PREPRINT

Zero Temperature Insulator-Metal Transition in Doped Manganites

G. Venketeswara Pai[1,2](*), S. R. Hassan[1,3](**) H. R. Krishnamurthy[1,3](***), and T. V. Ramakrishnan[1,3](*)

[1] *Centre for Condensed Matter Theory, Department of Physics, Indian Institute of Science, Bangalore - 560012, India*

[2] *The Abdus Salam International Centre for Theoretical Physics, Strada Costiera 11, 34014 Trieste, Italy*

[3] *Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore-560064, India*

PACS. 75.30.Vn – Colossal Magnetoresistance.

Abstract. – We study the transition at $T = 0$ from a ferromagnetic insulating to a ferromagnetic metallic phase in manganites as a function of hole doping using an effective low-energy model Hamiltonian proposed by us recently. The model incorporates the quantum nature of the dynamic Jahn-Teller(JT) phonons strongly coupled to orbitally degenerate electrons as well as strong Coulomb correlation effects and leads naturally to the coexistence of localized (JT polaronic) and band-like electronic states. We study the insulator-metal transition as a function of doping as well as of the correlation strength U and JT gain in energy E_{JT}, and find, for realistic values of parameters, a ground state phase diagram in agreement with experiments. We also discuss how several other features of manganites as well as differences in behaviour among manganites can be understood in terms of our model.

The colossal magneto-resistance(CMR) exhibited by manganites ($Re_{1-x}A_xMnO_3$, $Re = La, Nd, Pr$ *etc.* and $A = Sr, Ca, Ba$ *etc.*) for a range of hole doping x around $x \sim 0.3$ and near the Curie temperature T_c, where they undergo a transition from a low temperature ferromagnetic metallic phase to a high temperature paramagnetic insulating phase, has led to a great deal of interest [1, 2] in these systems, which also show a variety of other interesting phenomena such as charge and orbital ordering and incipient phase separation. The interplay of orbital degeneracy of the itinerant e_g electrons of Mn, their coupling to lattice degrees of freedom, especially to degeneracy removing Jahn-Teller(JT) phonons, strong Coulomb correlation effects and related Hund's rule coupling (between the e_g electrons and the t_{2g} core spins of Mn) are believed to be responsible for these phenomena, but achieving a detailed theoretical understanding has been a major challenge.

We have recently proposed [3, 4] a new effective low-energy Hamiltonian starting from the two qualitatively different coexisting vibron [5] states at the each site of the lattice, one

(*) Email : venkat@ictp.trieste.it
(**) Email:hassan@physics.iisc.ernet.in
(***) Email:hrkrish@physics.iisc.ernet.in
(*) Email: tvrama@physics.iisc.ernet.in

consisting of localized JT polarons [6], which we label ℓ, and the other, which we label b, dispersive and forming a broad band as outlined below. In the presence of strong correlation U and ferromagnetic Hund's rule coupling J_H on site between e_g and t_{2g} spins this leads [3, 4] to a consistent description of many known features of these systems such as the finite temperature insulator metal transition (IMT) near T_c for a range of x, CMR, the existence of a ferromagnetic insulating phase at low doping, good metallic behaviour of electron doped systems, etc., and a heuristic understanding of several other features, such as the isotope effect on T_c and the *two-phase coexistence* seen by a variety of experimental probes over a range of x and T [2, 7]. In this paper, we present in detail our theory for the *ground state behaviour of manganites in the ferromagnetic state* as a function of doping x (for $x < x_{co}$ where charge ordering occurs) in terms of the Falicov-Kimball model (FKM) [8] involving the ℓ and b states.

The un-doped compound, eg. $LaMnO_3$ is an $Mn-O$ bond (JT) distorted but structurally ordered, A-type anti-ferromagnetic insulator with ferromagnetic order of the t_{2g} spins in plane (defined by the JT distortion pattern) and anti-ferromagnetic order perpendicular to it. On hole doping, say with Sr, anti-ferromagnetism disappears at $x = x_{c1} = .08$ and the ground state is a ferromagnetic insulator till $x = x_c = .16$, beyond which it is a ferromagnetic metal. For $LaCa$, $x_{c1} = 0.1$ and $x_c = 0.18$ whereas for $NdSr$, $x_{c1} = 0.18$ and x_c is not accurately known. The occurrence of the fully ferromagnetic insulating phases and the IMT at such large values of x cannot be understood in a model for manganites with only e_g electron double exchange caused by J_H [1, 9]. For, since doping generates holes (unoccupied sites) in the e_g band, one expects a metal especially when the t_{2g} spin alignment is ferromagnetic, since the e_g electrons can then move without hindrance. This is true even for large U.

