

## A new theory of doped manganites exhibiting colossal magnetoresistance

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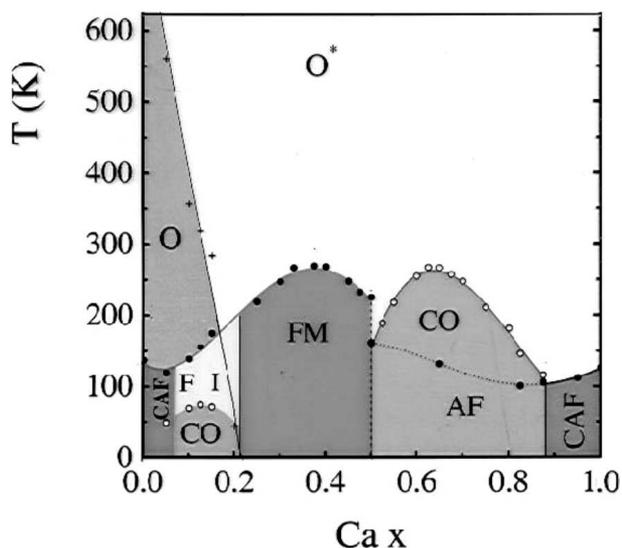
**Abstract.** Rare earth manganites doped with alkaline earths, namely  $\text{Re}_{1-x}\text{A}_x\text{MnO}_3$ , exhibit colossal magnetoresistance, metal insulator transitions, competing magnetic, orbital and charge ordering, and many other interesting but poorly understood phenomena. In this article I outline our recent theory based on the idea that in the presence of strong Jahn–Teller, Coulomb and Hund’s couplings present in these materials, the low-energy electronic states dynamically reorganize themselves into two sets: one set ( $\ell$ ) which are polaronic, i.e., localized and accompanied by large local lattice distortion, and another ( $b$ ) which are non-polaronic and band-like. The coexistence of the radically different  $\ell$  and  $b$  states, and the sensitive dependence of their relative energies and occupation upon doping  $x$ , temperature  $T$ , magnetic field  $H$ , etc., underlies the unique effects seen in manganites. I present results from strong correlation calculations using dynamical mean-field theory and simulations on a new 2-fluid model which accord with a variety of observations.

**Keywords.** Colossal magnetoresistance; manganites; Jahn–Teller polarons; strong correlation.

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### 1. Introduction

Doped perovskite manganites  $\text{Re}_{1-x}\text{A}_x\text{MnO}_3$ , where Re is a rare earth ion such as La, Pr, Nd etc., and A an alkaline earth ion, such as Ca, Sr, Ba etc., have been a focus of major research activity following the discovery [1] that their magnetoresistance is two or more orders of magnitude larger than in normal metals (colossal magnetoresistance or CMR). All of them show a bewildering variety of phases and phase transitions involving electronic, magnetic and structural changes [2–4] depending on the doping  $x$ , temperature  $T$ , and ionic species Re and A as well as external perturbations. For example, figure 1 shows the phase diagram of  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ . It has an insulating, Mn–O bond (Jahn–Teller) distorted but structurally ordered, antiferromagnetic phase for small  $x$ . There is a transition at low  $T$  first to a ferromagnetic insulator, next to a ferromagnetic metal at  $x \simeq 0.2$ , and thence to a charge ordered insulating phase for  $x \gtrsim 0.5$ . On heating the material in the regime  $0.2 \lesssim x \lesssim 0.5$ , the ferro-metal transforms to a paramagnetic insulator



**Figure 1.** The phase diagram of  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  in the doping  $x$  and temperature  $T$  plane (adapted from ref. [14]). Various kinds of antiferromagnetic insulator (AF), ferromagnetic insulator (FI), ferromagnetic metal (FM) and charge/orbitally ordered insulator (CO/OO\*) are shown. O and O\* are orthorhombic (Jahn–Teller distorted) and orthorhombic (octahedron rotated) structural phases. Both the O\* phase and the high temperature part of the O phase (i.e. that *not* marked CAF, FI/CO) are paramagnetic and insulating, namely PI.

above  $T_c \gtrsim 250$  K, with CMR near  $T_c$ . The phase diagram varies considerably with the ‘A-site’ ionic species. For example,  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  has a *paramagnetic metallic* phase for  $0.175 \lesssim x \lesssim 0.5$  and shows no charge/orbital order, while  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  has *no metallic phases (even ferromagnetic)* [2–4]. Two other characteristic features are very striking. First, physical properties are extremely sensitive to small perturbations; examples being the CMR itself, the unusually large strain and ion size effects [5–7], the ‘melting’ of the charge/orbital order for anomalously small magnetic fields and a metal-to-insulator transition induced by the electronically benign substitution of  $\text{O}^{16}$  by  $\text{O}^{18}$  [8]. Secondly, over a wide range of  $x$  and  $T$ , many experiments seem to show the coexistence [4] of two very different types of regions, one insulating and locally lattice distorted and the other metallic and undistorted. The regions can be static [9,10] or dynamic [10–12]; with sizes varying from 100 Å [13] to 3000 Å [9]. All these observations suggest that metallic and insulating phases are always very close in free energy.

