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Colossal magnetoresistance manganites: A new approach[¶]

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Abstract. Manganites of the $LA_{1-x}Ca_xMnO_3$ family show a variety of new and poorly understood electronic, magnetic and structural effects. Here we outline a new approach recently proposed by us, where we argue that due to strong Jahn–Teller (JT) coupling with phonons the twofold degenerate e_g states at the Mn sites dynamically reorganize themselves into localised, JT polarons ℓ with exponentially small inter-site hopping, and band-like, nonpolaronic states b, leading to a *new 2-band model for manganites* which includes strong Coulomb and Hund's couplings. We also discuss some results from a dynamical mean-field theory treatment of the model which explains quantitatively a wide variety of experimental results, including insulator–metal transitions and CMR, in terms of the influence of physical conditions on the relative energies and occupation of the ℓ and b states. We argue that this microscopic coexistence of the two types of electronic states, and their relative occupation and spatial correlation is the key to manganite physics.

Keywords. Manganites; colossal magnetoresistance; strongly correlated electron systems; metal–insulator transitions and other electronic transitions; Jahn–Teller polarons and electron–phonon interaction.

1. Introduction

In this paper we outline the main ideas and some results from a new theory of doped manganites proposed recently by us, after a brief introduction. More details can be found in references [1–4].

The discovery of colossal magneto-resistance in $La_{0.7}Ca_{0.3}MnO_3$ nearly a decade ago[5] has triggered an explosion of interest in rare earth manganites doped with alkaline earths, namely $Re_{1-x}A_xMnO_3$ (Re – rare earth, A – alkaline earth). They show a bewildering variety of intertwined electronic, magnetic and structural phenomena[6,7] such as: metal–insulator transitions both as a function of x and temperature T, with the latter accompanied by ferromagnetic Curie transition and colossal magneto-resistance (CMR), two or more orders of magnitude larger than normal; charge/orbital ordering and its melting for

[¶]Dedicated to Professor C N R Rao on his 70th birthday

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anomalously small magnetic fields; giant isotope effect on T_c. Two new features common to these systems are the following. First, two very different 'phases', one insulating, with lattice distortion, and another metallic, without lattice distortion, coexist over a wide range of x and T on length scales ranging from of 10 to 10^3 Å; the coexistence can be static or dynamic.[8] Secondly, physical properties are extremely sensitive to small changes at all length scales.[9] This complex behaviour is a major challenge to our understanding of solids. Three strong local interactions involving the e_g electrons, namely the ferromagnetic Hund's rule exchange coupling J_H between e_g and t_{2g} spins, their interaction of strength g with Jahn–Teller (JT) phonons, and coulomb correlation U are believed to be responsible for the phenomena, but in ways that have so far not been very clear.

The earliest theoretical approaches,[10] commonly referred to as double exchange theories, considered solely the Hund's rule exchange J_H. However, only a metallic state is possible in this case. A theory due to Millis, Mueller and Shraiman[11] additionally included the effect of the coupling g, but treated the local *JT* lattice distortion classically, as annealed static disorder, and neglected U. A polaronic insulating phase also occurs now for large enough g, but the predicted results do not resemble experiments; for example at $x \neq 0$, one finds only metal–metal or insulator–insulator Curie transitions, unlike the commonly observed metal–insulator transition. The magneto-resistance while large is not colossal and there is no isotope effect. There are many other models designed to address specific effects, but no theoretical ideas which explain the novel general features of manganites cohesively.

We have recently proposed a new approach which includes the most crucial effects of all the three strong local interactions, starting with the coupling of the e_g electrons to *JT* phonons. If the *JT* modes are treated quantum-dynamically and not classically,[11] this coupling leads to a lattice polaronic state at each site, which we label ℓ, with negligible inter-site hopping between these due to the exponentially small overlap[12] of the initial and final state phonon wavefunctions at the polaron site. Since the e_g orbital at each site is doubly degenerate initially, there is another orthogonal set of states which we label b, which have their largest amplitudes at the fraction (x or more) of hole sites where the polaron is not, since their occupancy on the polaron site costs a large mutual repulsion U. The (bare) hopping amongst these b states is not reduced and they form a broad band whose properties are strongly affected by the other two strong interactions present in the system, namely the on site repulsive scattering from the ℓ polarons (U) and the coupling to the t_{2g} spins (J_H). The inevitable atomic level occurrence of these two very different kinds of states is, we believe, the essential new feature of manganites. We outline below how such a description can arise from a conventional microscopic model of e_g electrons and lattice phonons with the interactions mentioned above.[13] On the basis of this we have proposed a new, correlated, Falicov–Kimball[14] like two electron species model for manganites and calculated a number of results using dynamical mean field theory (DMFT). These compare very well with experiments. So as to bring out most clearly the implications of the model, we have ignored spatial correlations of the orbital structure or of the occupancies of the ℓ/b electron states at different sites and also the weak intersite coupling of ℓ polarons. The results obtained are thus for a homogeneous orbital liquid phase which is appropriate for $0{\cdot}1 \lesssim x \lesssim 0{\cdot}5$, and for not too low temperatures. Our theory can be extended to include spatial correlations and intersite ℓ coherence.