We outline below (see ref. [3] for details) how the FKM [8] describing the correlated ℓ and b states arises in the context of manganites at $T = 0$ from a conventional lattice model with two e_g orbitals per site, large electron JT phonon coupling g and perfect spin alignment resulting from a *new ferromagnetic 'virtual double exchange' coupling* J_F. We treat it using dynamical mean field theory (DMFT) [10], and show that the b band has a *reduced effective width*, $2D$, roughly equal to $\sqrt{x}$ times its bare width $2D_0$ for large U. Hence, below a critical doping x_c the b band bottom lies above the localized JT polaronic ℓ levels of energy $-E_{JT}$, which are then the only ones occupied, leading to an insulator. For larger x, the b-band bottom lies below the ℓ level, so the system is metallic. The ferromagnetism is largely due to J_F (with a small contribution from conventional double exchange in the metallic phase). Thus the observed $T = 0$ pattern of phases and phase transitions follows naturally from our picture [11]. We discuss the ground state properties of the FKM as a function of the hole doping (x) and the model parameters, namely U, D_0 and E_{JT}, and show that for realistic values of these parameters, the calculated phase boundary is in good agreement with experimental trends. We conclude by discussing some other implications of our work in regard to experiments. A detailed discussion of the finite temperature properties of our model, including the ferro metal- para insulator transition and the CMR, is presented elsewhere [3].

We start with a model with two degenerate e_g orbitals per site and strong degeneracy breaking electron JT phonon coupling g. For large g, at each site there will be one *vibron* solution [5], labelled ℓ, with its energy reduced for single occupancy due to a large JT distortion by an amount $E_{JT} = (g^2/2K) \simeq 1eV$ [12] where K is the force constant of the JT phonon mode. The orthogonal vibron solution [5], labelled b , is not JT distorted, and hence has no gain in JT energy. Inter-site hybridization of the ℓ states is reduced by the phonon overlap or Huang-Rhys factor [13] $\eta = exp(-E_{JT}/2\hbar\omega_0)$, which for manganites is $\sim (1/200)$ since $(E_{JT}/\hbar\omega_0) \simeq 10$. As a first approximation, we neglect this altogether and treat the ℓ states as site localized. Inter-site hybridization amongst the b electrons is not suppressed. They hence form a broad band. In the presence of large U the b states have their largest amplitudes on

hole sites (x) as they are strongly repelled from the polaronic sites ℓ. In the presence of large J_H the spins of both ℓ and b electrons are aligned parallel to the t_{2g} core spins.

An additional consequence [3] of the existence of JT distorted, localized ℓ states is that *virtual, adiabatic* hopping processes involving them *in the presence of large U and J_H* (where an ℓ electron at site i quickly hops to an *empty neighbour j* and back, with an intermediate state energy cost of $2E_{JT}$ due to the unrelaxed lattice distortion at i) give rise to a *new, major, doping dependent ferromagnetic nearest neighbour exchange coupling J_F* between the t_{2g} core spins of order $t^2(1-x)x/(2E_{JT}S^2)$. In the ground state for $x > x_{c1}$ when this interaction dominates the anti-ferromagnetic super-exchange, the t_{2g} are fully ferromagnetically polarized; then so also are the e_g (both ℓ and b) spins due to the large $J_H(>> t)$. Hence the spin degrees of freedom are frozen.