The active degrees of freedom in the doped manganites are believed to be the two-fold degenerate  $e_g$  electrons and the  $t_{2g}$  core spins of Mn, and the Jahn–Teller (JT) optical phonon modes of the oxygen octahedra surrounding the Mn sites. There are three strong interactions present, namely the large on-site  $d-d$  repulsion  $U \simeq 5$  eV [15,16] amongst the  $e_g$  electrons, the large ferromagnetic Hund’s rule coupling  $J_H$  between  $e_g$  and  $t_{2g}$  spins ( $\simeq 1$  to 2 eV [15,16]), and the strong JT

mode –  $e_g$  electron coupling  $g$  which splits the doubly degenerate  $e_g$  level by about  $2E_{\text{JT}} \simeq 1 \text{ eV}$  [17,18]. All the interactions are larger than or comparable to the  $e_g$  electron kinetic energy scale (band width  $W \equiv 2D_0$  is  $\simeq 2 \text{ eV}$  [15,16]).

However, just the knowledge of these interactions does not lead to simple and obvious explanations of all the observed phenomena. For example, one expects that doping  $\text{LaMnO}_3$  (a Mott insulator) with Ca introduces mobile holes in the Mn-d band so that one should get a metal at least in the para/ferro phases; but one has an insulator till  $x \simeq 0.20$ . Most previous theoretical efforts [19–22,4] neglect one or the other of the interactions, make further approximations, and seem inadequate in one way or another. The earliest theoretical approaches [19], commonly referred to as double exchange theories, considered solely the Hund’s rule exchange  $J_{\text{H}}$ . One can account for the ferromagnetism in this way, as the  $e_g$  electrons gain the maximal kinetic energy if the Mn core spins are parallel, but then the doped phase is *always metallic*. A theory due to Millis, Mueller and Shraiman [20] additionally includes the effect of the JT coupling  $g$ , but treats the JT distortions classically, as annealed static disorder, and neglects  $U$ . A polaronic insulating phase does occur for large enough  $g$ , but for  $x \neq 0$ , one finds either metal–metal or insulator–insulator Curie transitions, unlike the commonly observed metal–insulator transition. The magnetoresistance is not colossal and there is no isotope effect. Dagotto and coworkers (see eg. ref. [4]) have done extensive numerical simulations of several models on finite sized lattices, and reported several instances of ‘phase separation’. The early simulations explored the competition between (double exchange induced) ferromagnetism and antiferromagnetic (super)exchange, amplification and generation of small-scale phase coexistence by disorder, and identified two kinds of magnetic domains with metallic and insulating regions. Later simulations explored similar issues including static JT couplings. Based on these, they suggested [4] that transport in manganites should be pictured in terms of a random resistor network arising from tunnelling between misaligned ferromagnetic metallic domains across insulating regions, and that the CMR arises from enhanced tunnelling due to field induced alignment of the magnetic domains. There are many other models designed to address specific effects, but there is no cohesive explanation of the novel general features of manganites.

I outline here a new approach to the physics of manganites developed by us recently [23–27] which we believe *takes into account all the three strong interactions, the double degeneracy of  $e_g$  orbitals as well as the quantum dynamics of phonons*. It leads to a simple physical description from which a qualitative understanding of many properties of manganites follows naturally, and detailed quantitative calculations of ground state and transport properties at finite temperatures can also be made.

## 2. Coexisting polaronic and band states and a new two-fluid model for manganites

Our theory is based on the key new idea that under the conditions present in the manganites, the electrons populating the doubly degenerate  $e_g$  states centered at the Mn sites spontaneously reorganize themselves into two types of electron fluids which coexist.