2 Coexisting polaronic and band states and a new model Hamiltonian for manganites

The electron JT phonon coupling has the Hamiltonian $H_{JT} = \sum_i H^i_{JT}$ with $H^i_{JT} \equiv g a^+_{i\alpha s} \boldsymbol{\tau} \cdot \mathbf{Q} i a_{i\alpha s}$, where a_{ias} with $\alpha = 1, 2$ create e_g electrons with spin s in the two degenerate e_g orbitals, namely $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ respectively, at site i. $\mathbf{Q}_i$ [$= (Q_{iz}, Q_{ix})$, or in polar coordinates, (Q_i, q_i)] labels the displacement of the *JT* modes at site i. We model the *JT* modes as Einstein oscillators, with force constant K_0 and frequency ω_0. $\mathbf{Q}_i$ is like a local pseudo-magnetic field splitting the pseudo-spin ½ levels α, hence H^i_{JT} has eigenvalues $\pm gQ_i$. In the basis of the corresponding eigenstates,[13] (which depend on q_i), we can write $H^i_{JT} = gQ_i(\tilde{\ell}^+_{is}\tilde{\ell}_{is} + b^+_{is}b_{is})$. The state $|\tilde{\ell}\rangle$ corresponding to the eigenvalue $-gQ_i$ leads to a local lattice instability when occupied, generating a *JT* polaron ℓ, with a lattice potential energy minimum of $E_{JT} = g^2/2K_0$ at a displacement $Q_0 = g/K_0$. The lattice potential for an electron in the state $|b\rangle$ (orthogonal to $|\tilde{\ell}\rangle$ and corresponding to the eigenvalue $+gQ_i$) has a minimum at $Q_i = 0$.

For large Q_0 i.e., for $(E_{JT}/2\hbar\omega_0) \gg 1$, hopping involving the ℓ polaronic states is reduced by the phonon overlap or Huang Rhys[12] factor $\eta = \exp-(E_{JT}/2\hbar\omega_0)$ even if the bare electrons are adiabatic. Since one has $(E_{JT}/2\hbar\omega_0) \simeq 5$ or 6 for $LaMnO_3$ (which has $E_{JT} \simeq 0{\cdot}7$ to 1 eV, and $\hbar\omega_0 \simeq 0{\cdot}07$ eV; see for example ref. 15), the effective ℓ electron intersite hopping $t^* \simeq t\eta \simeq (t/200) \simeq 12$ K is very small, corresponding to a bandwidth $2D^* = 2zt^* \simeq 150$ K. As a first approximation we neglect it altogether. By contrast, the intersite hopping $t_{ij}(q_i, q_j)$ within the manifold of b states is not reduced, so that they form a broad band (of width $\simeq 2$ eV). For the orbital liquid phases considered here, the hopping $t_{ij}(q_i, q_j)$ can then be averaged over the distribution of angles (either thermal or quantum mechanical or both, the latter being due to the lattice kinetic energy term which goes as $\dot{q}_i^2$) leading to an effective nearest neighbour hopping amplitude $\bar{t}$. Thus our picture is that, in manganites, polarons (ℓ) accompanied by large local *JT* lattice distortions persist into the metallic regime ($x \lesssim 0{\cdot}3$, $150\text{ K} \lesssim T \lesssim T_c$), which is consistent with fast local measurements,[16] and furthermore, that they coexist with band-like (b) electrons.