Thus we are led to effectively spin-less localized ℓ and mobile b electrons with a strong local Coulomb repulsion U. The relevant effective Hamiltonian is just the Falicov-Kimball model (FKM) [3,4,8] , given by

$$H_{eff} = -\sum_{\langle ij\rangle} \bar{t}_{ij} b_i^\dagger b_j - (E_{JT}+\mu)\sum_i \ell_i^\dagger \ell_i - \mu \sum_i b_i^\dagger b_i + U\sum_i n_{bi} n_{\ell i} \tag{1}$$

Here $b_i^\dagger$ and $\ell_i^\dagger$ create the band and localized polaronic states described above at site i, and $\bar{t}_{ij}$ are effective, orbitally averaged [14] inter-site hopping amplitudes for the b states. The chemical potential μ *is determined by the doping-dependent constraint* that the total number of e_g electrons is $(1-x)$ per site. The relevant parameter regime of H_{eff} we are interested in for manganites corresponds to $\bar{t} \sim 0.2\,eV$ [15], U very large ($\sim 5-8\,eV$ [15]) and E_{JT} in the range $0.5-1.0\,eV$ [15,12].

While there are no known techniques for exactly solving H_{eff}, a dynamical mean field theory(DMFT) treatment of it can be carried out exactly [10]. In this approximation, which is exact in infinite dimensions, and quite accurate for three dimensions [10], the lattice problem is mapped to a single site problem embedded in a self consistent effective medium or electron bath that represents all the other sites of the lattice. We assume that the system is homogeneous [14]. The b electron self energy $\Sigma_{ij}(\omega)$ due to the interactions U is site local i.e. $\Sigma_{ij}(\omega) = \delta_{ij}\Sigma(\omega)$, and is determined from the single site or local effective action

$$\mathcal{S}_{eff} \;=\; -\int_0^\beta \int_0^\beta d\tau d\tau' b^\dagger(\tau)\mathcal{G}^{-1}(\tau-\tau')b(\tau') + \beta(-E_{JT}-\mu)n_\ell + Un_\ell \int_0^\beta d\tau n_b(\tau) \tag{2}$$

Here $b^\dagger(\tau)$ and $b(\tau')$ are fluctuating fermionic Grassmann fields, $n_\ell = 1$ or 0 corresponding to the ℓ state being occupied or not, and $\mathcal{G}(\tau)$ is the bare on site local propagator in the presence of the effective medium. The local partition function, obtained by summing $exp(-S_{eff})$ over all the configurations, is expressible as $Z_{local} = Z_0 + Z_1$. Here Z_0, Z_1 are *constrained partition functions* corresponding to $n_\ell = 0,1$ respectively, and are calculable using standard techniques [10] in terms of $\mathcal{G}(\omega^+)$,the Fourier coefficients of $\mathcal{G}(\tau)$ analytically continued to real frequencies. Explicitly, $Z_0 \equiv exp(\beta\alpha_0(T))\,; Z_1 = exp(\beta\alpha_1(T)) \times exp\left[-\beta(-E_{JT}-\mu)\right]$; where

$$\alpha_m(T) = \pi^{-1}\int d\omega n_F^-(\omega-\mu)\, Im\left\{\ell n(\mathcal{G}^{-1}(\omega^+) - U\delta_{m1})\right\}\,, \tag{3}$$

$n_F^-(\omega)$ being the Fermi function $[1+exp(\beta\omega)]^{-1}$. The local single particle Green's function $G(\omega^+)$ is given by

$$G(\omega^+) = -\langle b b^+\rangle_{S_{eff}} = w_0\mathcal{G}(\omega^+) + w_1(\mathcal{G}^{-1}(\omega^+) - U)^{-1} \tag{4}$$

with $w_1 \equiv Z_1/(Z_0+Z_1) = \bar{n}_\ell$ and $w_0 = (1-w_1)$ being the annealed probabilities for the ℓ state being occupied and empty respectively. The condition that the average e_g occupancy $\bar{n}_\ell + \bar{n}_b = (1-x)$ determines the chemical potential μ. A re-normalized or effective ℓ electron energy can be defined by writing $w_1 = n_F^-(\epsilon_\ell^* - \mu)$, whence $\epsilon_\ell^* = -E_{JT} + \alpha_0(T) - \alpha_1(T)$. Clearly, at $T=0$, μ is necessarily pinned to ϵ_ℓ^* as long as $\bar{n}_\ell$ is non zero.