Our proposal is that for all doping  $x$  the majority of the  $e_g$  electrons form a fluid of localized polarons, which we label ( $\ell$ ). They are accompanied by strong local JT distortions with a magnitude  $Q_0$  ( $\simeq g/K$  in the large  $g$  limit, where  $K$  is the force constant for the JT phonons), thereby gaining local JT energy  $E_{JT}$  ( $\simeq g^2/(2K)$ ). The direction of the JT distortion, specified by an angle  $\Theta_i$ , which also determines the orbital state of the polaron, can vary from site to site, and even at a given site on long time-scales. In the metallic regime for  $x < 0.5$ , the orbital angles typically have only short range correlations, corresponding to an *orbital liquid* state. States with long range orbital order are also known, e.g., at  $x = 0.5$ . The quantum coherent hopping of the  $\ell$  polarons is much reduced because of the Huang–Rhys or JT-distortion wave-function overlap factor (by  $\eta \sim \exp\{-(E_{JT}/2\hbar\omega_0)\} \ll 1$  where  $\hbar\omega_0 \simeq 0.05$  eV is the JT optical phonon energy) and can be neglected to a first approximation.

The second  $e_g$  electron fluid is a fluid of broad band, non-polaronic electrons (labelled ( $b$ )) which are mobile through the solid, thereby gaining kinetic energy. There is a strong repulsion between the two fluids, as double occupancy on a polaronic site costs a large extra energy  $\bar{U} = (U+2E_{JT})$ . So the  $b$  electrons, which, as we show, are always small in number, mostly run around on the fraction  $[\sim x]$  of sites which are typically unoccupied and undistorted. Both types of electrons have a strong Hund's coupling  $J_H$  with the  $t_{2g}$  core spins. Over long time-scales, sites can exchange roles, between being hosts for  $\ell$  polarons and being empty and hosts for  $b$  electrons.

While the bare  $b$  hopping amplitude among neighboring (empty) sites is of order  $t$ , the effective bandwidth  $2D$  (lower Hubbard band) of the  $b$  electrons can get reduced much below its bare value  $2D_0$  ( $\sim 2zt$ ) because their motion is inhibited, due to  $U$ , by repulsion from the sites occupied by the  $\ell$  polarons, and due to  $J_H$ , by the misalignment of neighboring core spins (which can be due to thermal disorder, or antiferromagnetic correlations arising from super-exchange). Roughly,  $2D$  increases with  $x$  as well as with  $T^{-1}$  and  $H$ , because the inhibition of  $b$  hopping due to large  $\bar{U}$  is reduced when there are more hole-sites, and that due to large  $J_H$  is reduced when the  $t_{2g}$  spin order is enhanced. When  $D$  is smaller than  $E_{JT}$ , all the electrons prefer to be  $\ell$ -like and the system is an insulator, whereas when  $D$  becomes bigger than  $E_{JT}$  a small fraction of the electrons are converted to being  $b$ -like, and the system becomes metallic. This is consistent with the persistence of many JT distorted sites well inside the metallic regime seen in several experiments [10, 11]. The delicate dependence of the relative energies and numbers of the  $b$  and  $\ell$  electrons on doping  $x$ , temperature  $T$ , magnetic field  $H$ , etc., underlies the ubiquity of the insulator–metal transitions seen in the doped manganites. The high sensitivity of the physical properties of manganites to other perturbations such as strain and ion-size alluded to the above arises because the ( $\ell$ ) states, being localized and lattice distorted, are strongly influenced by such perturbations, which in turn affects the delicate relative stability of  $\ell$  and  $b$  states.

Finally, the existence of the localized polaronic  $\ell$  states *in the presence of large  $U$  and  $J_H$*  give rise to a *new, occupancy dependent, ferromagnetic nearest neighbour exchange coupling* between the  $t_{2g}$  core spins which we refer to as ‘virtual double exchange’. This comes about due to *virtual, fast (adiabatic) hopping* processes of the  $\ell$  electrons to neighboring sites and back, i.e., leaving the local lattice distortion unrelaxed, by paying an energy cost of  $2E_{JT}$  in the intermediate state. For large  $U$  this can happen only if the neighboring state is empty, and for large  $J_H$  only if the  $t_{2g}$  spins on the two sites are parallel. (Otherwise the energy of the intermediate state

increases by  $U$  and  $J_H$  respectively.) For  $E_{JT} \gg t$ , from second-order perturbation theory the interaction can be seen to be of the form

$$\left(\frac{\bar{t}^2}{2E_{JT}}\right) \frac{1}{2}(\hat{\Omega}_i \cdot \hat{\Omega}_j + 1)[n_{\ell i}(1 - n_j) + n_{\ell j}(1 - n_i)]. \quad (1)$$

Here, for simplicity we have ignored the dependence of the hopping amplitudes on the angles  $\Theta_i$  etc. (extensions in contexts with orbital ordering effects where one must include these are discussed in ref. [26]), and used an orbitally averaged effective hopping amplitude  $\bar{t} \sim t$ . We have also approximated the  $t_{2g}$  spins as classical spins of fixed length  $S = \frac{3}{2}$ , i.e.,  $\vec{S}_i = S\hat{\Omega}_i$  where  $\hat{\Omega}_i$  is a unit vector. The  $\frac{1}{2}(\hat{\Omega}_i \cdot \hat{\Omega}_j + 1)$  factor comes from large  $J_H$ , and the occupancy dependent terms comes from large  $\bar{U}$ . We believe that this term (and longer range extensions which become important if  $E_{JT}$  is not very large compared to  $t$ ) is crucially responsible for many features of doped manganites, in particular the ubiquitous appearance of ferromagnetic correlations upon doping.