Under the above conditions, we propose that the electronic and magnetic properties of manganites can be described by the following *new model Hamiltonian*,[13] which we label $H_{\ell b}$:

$$H_{\ell b} = -E_{JT}\sum_{is}\ell^+_{is}\ell_{is} + \sum_{is}b^+_{is}b_{is} - m\sum_{is}(n_{\ell is} + n_{bis})$$

$$+U\sum_{is}n_{\ell is}n_{bis} - J_H\sum_i \mathbf{s}_i\cdot\mathbf{S}_i - J_F\sum_{\langle ij\rangle}\mathbf{S}_i\cdot\mathbf{S}_j + g\,\mathbf{H}\cdot\sum_i\mathbf{S}_i\ . \qquad (1)$$

Equation (1) contains *all the three strong local interactions*. The *JT* coupling reorganises the e_g states into localised polaronic and band states (ℓ, b). The former gains the *JT* energy E_{JT}. The two other strong interactions, namely U and J_H ($\simeq 5$ eV and 2 eV respectively, see ref. 17) are explicitly present in (1). We work in the large J_H limit, whence the e_g spins are forced to be parallel to the t_{2g} spins, so that only the coulomb repulsion between parallel spin ℓ and b electrons retained in (1) is relevant.

Our model Hamiltonian also includes a *new, doping dependent ferromagnetic* exchange J_F that is *made possible by the JT effect, large J_H and large U.* It arises from a 'virtual double exchange' process, in which an ℓ electron at site i hops *quickly to an empty nearest neighbour site j* and back, the intermediate state energy due to the *unrelaxed lattice distortion* being $2E_{JT}$. We find[13] $J_F \simeq \bar{t}^{\,2}(1-x)x/(2E_{JT}S^2)$. The last term in (1) is the coupling to the external magnetic field, ignoring the smaller contribution from e_g spins. The chemical potential is determined by the global constraint on the total number of electrons ($(1-x)$ per site). Since we assume the system is homogeneous, this constraint becomes local, i.e.

$$\langle n_{\ell i}\rangle \equiv \bar{n}_\ell\,,\ \langle n_{bi}\rangle \equiv \bar{n}_b \quad \text{with} \quad \bar{n}_\ell + \bar{n}_b = (1-x). \tag{2}$$

3. Results and discussion

We solve the Falicov–Kimball like model (1) exactly in the dynamical mean field theory (DMFT) or CPA, exact for $d = \infty$.[13,18] We assume the t_{2g} core spins to be classical, i.e. $\mathbf{S}_i = \mathbf{S}\hat{\Omega}_i$ where $\hat{\Omega}_i$ are unit vectors, treat the interaction between them in the Curie-Weiss mean field approximation, and work in the $J_H \to \infty$ limit (since $SJ_H/\bar{t} \gg 1$). The local self energy $\Sigma_{ii}(\omega)$ of the b electrons and the mean magnetization $m = \langle\hat{\Omega}_i\rangle$ are determined self-consistently. Then we calculate the b electron propagator $G_{ij}(\omega)$ and thus the spectral density or the b density of states (DOS) which decides the relative occupation of the ℓ and the b states. We also calculate the current–current correlation function (the Kubo formula) which determines the electrical (and optical) conductivity, as it can be expressed entirely in terms of $G_{ij}(\omega)$, vertex corrections being negligible for $d = \infty$. The DMFT results are quite accurate for $d = 3$, since spatial correlations involving different sites are small for the orbital liquid discussed here. We describe below some of the results obtained by us for the model (1) using the above procedure.[13,18]

Our results for the DOS for different values of x and T are shown in figure 1, the other parameters being $E_{JT} = 0{\cdot}5$ eV, the bare b bandwidth $2D_0 = 2{\cdot}4$ eV, $U = 5{\cdot}0$ eV and $J_F = 2{\cdot}23$ meV. The *effective b bandwidth* $2D$ of the re-normalised DOS vanishes as $x \to 0$ for large U, so that for small x the b band bottom lies above the ℓ levels. Only the latter are thus occupied and the system is an insulator (e.g. figure 1a), ferromagnetic because of the exchange term J_F. This is not possible in a pure double exchange model where ferromagnetism and metallicity go together.[6,7,10,19] As x increases, so does D, and beyond a critical x_c for which $D = E_{JT}$, the low temperature state is a ferromagnetic metal, with both b and ℓ states occupied though most of the e_g electrons are in the latter state [e.g. for $(1-x) = 0{\cdot}7$, $\bar{n}_l = 0{\cdot}66$ and $\bar{n}_b = 0{\cdot}04$ in figure 1b]. For this doping, as T increases, the t_{2g} spins disorder, the effective b electron hopping decreases (conventional double exchange), and D decreases enough that the system becomes an insulator (figure 1c). The transition occurs very close to the Curie temperature because of the strong positive feedback between D and the magnetization m. The carriers in the paramagnetic insulating state are b electrons excited across a relatively small effective band-gap.