In the DMFT [10] Eq. 4 relating $G(\omega^+)$ and $\mathcal{G}(\omega^+)$ for our model has to be supplemented by two other equations: namely the Dyson equation, $G^{-1}(\omega^+) = \mathcal{G}^{-1}(\omega^+) - \Sigma(\omega^+)$, and the self consistency relation which expresses the local Green's function in terms of the lattice Green's function, as $G(\omega^+) = \int d\epsilon D_0(\epsilon)/(\omega^+ + \mu - \epsilon - \Sigma(\omega^+))$, where $D_0(\epsilon)$ is bare density of states (DOS) for the b-band. These coupled equations for $\mathcal{G}, G$ and Σ have to be solved self-consistently, and typically numerically, to obtain all the quantities of direct physical interest. The self consistency relation becomes algebraic, considerably simplifying such calculations, for a semicircular DOS, i.e., for $D_0(\epsilon) = (2/\pi D_0^2)\sqrt{D_0^2 - \epsilon^2}$ where D_0 is the half bandwidth. This DOS, exact for the Bethe lattice in infinite dimensions [10], is fairly accurate for our model in 3d, especially for trends and magnitude estimates [16]. Hence we confine ourselves to the semicircular DOS results in this paper. In this case, $G(z) = 2/(z + \sqrt{z^2 - D_0^2})$ where $z \equiv (\omega^+ + \mu - \Sigma(\omega^+))$ is complex. Using this result, Eq. 4, the Dyson equation, and the equations for w_0, w_1 we have numerically solved the DMFT equations self-consistently for a wide range of values for the correlation U, JT polaronic energy E_{JT}, bare bandwidth $2D_0$ and doping x. The results are discussed below. A broad perspective of the trends in these can be obtained in the simpler limit when $U \to \infty$. Hence we discuss these first.

In the $U \to \infty$ limit, the DMFT equations stated above (for the semicircular DOS) can be solved analytically. The local Green's functions have the simple form

$$G(\omega^+) = 2w_0/\left(\omega^+ + \mu + \sqrt{(\omega^+ + \mu)^2 - D^2}\right) = w_0 \mathcal{G}(\omega^+)$$

with $D \equiv \sqrt{w_0} D_0$. The local spectral function or re-normalized DOS of the b-band is simply $\rho(\omega) = 2\sqrt{D^2 - (\omega+\mu)^2}/(\pi {D_0}^2)$, i.e., once again of the semi-circular form, but with a reduced effective bandwidth $2D$, and reduced weight w_0. At $T=0$, $\bar{n}_b$, $w_0 = 1 - \bar{n}_\ell$ and ϵ_ℓ^* can hence be evaluated from (numerically solving) the equations:

$$\epsilon_\ell^* = -E_{JT} + (\mu \bar{n}_b / w_0);$$

$$\bar{n}_b = (w_0 - x) = (w_0/\pi)\left\{ sin^{-1}(\mu/D) + (\pi/2) + (\mu/D)\sqrt{1 - (\mu/D)^2} \right\} \theta(\mu + D).$$

In addition, when $\bar{n}_\ell \neq 0$, there is the pinning condition $\epsilon_\ell^* = \mu$. These equations have the self consistent solution $\bar{n}_b = 0$, $\epsilon_\ell^* = -E_{JT} = \mu$, for $E_{JT} > D \equiv \sqrt{w_0} D_0 = \sqrt{x} D_0$, since $w_0 = x$ for $\bar{n}_b = 0$. Thus we have the analytic result that for $x < (E_{JT}/D_0)^2$ the effective half bandwidth $D = \sqrt{x} D_0$, the localized ℓ levels lie lower than the b band bottom, only the former are occupied and the system is an insulator. The $T=0$ electrical gap between the occupied ℓ levels and the unoccupied b band bottom in this ferro-insulator phase is given by $\Delta = E_{JT} - D = E_{JT} - \sqrt{x} D_o$. The critical doping for the $T=0$ ferro-insulator to ferro-metal transition, determined by the vanishing of Δ, is thus $x_c = (E_{JT}/D_0)^2$. As x increases beyond x_c, the system becomes a ferromagnetic metal, with ϵ_ℓ^* the re-normalized ℓ level lying above the b band bottom. $\bar{n}_b$ increases with x ,till at some value x_{c2}, $\bar{n}_b = (1 - x_{c2})$ so that $\bar{n}_\ell = 0$. Beyond x_{c2}, only the b band is occupied.

