 0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for  $x = 0.33$  [17], and about  $0.03 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for  $x = 0.25$  [8], which lie in the range typical of polaronic conductors like  $\text{TiO}_2$  at room temperature [15]. We have fitted the observed resistivity to the above expression (figure 3(c)) using for  $\omega_0$  a value of 50 meV, which is close to the phonon cut-off in LCMO (50–70 meV [41]). The fit indicates that the activation energy is close to  $E_a = 300 \text{ meV}$ . A crossover from tunnelling to hopping occurs at around the critical temperature  $T_c$ , which is not very different from  $\hbar\omega_0/2k_B$  [42]. Agreement with the experiment (figure 3(c)) supports the idea that the temperature dependence of the resistivity is due primarily to CCDC. The temperature dependence of the small-polaron mobility then allows the resistivity far away from the transition *both* above and below  $T_c$  to be explained.

## 5. Anomalous specific heat

The carrier-density collapse is also evident through anomalies in thermodynamic quantities. Indeed, we have shown above that the ferromagnetic transition is first order, or second order close to first order, as observed. The thermodynamic potential changes rather abruptly in the vicinity of the phase transition and this results in a sharp peak in the specific heat  $C$  (figure 4), which has been observed [43]. Note that this is *not* a result of critical fluctuations as suggested earlier [43], since they are absent or severely suppressed when the phase transition is first order, or close to it. We see that our theory is in quantitative agreement with the experiment for this anomalous thermodynamic quantity.

## 6. Triplet bipolarons

Let us now discuss the modification which arises if we include exchange between O holes bound into bipolarons. This exchange generally induces a splitting  $J_{st}$  between singlet and



**Figure 4.** The calculated anomalous part of the specific heat for different values of the magnetic field  $H$ . Inset: the experimental results for  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  [42] (the thin solid curve is a guide to the eye).

triplet states of the bipolaron. This changes somewhat the thermodynamic potential of the bipolarons, since the triplet is subject to a Zeeman splitting. The factor  $D$  is then

$$D = 1 + e^{-J_{st}/k_B T} \sinh(3\xi/2) / \sinh(\xi/2) \quad (26)$$

as it accounts for thermal excitations of singlet bipolarons into the triplet state, separated from the singlet by the energy  $J_{st}$ . The parameter

$$\xi = (\tilde{J}_{pd} S \sigma + V_{bp} m + g \mu_B H) / k_B T \quad (27)$$

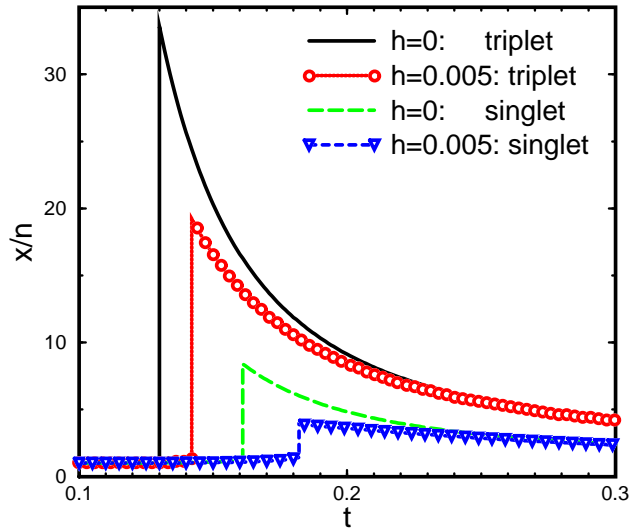
depends on exchange interaction of the bipolarons with  $\text{Mn}^{3+}$  spins given by the exchange constant  $\tilde{J}_{pd}$ , and with delocalized polarons, given by the exchange constant  $V_{bp}$ . Note that  $D = 4$  at  $J_{st}/k_B T \ll 1$ , whereas  $D = 1$  for  $J_{st}/k_B T \gg 1$ , which reflects the higher statistical weight of triplet states compared to singlets.