The normal super-exchange coupling between  $t_{2g}$  core spins on neighboring sites is of order  $\bar{t}^2/U$ , and its sign depends on the nearest neighbor orbital correlations [28]. For example, in  $\text{LaMnO}_3$  it is antiferromagnetic along the  $c$  axis, and ferromagnetic in plane. Conventional double exchange can, in principle, explain metallic ferromagnetism in the manganites, but would be unable to account for ferromagnetism in their insulating phases in the absence of orbital correlations. The above mechanism yields a ferromagnetic coupling which is clearly much larger (as  $E_{JT} \ll U$ ), and therefore dominates the super-exchange for all intermediate doping, operates even in the insulating states and even in the orbital liquid phase. In a homogeneous orbital liquid approximation which seems appropriate in the orbital liquid regime, the above term translates to an effective, average ferromagnetic interaction roughly of order  $x(1-x)\bar{t}^2/(2E_{JT}S^2) \simeq 2\text{meV}$  for  $x = 0.3$ . Our calculations suggest that this *virtual double exchange due to the localized  $\ell$  electrons*, and not conventional double exchange due to mobile  $e_g$  electrons as hitherto believed, is the dominant source of ferromagnetism and of the ferromagnetic transition temperature  $T_c$  in the hole doped manganites, even in their metallic phases.

Based on the above ideas, and for the purposes of making detailed, quantitative calculations and predictions, we have proposed [23–25] the following new two-fluid model Hamiltonian for the orbital liquid regime of doped manganites:

$$\begin{aligned} H_{\ell b} = & -(E_{JT} + \mu) \sum_{i,\sigma} \ell_{i\sigma}^+ \ell_{i\sigma} - \mu \sum_{i,\sigma} b_{i\sigma}^+ b_{i\sigma} \\ & - \bar{t} \sum_{\langle ij \rangle, \sigma} b_{i\sigma}^+ b_{j\sigma} + \bar{U} \sum_{i,\sigma} n_{\ell i\sigma} n_{b i\sigma} + H_s. \end{aligned} \quad (2)$$

Here  $\ell_{i\sigma}^+$  and  $\ell_{i\sigma}$  create and destroy the JT polaronic state of energy  $-E_{JT}$  and spin  $\sigma$ , localized at site  $i$ . The broad band electrons, created by the operator  $b_{i\sigma}^+$ , have mean energy zero, and hop with the orbitally averaged effective amplitude  $\bar{t}$ . The two repel each other on site with energy  $U$ . The common chemical potential  $\mu$  is determined by the constraint that the filling, i.e., the average number of  $e_g$  electrons per site must be determined by the doping  $x$  according to

$$N^{-1} \sum_{i\sigma} (\langle n_{\ell i\sigma} \rangle + \langle n_{bi\sigma} \rangle) \equiv N^{-1} \sum_i (\bar{n}_{\ell i} + \bar{n}_{bi}) = (1-x). \quad (3)$$

The term  $H_s$  in eq. (2) models the spin-dependent interactions, and is given by

$$H_s = -J_H \sum_i \vec{s}_i \cdot \vec{S}_i - J_F \sum_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j - \gamma \sum_i \vec{S}_i \cdot \vec{h}. \quad (4)$$

It includes the strong ferromagnetic Hund's rule coupling  $J_H$  between the  $e_g$  spins  $\vec{s}_i$  ( $\equiv (\vec{s}_{\ell i} + \vec{s}_{bi})$ ) and the  $t_{2g}$  spins  $\vec{S}_i$ , a net effective ferromagnetic exchange coupling  $J_F$  between these  $t_{2g}$  spins (from the mechanism alluded to the above), and the interaction of the latter with an external magnetic field  $\vec{H}$ .