Thus our theory leads naturally to an insulating (ferromagnetic) state for $x < x_c$, a ferro-metallic state with coexisting band b and localized ℓ electrons for $x_c < x < x_{c2}$, and a metal with only b electrons and bandwidth $2D_0$ for $x > x_{c2}$. Indeed, for x close to 1 ("electron

doped limit") there are surprisingly successful calculations [17] of (magnetic) ground states based on a model of independent broad band tight binding electrons moving in appropriate magnetic superstructures of t_{2g} spins which have AF super-exchange interactions, completely ignoring JT interactions. Our theory provides a rationalization for this.

Detailed zero temperature results from our theory are shown in Figs. 1(a)-(c) and in Fig. 2. We choose $E_{JT} = 0.5\,eV$ and $D_0 = 1eV$. Fig. 1(a) shows the variation of the re-normalized ℓ level and the b band edge positions ($U = \infty$, full line, $U = 5eV$, a realistic value, dotted line) with doping x. The effective b bandwidth $2D$ becomes very small (0 for $U = \infty$) as $x \to 0$. The physical reason is that, as mentioned before, the b electrons reside mostly on the hole sites(fraction x), being strongly repelled from those occupied by ℓ polarons (with repulsion energy $U >> 2D$). At $x = x_c$ ($= 0.25$ for $U = \infty$, and very nearly this value for $U = 5\,eV$), the band bottom crosses the ℓ level. The system is metallic for $x > x_c$, with both $\bar{n}_b$ and $\bar{n}_\ell$ being nonzero, as shown in Fig. 1(b). We note that in the 'metallic' regime $x_c < x < 0.5$, $\bar{n}_b$, the average band occupancy, is small, eg. at $x = 0.4$, $\bar{n}_b \simeq .08$. For the set of parameters chosen, the ℓ level empties out completely for $x = x_{c2} \simeq 0.72$, and beyond this only band states are occupied. Double exchange and anti-ferromagnetic super-exchange describe the magnetic behaviour of the system in this regime. In Fig. 1(c), the effective band or electrical gap is shown as a function of x. The gap vanishes smoothly as $x \to x_c$ and rises as $x \to 0$ to a value E_{JT}, and not U; this should be the electrical gap seen at any finite x no matter how small, or in a $T \neq 0$ experiment. Fig. 2 shows how the $T = 0$ insulator metal boundary (x_c) shifts as a function of D_0 and U. x_c increases as D_0 decreases, and as U increases. We note that all physical quantities for $U = 5eV$ are close to those for $U = \infty$.

We now briefly compare our results with observed material trends and experimental numbers where available. One of our predictions is that of a ferromagnetic but insulating ground state (FI) for $x < x_c$. The former arises from the new virtual double-exchange coupling J_F described earlier; the state is insulating because the effective b half bandwidth $D < E_{JT}$ for $x < x_c$. In contrast, the ferromagnetic state is necessarily metallic if it arises solely due to double exchange [9]. Experimentally, all doped manganites have an insulating, fully polarized ferromagnetic state, for $x_{c1} < x < x_c$; *eg.* for $LaCa$, $x_{c1} = 0.10$ and $x_c = 0.18$. In our calculations, $x_{c1} = 0$ (because we have neglected the small, orbital order dependent, anti-ferromagnetic exchange important at small x [11]), while the critical doping x_c for the insulator-metal transition at $T = 0$ depends on material parameters roughly as $x_c = (E_{JT}/D_0)^2$ (cf. Fig. 2). This prediction can not be directly compared with experiment since the systematics of E_{JT} and D_0 are not precisely known. It is however believed [18] that the bare half-bandwidth D_0 decreases in the sequence $LaSr$, $LaCa$, $NdSr$ (and $PrCa$), because of cation size and its effect primarily on the Mn-O-Mn bond angle and via this on the nearest neighbour hopping, while E_{JT} does not change much. The observed x_c for this sequence has values 0.16, 0.18, and $\gtrsim 0.20$, the trend being consistent with our prediction. The puzzle as to why some manganites (eg. $PrCa$) have only insulating ground states unlike the above can be understood within our theory in terms of the characteristic values of (E_{JT}/D_0) appropriate to the materials (eg., from Fig. 2, for $E_{JT} \sim .5\,eV$, the ferro-insulator extends up to $x = .5$ if $D_0 \lesssim 0.7\,eV$).