Our theory also gives a very good account of transport properties. Figure 2 shows the electrical resistivity with the model parameters (given in the caption) chosen to fit T_c and $\rho(T_c)$ for $Nd_{0{\cdot}7}Sr_{0{\cdot}3}MnO_3$ and $La_{0{\cdot}7}Ca_{0{\cdot}3}MnO_3$. We clearly see the sharp paramagnetic insulator (PI) to ferromagnetic metal (FM) transition in the NdSr case, the former having an effective electrical gap of ~ 850 K (the experimental value is $\simeq 1250$ K).[20] The resistivity drops just below T_c to about 2 mΩcm, characteristic of a strongly disordered

metal. Experimentally, the resistivity decreases from about this value to ~ 50 $m\Omega$cm well below a characteristic temperature $T^* \simeq 150$ K. We believe that the latter effect is due to intersite ℓ polaron coherence neglected here, which reduces b electron scattering. A small increase in the bare bandwidth $2D_0$ reduces the high temperature ($T > T_c$) resistivity enormously, as shown in figure 2 where D_0 is increased from 1·05 to 1·15 eV and J_F from 1·95 to 2·23 meV, the parameters being appropriate for the NdSr and LaCa cases respectively. The broad reason is that the carrier (b electron) density and hence $\sigma(T) = [\rho(T)]^{-1}$ depends exponentially on $(E_{JT} - D)$. This is also the reason for the extremely strong dependence of $\rho(T)$ and the metal insulator transition T_c on pressure[21] which can be fitted assuming D_0 to increase with pressure at a reasonable rate of 0·01 eV/kbar while E_{JT} is constant. Colossal magnetoresistance is also due to the field induced t_{2g} spin alignment (maximum near T_c) increasing D and thus $\bar{n}_b$ or $\sigma(T)$ exponentially. Our results for $\rho(T)$ at 7 Tesla show this. Details of these calculations and the materials systematics are discussed elsewhere.[1–4] For example with increasing D_0, the Curie transition changes from insulator–insulator to insulator–metal and then to metal–metal. The fractional magnetoresistance decreases exponentially with increasing T_c. Both trends are observed experimentally.

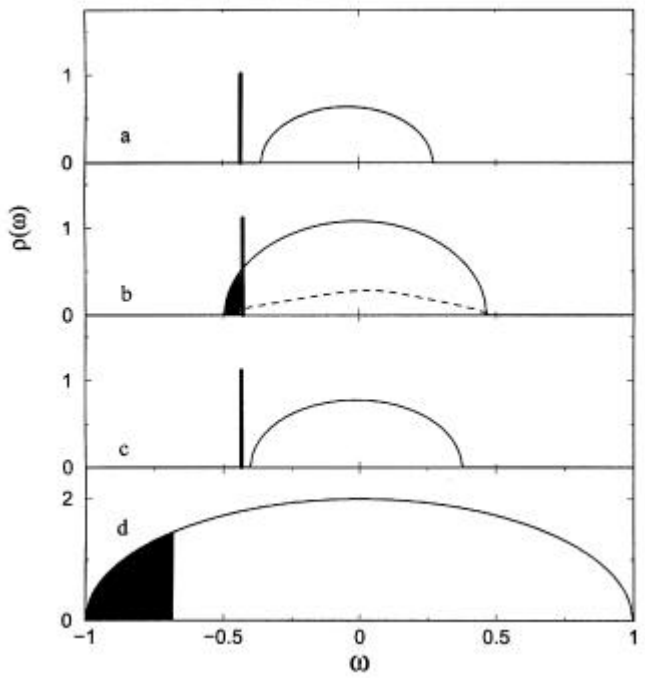

Figure 1. Density of states for the b band for up-spin (full line) and down-spin (dashed line) for various values of doping x and temperature T, with parameters $E_{JT} = 0{\cdot}5$ eV, $D_0 = 1{\cdot}2$ eV, $U = 5{\cdot}0$ eV and $J_F = 2{\cdot}23$ meV. (a) $x = 0{\cdot}1$, $T = 0$; ferromagnetic insulator. (b) $x = 0{\cdot}3$, $T = 180$ K; ferromagnetic metal. (c) $x = 0{\cdot}3$, $T = 350$ K ($> T_c = 240$ K); paramagnetic insulator. (d) $x = 0{\cdot}8$ (electron doped), $T = 230$ K; paramagnetic metal. The occupied b states are indicated by black shading and the effective ℓ level by a thick line. (Figure adapted from ref. 1.)