It is assumed, as is usually the case, that the triplet states lie higher in energy than the singlet state,  $J_{st} > 0$ . If the singlet–triplet splitting becomes smaller than the gap,  $J_{st} \lesssim \Delta$ , then, because of the higher number of the triplet states, their thermal population leads to a deeper minimum in the density of polarons and, therefore, to a larger jump in resistivity (figure 5). The dependence of the population of the triplet states on the external field makes the system somewhat less sensitive to the field. We make an essential assumption that  $J_{st} > 0$  and that the exchange between spins on Mn and triplet bipolarons,  $\tilde{J}_{pd}$ , is suppressed to values  $\ll J_{pd}$  because the bipolarons are strongly localized (we also expect that the exchange constant  $V_{bp}$  is the smallest one in (27)). Otherwise, the triplet bound pairs, if they were formed in the paramagnetic phase, can survive in the ferromagnetic phase, thus reducing or eliminating the carrier-density collapse.

The equation (19) is changed to read

$$y^2 = \frac{x - n}{(2 - x + n)v^2 D} \exp(-2\delta/t) \quad (28)$$

whereas the main system of equations (16)–(19) remains the same.  $D$  is given by equation (26). The effect of triplet bipolarons on the thermodynamics of doped manganites becomes



**Figure 5.** The inverse polaron density  $x/n$  for different magnetic fields for a system with triplet and singlet bipolarons versus temperature  $t \equiv 2k_B T/J_{pd}S$ . ( $\Delta/J_{pd}S = 0.5$ , doping  $x = 0.25$ , and we assume  $J_{st} \ll \Delta$ .) The jump in carrier density is much larger in a system with triplet bipolarons, but the critical temperature and sensitivity of the critical temperature to the magnetic field is lower in comparison with the case for singlet bipolarons. For the notation see the caption to figure 2.

insignificant when  $J_{st}/\Delta > 1$ , and the results are similar to the case in which only singlet bipolarons are involved. The polaron density at the transition  $n_c$  is determined by

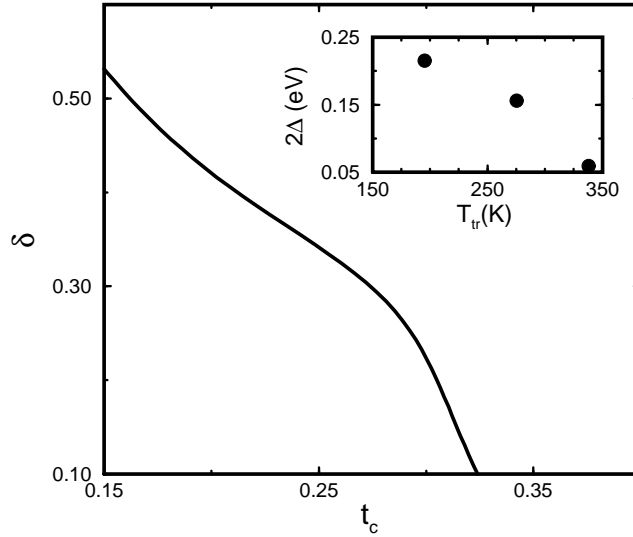
$$n_c^{1/2} \ln \frac{2(x - n_c)}{Dn_c^2[1 - (x - n_c)/2]} = 2^{3/2}\delta \quad (29)$$

which is similar to the case of singlet polarons and also indicates a crossover from first- to second-order phase transition. We compare the carrier-density collapse in a system with triplet bipolarons to that with singlet bipolarons alone in figure 5. The jump in the carrier density at the transition is a few times larger in this case as compared to that for singlet bipolarons. At the same time the critical temperature shifts to lower values, and the sensitivity to external magnetic field slightly reduces.

## 7. Tunnelling gap and giant isotope effect

Recent tunnelling measurements have shown that in the vicinity of  $T_c$  a gap in the quasi-particle spectrum opens up [24, 25]. Again, it is difficult to reconcile this gap with the notion of a (half-) metallic ferromagnetic state below  $T_c$  [44]. In half-metallic ferromagnets, like  $\text{CrO}_2$  or  $\text{Fe}_3\text{O}_4$ , there is a band gap for electron states of only *one* spin direction. The opposite-spin electrons have no gap at the Fermi level, similar to a standard metal situation. These states will contribute to tunnel current as in conventional metals, so there would be *no* temperature-dependent gap feature in the tunnel spectroscopy [44] like the one observed for the doped manganites [24].