The electrical activation energy in the Ferro-insulator state goes as $\Delta_{eff} = D_0(\sqrt{x_c} - \sqrt{x})$ for large U in our theory. This dependence cannot be compared with experiment, since there are no measurements of activation energies close to $T = 0$; the only experimental results we are aware of [19] are for $T > T_c$, in the paramagnetic phase. The corresponding gaps are not expected to go to zero at x_c. However, this high $T(> T_c)$ activation energy does decrease as $x \to x_c$ as expected from our theory.

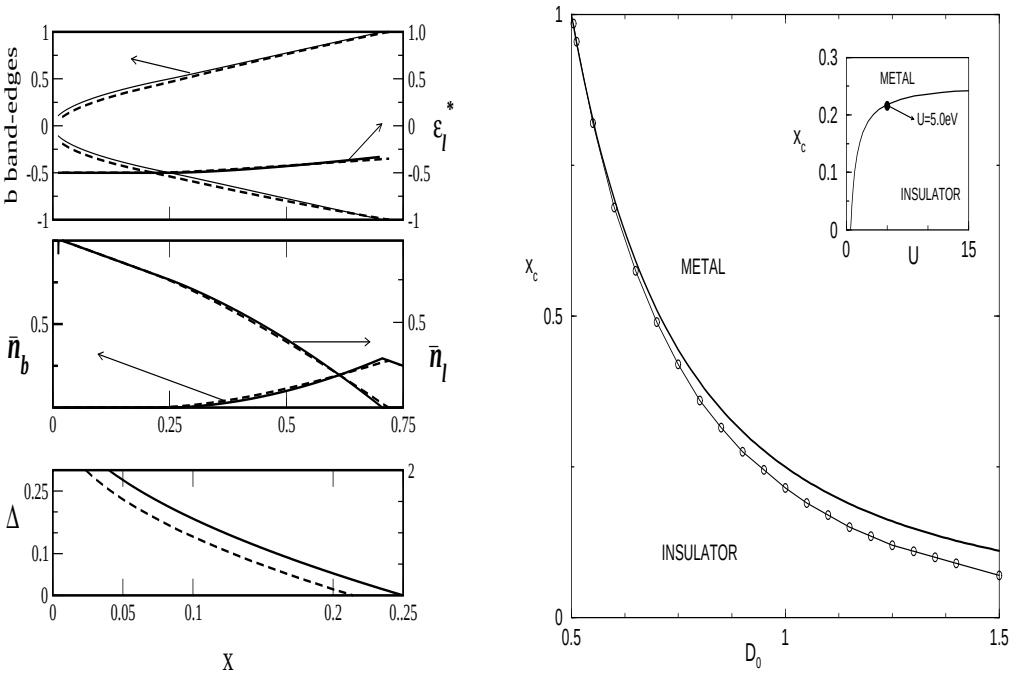

Fig. 1 – (a) Variation of b band edges and the effective ℓ level ϵ_ℓ^*, in units of D_0, with doping x. (b) The number $\bar{n}_l$ (of localized JT polaronic ℓ electrons) and $\bar{n}_b$ (of band electrons), per site, as a function of x. (c) The $T = 0$ insulating gap $\Delta \equiv (E_{JT} - D)$, as a function of x. In all the cases $E_{JT} = 0.5\,eV$ and $D_0 = 1\,eV$. The full line corresponds to $U = \infty$ and long dashed line to $U = 5\,eV$.
Fig. 2 – The critical concentration x_c for the $T = 0$ insulator metal transition as a function of D_0 the bare b half-bandwidth, in eV. The full line corresponds to $U = \infty$ and line with circles to $U = 5\,eV$. The inset shows x_c as a function of U/D_0 for $E_{JT} = 0.5\,eV$ and $D_0 = 1\,eV$. The point corresponding to $U = 5\,eV$ is marked by a filled circle.

An additional consequence of our model is that in the ferromagnetic metallic ground state, the concentration of mobile (b) electrons is rather small (Fig. 1(b)), and *not* $(1-x)$, the total number of e_g electrons per site. This is exactly the inference from the small Drude weight, *i.e.* the integrated optical conductivity, which is a direct measure of the effective number of carriers. For example, Okimoto *et. al.* [20] find $n_{eff} \simeq 0.06$ for $LaSr$ at $x = 0.3$. Our results for $\bar{n}_b$ quoted above are very much in this range of smallness. A related consequence of our theory, arising from the fact that the large majority of the e_g electrons are in polaronic ℓ states even in the metal, is the persistence of local polaronic distortions well into the metallic phase, for which there is considerable experimental evidence [6]. Thus our results provide a natural explanation for several unusual ground state properties of manganites.