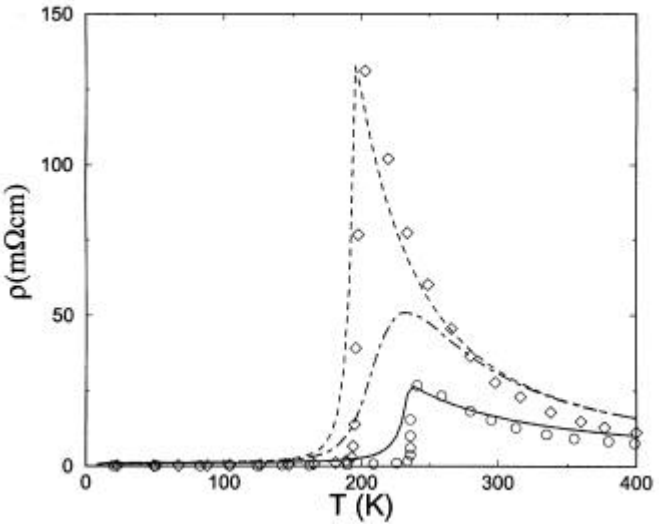

Figure 2. Electrical resistivity and CMR in the *JT* polaron–broad band model for $E_{JT} = 0{\cdot}5$ eV, $U = 5$ eV and $x = 0{\cdot}3$. D_0 and J_F are chosen so as to reproduce the experimental[20] T_c and $\rho(T_c)$ of $Nd_{0{\cdot}7}Sr_{0{\cdot}3}MnO_3$ ($D_0 = 1{\cdot}05$ eV, $J_F = 1{\cdot}95$ meV) and of $La_{0{\cdot}7}Ca_{0{\cdot}3}MnO_3$ ($D_0 = 1{\cdot}15$ eV, $J_F = 2{\cdot}23$ meV). Full line: theory (LaCa); circle (○): experiment (LaCa); dashed line: theory (NdSr); diamond (◇): experiment (NdSr). Calculated $\rho(T)$ at $H = 7$ Tesla (dash-dotted line) is shown for $Nd_{0{\cdot}7}Sr_{0{\cdot}3}MnO_3$. (Figure taken from ref. 2.)

A number of specific as well as general properties of manganites follow from our theory. The small weight of the Drude peak in the measured optical conductivity $\sigma(\omega)$ of metallic manganites[22] corresponds to an effective carrier density per site $n_{\text{eff}} \simeq 0{\cdot}06$ and decreasing strongly towards zero as $T \to T_c$, whereas its bare value is $(1 - x) \simeq 0{\cdot}7$ and independent of temperature. In our model the low frequency $\sigma(\omega)$ is due only to the b electrons since the ℓ polarons contribute only to a mid-infrared ($\hbar\omega \simeq 2E_{JT}$) peak. Hence $n_{\text{eff}} \simeq n_b$, which is indeed of the observed order of smallness, and furthermore decreases with T and reaches a minimum at T_c, as suggested by figures 1b and c and borne out by detailed calculations[1–4] of $\bar{n}_b(T)$. The strong electron hole asymmetry of manganites, e.g. the metallic character[23] of the paramagnetic phase in the electron doped regime ($(1 - x \simeq n_e \ll 1)$ is a puzzle, since with strong local *JT* coupling, the few carriers should form a dilute polaronic insulator. However, in our picture, in this limit the b band is uncorrelated and the broadest possible, the few carriers present occupy its lowest states as depicted in figure 1d; there are no ℓ polarons or lattice distortions and the system is indeed a metal.