We note that within the framework of our theory there should be a temperature-dependent gap  $\Delta$  related to the breakdown of a bipolaron into two polaronic carriers. The density of bipolarons peaks at  $T_c$ , whereas the polaron density dips there (figures 1, 2) and, therefore,



**Figure 6.** The relation between the gap  $\delta \equiv \Delta/J_{pd}S$  and the critical temperature  $t_c \equiv 2k_B T_c/J_{pd}S$  calculated from the present theory. Inset: the tunnelling gap in the density of states for samples with different temperatures of the transition:  $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ ,  $T_{tr} = 196$  K;  $(\text{NdLa})_{0.73}\text{Pb}_{0.27}\text{MnO}_3$  ( $T_{tr} = 275$  K);  $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$  ( $T_{tr} = 338$  K) [24]. For the notation see the caption to figure 2.

the gap feature in the tunnelling  $I$ - $V$  curves will be most pronounced in this region, as observed [24]. Spin-polarized polarons will provide a gapless background for the tunnelling current, which is least important in the vicinity of the transition temperature. We note that STM should also be sensitive to the presence of the one-particle charge-transfer gap between filled Mn  $d$  and empty O  $p$  states. In addition to the temperature dependence, we can predict how the gap feature will depend on the critical temperature of the transition (figure 6). Namely, as already follows from our discussion, with the increase of  $\Delta$  the critical temperature  $T_c$  goes down [38]. Very similar behaviour has indeed been observed experimentally for samples with different critical temperatures (figure 6, inset) [24].

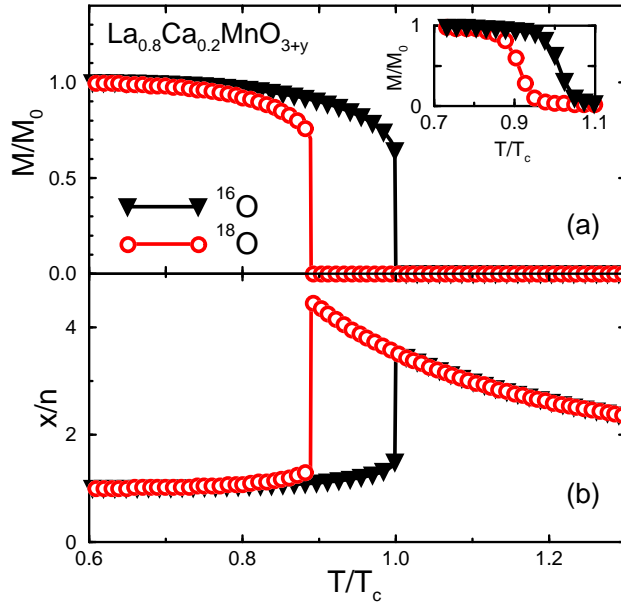
The giant isotope effect in  $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ , where a shift of  $-21$  K in  $T_c$  was observed as a result of  $^{16}\text{O}$ -to- $^{18}\text{O}$  substitution [16], is quantitatively explained within our approach. Namely, the gap is given by [45]

$$\Delta = 2E_p - V_C - \frac{1}{2}W \quad (30)$$

where  $E_p$  is the polaron level shift,  $V_C$  is the Coulomb repulsion between bound polarons, and  $W = W_0 \exp(-g^2)$  is the polaron bandwidth renormalized from the bare value  $W_0$  with the electron-phonon interaction constant  $g^2$  [15]. The *only* quantity in (30) that depends on ionic mass is the polaronic exponent  $g^2 = \gamma E_p/(\hbar\omega) \propto M^{1/2}$  [15], where  $\gamma < 1$  is a numerical coefficient depending on the radius of the electron-phonon interaction [35]. As immediately follows from this relation, isotope substitution will change the gap  $\Delta$  in the following way:

$$\Delta_{18} = \Delta_{16} + Wg_{16}^2(\sqrt{18/16} - 1) \quad (31)$$

where indices mark the quantities for the corresponding isotopes of oxygen. According to (31)  $\Delta_{18}$  is *always* larger than  $\Delta_{16}$ . This automatically leads to a lowering of  $T_c$  as a result of the isotope substitution, as observed [16], in figure 7. The resistivity, on the other hand, is *larger* in  $^{18}\text{O}$ -substituted samples, and this correlation seems to be supported by recent experiments [46].



**Figure 7.** The isotope effect on the magnetization (a) and the inverse carrier density (b) of  $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_{3+y}$  calculated in the present theory. Inset: experimental results [16]. The substitution  $^{16}\text{O} \rightarrow ^{18}\text{O}$  leads to increased resistivity (b).

Note that the *single parameter* defining the isotope effect on the magnetic transition and the resistivity jump is  $Wg_{16}^2$ , since neither  $E_p$  nor  $V_C$  depend on the ion mass.