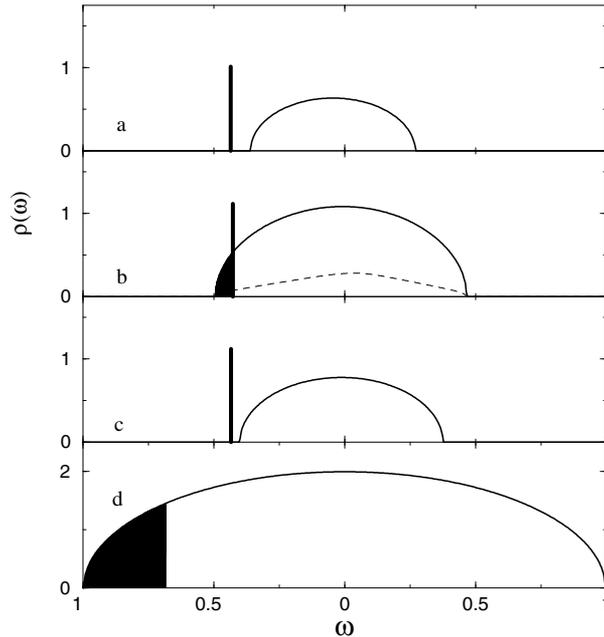
The above model Hamiltonian can be easily motivated from the microscopic Hamiltonian for the manganites in the limit of strong JT interaction. See refs [23,25] for a more detailed discussion. We believe that it is the appropriate low energy Hamiltonian in the orbital liquid regime, albeit with renormalized parameters, even when  $E_{JT}$  is of order  $t$  so that  $D_0 \gg E_{JT}$ . For, due to the competing effects of the various interactions such as  $U$ ,  $J_{AF}$  and filling, the motion of the  $e_g$  electrons gets inhibited leading to loss of kinetic energy, so the majority of the electrons would rather become localized polarons and gain JT energy even in this case.

### 3. DMFT of the two-fluid model, results and discussion

$H_{\ell b}$  is similar to the well-known Falicov–Kimball [29] model (FKM) for non-hybridizing localized ( $f$ ) electrons interacting with itinerant ( $d$  or  $p$ ) electrons. At  $T = 0$ , in the ferromagnetic phase, it reduces to the FKM. The  $b$  electrons hop in an annealed random medium, strongly repelled (repulsion  $\bar{U}$ ) from sites with static  $\ell$  electrons; hence for large  $\bar{U}$  their amplitude is largest on the hole sites. We assume that the randomness is homogeneous, i.e.  $\bar{n}_{\ell i} = \bar{n}_{\ell}$  and  $\bar{n}_{bi} = \bar{n}_b$  such that  $\bar{n}_{\ell} + \bar{n}_b = (1-x)$ . At  $T \neq 0$ , there is also annealed randomness in  $\Omega_i$ , which scatters  $b$  electrons via  $J_H$ . For strong  $U$  and  $J_H$ , we have solved this problem [23–25] using dynamical mean field theory (DMFT) [30] which is exact at dimensionality  $d = \infty$ , and is quite accurate for  $d = 3$ . We have calculated thermodynamic properties (the occupancies  $\bar{n}_{\ell}$ ,  $\bar{n}_b$ , the magnetization  $m \equiv \langle \vec{S}_i \rangle$ , the specific heat, etc.), spectral behavior (the  $b$  band self-energy, propagator, density of states (DOS), etc.) and transport (resistivity, magnetoresistance, optical conductivity, etc.). Results for a realistic tight binding band structure and for semicircular density of states with bare half bandwidth  $D_0$  are close. Here I present some results for the latter case where exact analytical results can be obtained in the  $U = \infty$ ,  $T = 0$  limit [24]. Whereas our specific results come from such calculations, many of the underlying physical mechanisms have a more general validity.

#### 3.1 Metal–insulator transitions

Figure 2 shows our results for the DOS for selected  $x$  and  $T$ . The effective  $b$  bandwidth  $2D$  vanishes as  $x \rightarrow 0$  for large  $U$  since the  $b$  electron is mainly at the  $xN$  hole sites. Thus for small  $x$ , the  $\ell$  level lies below the effective  $b$  band bottom;



**Figure 2.** Density of  $e_g$  electronic states (level  $\ell$  and band  $b$ ) for up-spin (full line) and down-spin (dashed line) for various values of doping  $x$  and temperature  $T$ , with parameters  $E_{JT} = 0.5$  eV,  $D_0 = 1.2$  eV,  $U = 5.0$  eV and  $J_F = 2.23$  meV. (a)  $x = 0.1$ ,  $T = 0$ ; ferromagnetic insulator. (b)  $x = 0.3$ ,  $T = 180$  K; ferromagnetic metal. (c)  $x = 0.3$ ,  $T = 350$  K ( $> T_c = 240$  K); paramagnetic insulator. (d)  $x = 0.8$  (electron doped),  $T = 230$  K; paramagnetic metal. The occupied states are indicated by a thick line ( $\ell$ ) or by black shading ( $b$ ). (Figure taken from ref. [25].)