The observed ubiquitous coexistence of two 'phases',[8] one insulating and lattice distorted, and the other metallic with no lattice distortion is rooted in the necessary presence of localized polaronic (ℓ) and band (b) states at the atomic level. Their static or dynamic spatial correlation is determined by their local dynamics and energetics as well as by lattice energies. These are influenced by x, T, global or local strain e.g. octahedral rotation, global anharmonicity, disorder, and intersite ℓ hopping. The other, connected, general property of manganites, namely extreme sensitivity to small changes,[9] is due to the relative balance of b and ℓ states being affected by small perturbations as seen above

(e.g. in CMR, and the large pressure dependence of T_c), as well as to the small bandwidth of polarons, and their strong coupling the lattice leading easily to very slow dynamics, glassiness etc.

Our approach can be extended to describe short or long-range charge/orbital order and intersite ℓ coherence. For the former one needs to explore the dependence of the thermodynamics via (1) on local degrees of freedom e.g. orbital angles θ_i, average occupancies $n_{\ell i}, n_{bi}$ and their spatial correlations. As lattice distortions, strain, disorder, coulomb interactions, anharmonicities, breathing modes etc. also couple to the above degrees of freedom, such terms need to be added as necessary to the Hamiltonian of (1). Intersite ℓ coherence arises essentially from the term $\tilde{t}\eta\sum_{\langle ij\rangle,s}(\ell_{is}\, b^{+}_{js} + hc)$, i.e. the hopping of an ℓ polaron to a b state on the next site. This term needs to be added to (1). Qualitatively, we see that ℓ polarons can then form a band of narrow width $2D^* = 2z\tilde{t}\,\eta \equiv k_B T^*$ with $T^* \simeq 150$ K. This accounts for the drop in resistivity seen in experiments[24] from $\rho(T \lesssim T_c) \sim 1$ or 2 mΩcm to about 50 mΩcm well below T^*. For $T \lesssim T^*$, since the ℓ polarons hop, the Jahn Teller effect is necessarily dynamic (unless there is long range orbital order), as seen by many probes.[6,25] Finally, we believe it is the origin of the giant isotope effect, since ℓ polaron hopping makes a double exchange contribution $T_c^l \simeq k_B^{-1} z\tilde{t}\eta(1-x)$ to the ferromagnetic T_c. This depends exponentially on $M_0^{1/2}$ because of the polaronic narrowing $\eta = \exp-(E_{JT}/2\hbar\sqrt{K_0/M_0})$. Our estimate for $\Delta T_c^{\ell} = T_c^{\ell}(O^{16}) - T_c^{\ell}(O^{18})$ is close to what is observed. The $\ell - b$ hybridisation is strongest in a metal because in it both the states are degenerate in energy; this broadens the ℓ band and thus reduces the polaronic distortion Q_0 which broadens the ℓ band further by increasing η. Because of this feedback, it is possible that *JT* polarons weaken and disappear deep in the metallic phase rather than becoming merely dynamic.

The *JT* polaron picture developed here differs from the one orbital Holstein polaron models often used. A broad b band is necessarily present here because of the critical double degeneracy of the e_g orbital. A classical treatment of the symmetry breaking *JT* lattice distortion leads[11] to *JT* polaron bands, as well as hole and 'anti'-*JT* bands all of comparable width. In our dynamical *JT* phonon picture, the former band (ℓ) is exponentially narrow, while the latter two merge into one broad b band. The consequences, as we have shown, are close to observations.

A general question of interest is the adiabatic to anti adiabatic crossover in a two $d(e_g)$ orbital model as g increases, and the conditions of coexistence of ℓ and b like states with exponentially separated timescales. We have argued that this happens in manganites and have explored the consequences in a simple model. There ought to be such a timescale/ energy separation in other systems with degenerate orbitals and strong symmetry breaking *JT* coupling, e.g. other oxides, organic solids and molecules.

Acknowledgements

We are particularly happy to make this contribution to the Special Issue of the Proceedings of the Indian Academy of Sciences as a part of the activities marking the seventieth year of Professor C N R Rao's life. This is because about nine years ago, Professor Rao started exploring manganites and with his discoveries, his infectious interest, as well as his unique gift for inspiring and continuing collaborations, made Bangalore a leading centre of research in this field. Our interest in the fascinating world of manganites and our knowledge of it owes much to this sustained effort. Over this long period, we came to realize that while the ingredients (the strong interactions present)

were known, how they give rise to the wide variety of strange behaviour was not, which motivated us to develop the theory outlined above.

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