## 8. Localization of polarons by disorder

We have also studied the localization of p holes due to a random field with a gap  $\Delta/2$  between localized impurity levels and the conduction band. The energy of polarons on impurity centres is given by

$$E_{i\uparrow(\downarrow)} = -\frac{\Delta}{2} - (+) \frac{1}{2} V_{ip} m - (+) \mu_B H \quad (32)$$

where  $V_{ip}$  is the exchange interaction between localized and delocalized polarons. The band diagram for this case is the same as that in figure 1 with the replacement of the bipolarons by localized polarons.

Assuming that the Hubbard repulsion prevents a double occupancy of the impurity centres, one can easily obtain the thermodynamic potential for impurities

$$\Omega_i = -k_B T \ln \left[ 1 + 2\nu y e^{\Delta/2k_B T} \cosh \left( \frac{\frac{1}{2} V_{ip} m + \mu_B H}{k_B T} \right) \right]. \quad (33)$$

The chemical potential is found to be

$$y = \frac{x - n}{2\nu n \cosh(\zeta)} \exp(-\delta/t) \quad (34)$$

where  $\zeta = (\frac{1}{2} V_{ip} m + \mu_B H)/k_B T$ , if we assume that the total number of impurity states is  $x$  ( $\equiv$  doping).

We have found similar features of the phase transition in zero field in the impurity case, as compared with the previous case with bipolarons. Thus, we obtain, by linearizing the system of equations of state (16)–(18) with (34), the following equation for the polaron density at the transition in zero field:

$$n_c^{1/2} \ln \frac{x - n_c}{n_c^2} = 2^{1/2} \delta. \quad (35)$$

Apparently, it has solutions only for  $\delta < \delta_c(x)$ . Therefore, the transition is first order for  $\delta \equiv \Delta/J_{pd}S > \delta_c(x)$  and second order for  $\delta < \delta_c(x)$ , with  $\delta_c(x)$  slightly larger than in the case of the bipolaron localization. This follows from the same consideration as in our previous discussion of equation (21).

The field sensitivity in the case of disorder-localized polarons is much lower than for the bipolarons. This stems from the different functional dependence of the chemical potential. The present approximations are valid in the limit  $y \ll 1$ , meaning that the polaron carriers are non-degenerate. In contrast to the case of the bound-polaron pair formation, in the impurity case the expression (34) for  $y$  is singular,  $y \propto 1/n$ , in the limit of small polaron density. This means that in the vicinity of the current-carrier-density collapse the value of  $y$  sharply increases in the case of polarons localized on impurities. As a result, the collapse becomes less pronounced, and transport becomes far less sensitive to an external field. We note also that equation (34) contains a factor depending on the external magnetic field in the denominator. This is in contrast with the case of bipolarons (28), where the field dependence is suppressed by a small factor  $\exp(-J_{st}/k_B T_c)$ . This field dependence, however, is small since always  $\mu_B H/k_B T_c \ll 1$ , and it quickly vanishes in the low-temperature phase when the exchange interaction sets in ( $m \neq 0$ ), as one can see from the expression for the parameter  $\zeta$  above. The singular behaviour of  $y$  as a function of the density for  $n \rightarrow 0$ , and the Zeeman splitting of the impurity states make the transition far less sensitive to the magnetic field. As a result, *no quantitative description of the experimental CMR data has been found with the localization of polarons due to disorder.*

## 9. Conclusions

In conclusion, we have developed a theory of the ferromagnetic–paramagnetic phase transition in doped magnetic charge–transfer insulators with a strong electron–phonon coupling. We have found that a few non-degenerate polarons in the p band polarize localized d electrons because of the huge density of states in the narrow polaronic band. For a sufficiently large p–d exchange  $J_{pd}S > \Delta$ , we have obtained a *current-carrier-density collapse* at the transition owing to the formation of immobile local pairs in the paramagnetic phase with the binding energy  $\Delta$  about twice that of the polaron level shift [15]. Depending on the ratio  $\Delta/(J_{pd}S)$ , the transition is first or second order [38].