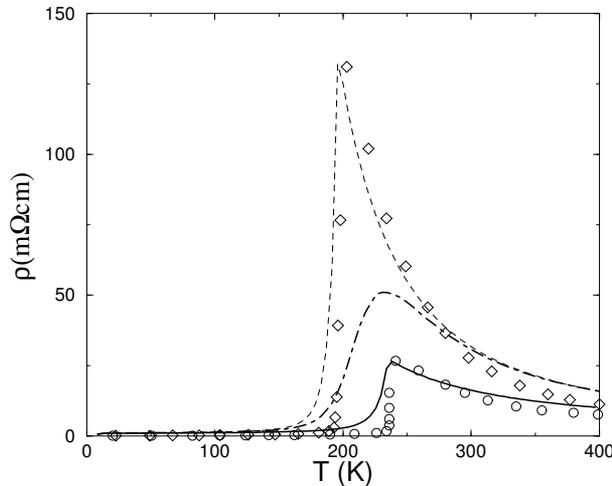
only the  $\ell$  states are occupied. Figure 2a shows the results for  $x = 0.1$  at  $T = 0$ , i.e., in the ferromagnetic ground state because of  $J_F$ . While the chosen  $E_{JT}$  is 0.5 eV, the self-consistently determined  $D$  is 0.42 eV  $< E_{JT}$ ; the system is a ferromagnetic insulator. This cannot happen in a pure double exchange model, where ferromagnetism and metallicity go together.

As  $x$  increases, so does  $D$ , whence  $D \rightarrow E_{JT}$  at a critical  $x_c$ , and we have a ferromagnetic metallic ground state for  $x > x_c$ . Figure 2b shows this for  $x = 0.3$  ( $> x_c = 0.17$  for the parameters used). Here both  $b$  band and  $\ell$  states are occupied, but most of the electrons (0.66 per site) are in the latter state though there is no long range JT order. Also, because  $T$  is non-zero, both spin-polarizations of the  $b$  band are now occupied. As the temperature increases,  $t_{2g}$  spins disorder, and reduce the effective  $b$  electron hopping via  $J_H$ , pushing the  $b$  band bottom above the  $\ell$  levels. Results for  $x = 0.3$  and  $T = 350$  K (figure 2c) show this. The system is now a paramagnetic insulator, with  $b$  states occupied thermally across a gap. This provides a simple picture of the thermally induced ferro-metal to para-insulator transition. For even larger doping (figure 2d), in the paramagnetic phase all the electrons become “ $b$ ” like, and one has a paramagnetic metal.

*3.2 Resistivity, CMR and material systematics*

Figure 3 shows the resistivity with model parameters chosen to fit  $T_c$  and  $\rho(T_c)$  data for  $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  [31]. The Curie and insulator to metal transition temperatures coincide because of strong feedback effects. As the  $t_{2g}$  spins align and  $m$  increases, so does the effective bandwidth  $D$ ; in turn, double exchange promoted ferromagnetism is stronger for larger  $D$ , so that  $m$  grows. The paramagnetic state is insulating, with an effective electrical gap  $\simeq 850$  K (the experimental value is  $\simeq 1250$  K [31]). The resistivity drops suddenly just below  $T_c$  as in experiment to a rather large value  $\simeq 2$  m $\Omega$  cm; but does not decrease much thereafter down to  $T = 0$  unlike experiments, where  $\rho(T)$  decreases to residual values of  $\simeq 50$   $\mu\Omega$  cm (11) below about  $T = 125$  K. We believe that the latter is due to inter-site  $\ell$  coherence, neglected here.

A small increase in  $2D_0$  reduces the high temperature resistivity  $\rho(T > T_c)$  enormously, as shown in figure 3 where we have increased  $D_0$  from 1.05 to 1.15 eV and  $J_F$  from 1.95 to 2.23 meV to fit  $T_c$  and  $\rho(T_c)$  for  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ . Broadly, this is because the density of current carrying  $b$  electrons and hence  $\sigma(T) = 1/\rho(T)$  depends exponentially on  $(E_{JT} - D_0)$ . This is also the general reason for the observed large variation of  $\rho(T > T_c)$  and  $T_c$  with strain and pressure. For example, the observed pressure variation [32] can be fitted assuming  $E_{JT}$  not to change, but  $D_0$  to increase with pressure at a reasonable rate of 0.01 eV/kbar. The cause of CMR



**Figure 3.** Electrical resistivity and CMR in the JT polaron and broad band model for  $E_{JT} = 0.5$  eV,  $U = 5$  eV and  $x = 0.3$ .  $D_0$  and  $J_F$  are chosen so as to reproduce the experimental [31]  $T_c$  and  $\rho(T_c)$  of  $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  ( $D_0 = 1.05$  eV,  $J_F = 1.95$  meV) and of  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  ( $D_0 = 1.15$  eV,  $J_F = 2.23$  meV). Full line: theory (LaCa); circle ( $\circ$ ): experiment (LaCa); dashed line: theory (NdSr); diamond ( $\diamond$ ): experiment (NdSr). Calculated  $\rho(T)$  at  $H = 7$  Tesla (dash-dotted line) is shown for  $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ . (Figure taken from ref. [25].)

is similar. A magnetic field aligns  $t_{2g}$  spins most effectively near  $T_c$ ; this alignment increases  $D$  via double exchange of  $b$  electrons and thus  $n_b$  exponentially. The calculated numbers for  $\rho(T)$  at 7 Tesla (figure 3) show that the magnetoresistance is indeed colossal. For a more detailed discussion of these results, as also the material systematics, see refs [23,25]. For example, we find that with increasing  $D_0$ , the Curie transition changes from insulator–insulator to insulator–metal to metal–metal. The fractional magnetoresistance decreases exponentially with increasing  $T_c$ . These trends are observed experimentally.

### 3.3 Other unusual properties

Several other unusual general properties of manganites can be understood in our theory. For example, the observed Drude weight in the metallic phase is small, corresponding to a carrier density  $n_{\text{eff}} \ll (1-x)$ , the  $e_g$  electron count. In our theory  $n_{\text{eff}} = \bar{n}_b$  which is very small (figure 2b). Our results for  $\bar{n}_b$  ( $T=0$ ) ( $\simeq 0.06$ ) and its strong decrease with temperature as  $T \rightarrow T_c$  agree closely with experiment for  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  [33]. Another example is of ‘electron-doped manganites’ with a low  $e_g$  electron density, which are better metals [34] *in the paramagnetic phase* than complementary ‘hole doped’ ones, contrary to expectation in naive small polaron models, where such systems should form a dilute polaronic insulator. What we find is that the  $b$  bandwidth is largest for low  $e_g$  electron density (negligible correlation effects) and the few  $e_g$  electrons present occupy the lowest  $b$  band states (figure 2d), the  $\ell$  level is empty and the system is a good metal in the paramagnetic state (unless prevented by possible Anderson localization).

Other unusual general effects such as ‘two phase coexistence’ and strong sensitivity to local lattice displacements also follow naturally from our model. As mentioned earlier, the former is due to the *simultaneous presence* of  $\ell$  (locally distorted, ‘insulating’) and  $b$  (undistorted, ‘metallic’) states, with very small energy differences (see figures 2b, 2c). The static or dynamic nature and the spatial range of the coexistence depend on  $x$ ,  $T$ , local lattice conditions, strain etc. The strong dependence of properties on the last two, an example being mesoscopic textures [5], is due to the fact that local environments strongly affect the energy, ‘shape’ (or orbital admixture) and inter-site overlap of the JT polaronic  $\ell$  states which are occupied over a wide range of  $x$  and  $T$ .

## 4. Concluding remarks

In principle, the JT distortion should be determined self-consistently and will vary with  $x, T$ , chemical species etc., and is not a fixed single octahedron constant as we have assumed. However, for  $x \lesssim 0.4$  (orbital liquid) and not too low temperatures, we believe that the latter assumption is reasonable.

Two approximations that we have made in our model are the neglect of inter-site  $\ell$  hopping, and the assumption that the system is an orbital liquid. The former can be included by adding to eq. (1) a term proportional to  $t\eta \sum_{\langle ij \rangle} (\ell_i^+ b_j + hc)$ . One consequence is that as polarons hop and form a band, the local JT effect becomes