We have explained the resistivity peak and the colossal magnetoresistance of doped perovskite manganites—figure 3—as the result of the current-carrier-density collapse due to the binding of polarons into local pairs (bipolarons). The density of these immobile pairs has a sharp peak at the 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 of p holes with the Mn  $d^4$  local moments, which tends to align the polaron moments and, therefore, breaks those pairs apart. The spin-polarized polaron band falls below the bipolaron band upon decrease in temperature, so all carriers are unpaired at  $T = 0$  if  $J_{pd}S - \Delta > W$ . Above  $T_c$ , the bipolaron density decreases because of thermal activation across the polaron binding energy. These competing interactions lead to the unusual

behaviour of CMR materials, the huge sensitivity of their transport to external field, and the very large negative magnetoresistance.

There is a crossover around the transition temperature from polaron tunnelling at low temperatures to polaron hopping, where the latter dominates at high temperatures. This explains the temperature behaviour of the resistivity over a wide temperature range around the transition. The ferromagnetic-to-paramagnetic transition is also accompanied by a sharp anomaly in the specific heat.

The present theory provides a natural explanation for the temperature-dependent gap feature in tunnelling spectra [24] and the giant isotope effect on the temperature of the ferromagnetic transition [16]. One of our main conclusions is that the highly polarized ferromagnetic phase of manganites is a polaron-doped semiconductor rather than a metal.

We expect the present theory to be general enough to also account for the giant magnetoresistance observed in pyrochlore manganites [47] and other systems [9]. It is worth mentioning in this regard that the present theory requires the presence of strong electron–phonon coupling of any origin, but it does *not* require the presence of Jahn–Teller distortions and/or the double-exchange mechanism. Note that the Jahn–Teller distortions and the double-exchange mechanism are certainly absent in, for instance, pyrochlore manganites, chromium spinels [9], and other CMR systems, so the ideas based on the double exchange cannot be applied there at all. It is believed that at least in perovskite manganites the local Jahn–Teller distortion may be involved in defining the crystal structure of the parent insulating phases [48], although tilting distortions of  $\text{MnO}_6$  octahedra are just a result of steric conditions [9, 49]. Apparently, the ratio of the sum of Mn and O ionic radii,  $r_{\text{Mn}} + r_{\text{O}}$ , and  $(r_{\text{La}} + r_{\text{O}})/\sqrt{2}$  (the misfit parameter) substantially differs from unity, thus making a cubic structure unstable and favouring a rotation of  $\text{MnO}_6$  octahedra [1, 49]. The tetragonal distortion of  $\text{MnO}_6$  is large; its symmetry corresponds to a notion of the Jahn–Teller local distortion. However, since the steric interaction is strong, it necessarily deforms the lattice, thus rendering the Jahn–Teller derivation, strictly speaking, inapplicable.

It is also believed that doping by divalent metals introduces holes into the  $\text{Mn}^{3+}$  d shell, since the doped systems are less distorted [50]. This argument, which may have supported the relevance of the double-exchange mechanism for at least perovskite manganites, contradicts the site-sensitive spectroscopic probes [22, 26], which show unambiguously that holes reside on O sites. It also neglects two important facts, that (i) the doping is heavy ( $\gtrsim 10^{21}$  carriers  $\text{cm}^{-3}$ ) and there is a substantial size difference between the impurity and host atoms and (ii) the O p holes are hybridized with the d states on  $\text{Mn}^{3+}$ , depending on the value of the charge-transfer gap. Both effects, together with screened Coulomb hole–hole repulsion, can apparently explain the observed changes in the lattice distortion upon doping without invoking the Jahn–Teller mechanism. These short-range interactions may well be responsible for the charge-ordered phases observed at some doping levels in manganites [9]. It would be interesting, in this regard, to perform quantum-chemical calculations of  $\text{MnO}_6$  clusters with holes doped onto O site(s).

Changes and the amount of disorder in the bond lengths are very important for characterizing the properties of polaronic systems. The reduction in bond-length distribution width as a result of cooling through  $T_c$  in doped manganites has been attributed to (at least partial) delocalization of doped carriers in the low-temperature ‘metallic’ phase. Since the data show that the carriers retain their polaronic character below  $T_c$ , and the residual width of the Mn–O bond-length distribution remains larger than that of  $\text{CaMnO}_3$  [50], where the Jahn–Teller  $\text{Mn}^{3+}$  ions are absent, the reduction of the width should be mainly related to instability of bipolarons in this temperature region. Breaking of polaron bound pairs below  $T_c$  may result in a reduction of bond-length distribution width, and we shall address this question elsewhere. It is worth repeating that whether or not the Jahn–Teller distortions play any role



in doped perovskite manganites and the exact location of the carriers are of no importance for the present scenario of the CMR.

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