dynamic below a temperature scale  $T^* \simeq 2z\eta\bar{t}/k_B \simeq 125$  K, as observed by several experimental probes [2–4]. Furthermore, the electrical resistivity  $\rho(T)$  due to scattering of  $b$  electrons by  $\ell$  polarons decreases below  $\sim 125$  K [35]. Finally, the giant isotope effect on  $T_c$  [35] is a consequence of inter-site  $\ell$  hopping. The latter leads to a ferromagnetic double exchange contribution to  $k_B T_c$  proportional to  $z\bar{t}\eta(1-x)$  which depends exponentially on  $M_0^{-1/2}$  since  $\eta = \exp[-\{E_{JT}/2\hbar\sqrt{K/M_0}\}]$ ; our estimate for  $[T_c(\text{O}^{16}) - T_c(\text{O}^{18})]$  is close to what is observed. A number of phenomena are characterized by long or short range orbital/charge order. These can be explored in our theory by considering the effect on the thermodynamics of relevant local quantities, i.e. orbital angles  $\Theta_i$ , and occupancies  $\bar{n}_{\ell i}$  and  $\bar{n}_{b i}$  (subject to the global constraint  $N^{-1} \sum (\bar{n}_{\ell i} + \bar{n}_{b i}) = (1-x)$ ).

*An unusual feature of the sharp polaron level at the Fermi energy in our model is that it has no prominent thermodynamic or spectroscopic manifestations.* Firstly, it does not lead to a large electronic specific heat; for, the internal energy  $U = [-E_{JT}n_\ell(T) + \int \epsilon \rho_b(\epsilon) f^-(\epsilon)]$  does not change much with  $T$  since  $(\Delta n_\ell/n_\ell) \lesssim 0.1$  and the few occupied  $b$  states have very nearly the same energy as  $-E_{JT}$  ( $(\Delta \epsilon_b/E_{JT}) \lesssim 0.05$ ; see figure 1b). We find a linear specific heat which is about that for a  $b$  band metal, as seen experimentally [3]. Secondly, no sharp  $\ell$ -like spectral feature is to be expected. The  $\ell$  excitation spectrum will be an incoherent continuum, starting from a weak (weight  $\propto \eta \simeq 1/200$ ) anti-adiabatic low energy part building up to adiabatic (Franck–Condon) higher energy features, as the fast removal of an  $\ell$  electron leads to highly excited lattice states (energy  $\sim 2E_{JT}$ ). Indeed, optical conductivity data in manganites do show [33] such an incoherent continuum.

Actually,  $H_{\ell b}$  by itself gives rise to macroscopic phase separation of  $\ell$  and  $b$  electrons. The homogeneous solution we have assumed in the DMFT is stabilized in a more realistic model which include long range Coulomb interactions with strength  $V_0$ , with repulsion between  $\ell$ - $\ell$ ,  $\ell$ - $b$  and  $b$ - $b$  electrons (treated in the Hartree approximation) and attraction between the  $\ell$  and  $b$  electrons and the (quenched) dopant ions. We have recently carried out [27] extensive simulations of such a model on finite lattices (of sizes up to  $20 \times 20 \times 20$ ). For realistic values of the long range Coulomb interaction parameter  $V_0$ , the simulation results are in excellent agreement with the above-described DMFT calculations made neglecting  $V_0$ . Furthermore, we find that the inhomogeneities encountered in such a realistic model exist only on the nano-scales that characterize the disorder due to doping. On longer length scales the system appears homogeneous, consistent with the DMFT description, but nevertheless exhibits colossal magnetoresistance as discussed above. This differs greatly from explanations [4] alluded to above, attributing the CMR to disorder frustrated large scale phase separation. It also suggests that the micro-scale inhomogeneities observed in doped manganites probably arise from extrinsic causes such as long-range strains arising from cracks, etc. For details, see ref. [27].

Finally, we have recently also extended [26] the 2-fluid ideas discussed above to include the effects of charge, orbital and antiferromagnetic order, as seen for example in the half-doped manganites. Starting from an adiabatic description of a reference JT distortion pattern that characterizes the phases with such order, we show that the two-fluid picture now emerges from a competition between canting of the core spins of Mn promoting mobile carriers and polaronic trapping of carriers

by JT *defects*. Using this we are able to provide explanations for such features as the magnetic field induced insulator–metal transitions and the smallness of the transition fields, as well as the observed asymmetry with respect to electron and hole doping of the half-doped materials, the insulator–metal transition on the electron doped side, and the persistence of insulating phases on the hole-doped side. For details see ref. [26].

In summary, we have argued that two types of electrons, one ( $\ell$ ) accompanied by local JT distortions (polaronic) and localized, and the other ( $b$ ) primarily moving on undistorted empty sites and extended, with well-separated time-scales coexist in manganites. We have proposed a new model based on these, including a new ‘virtual double exchange’ mechanism for ferromagnetism. Even a simple DMFT treatment of this model explains many aspects of manganites that were hitherto not well-understood. Extensions of theory including long range Coulomb interactions, inter-site  $\ell$ – $b$  coherence effects, charge and orbital ordering, etc., in progress, have the promise of providing a complete theory of manganite physics.

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