In summary, we have presented here a new coexisting polaron/broad band electron model for manganites, which revives the Falicov-Kimball model in a new, hitherto unexpected and unexplored, setting. We have completely solved the model in this new context within the DMFT, and shown that this leads to a physical explanation and a quantitative theory of many characteristic and hitherto puzzling ground state properties of doped manganites in the doping regime $0.1 < x < 0.5$.

SRH and GVP thank the Council of Scientific and Industrial Research (India) for partial financial support. HRK would like to acknowledge support from the Indo-French Centre for

the Promotion of Advanced Research through its grant no. 2400-1.

REFERENCES

[1] *Colossal Magnetoresistive Oxides*, edited by Y. Tokura (Gordon and Breach, London) 2000; *Colossal Magnetoresistance, Charge Ordering and Related Properties of Manganese Oxides*, edited by C. N. R. Rao and B. Raveau (World Scientific, Singapore) 1998; M. B. Salamon and M. Jaime, *Rev. Mod. Phys.*, **73** (2001) 583.

[2] E. Dagotto, T. Hotta, and A. Moreo, *Phys. Rep.*, **344** (2001) 1.

[3] T. V. Ramakrishnan, H. R. Krishnamurthy, S. R. Hassan and G. Venketeswara Pai, cond-matt/0308376, *submitted for publication*; cond-matt/0308396, to appear as a chapter in *Colossal Magnetoresistive Manganites*, edited by T. Chatterji (Kluwer Academic Publishers, Dordrecht, Netherlands) 2003

[4] G. Venketeswara Pai, *Ph. D. Thesis* (Indian Institute of Science, Bangalore) 2001 *unpublished*; S. R. Hassan , *Ph. D. Thesis* (Indian Institute of Science, Bangalore) 2003 *unpublished*.

[5] M. D. Sturge, *The Jahn-Teller Effect in Solids , in Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic Press, NewYork) **20** (1967) 91-211; I. B. Bersuker and V. Z. Polinger, *Vibronic Interactions in Molecules and Crystals* (Springer-Verlag, Berlin) 1989

[6] Louca, D. et. al., *Phys. Rev. B*, **56** (1997) R8475; C. Meneghini, C. Castellano, S. Mobilio, Ashwani Kumar, S. Ray and D.D. Sarma, *J. Phys. Condensed Matter*, **14** (2002) 1967; V. Hardy, A. Wahl, and C. Martin, *Phys. Rev. B*, **64** (2001) 064402; Takuya Satoh and Yoshinao Kikuchi, *Phys. Rev. B*, **65** (2002) 125103; Xianming Liu, Hong Zhu, and Yuheng Zhang, *Phys. Rev. B*, **65** (2002) 024412; *Phase Transit.*, **75** (2002) 935; *J. Phys. Chem. Solids*, **63** (2002) 943; *Phys. Rev. B*, **67** (2003) 054413.

[7] M.Uehara, S.Mori, C.M. Chen, and S-W.Cheong, *Nature*, **399** (1999) 560; Heffner, R. H. et al., *Phys. Rev. Lett.*, **85** (2000) 3285.

[8] L. M. Falicov and J. C. Kimball, *Phys. Rev. Lett.*, **22** (1969) 997.

[9] N. Furukawa, *Journal of the Physical Society of Japan*, **64** (1995) 2734

[10] A. Georges, G. Kotliar, W. Krauth and M. J. Rozenberg, *Rev. Mod. Phys.*, **68** (1996) 13; U. Brandt and C. Mielsch, *Z. Phys.*, **75** (1989) 365, *ibid*, **79** (1990) 295, *ibid*, **82** (1991) 37.

[11] We do not address the phase transition from the ferro-insulator to the anti-ferro insulator as x decreases, which requires a careful treatment of competing exchange interactions and orbital ordering effects present at small x, in this paper.

[12] A. J. Millis, *Phil. Trans. R. Soc. Lond. A*, **356** (1998) 1437.

[13] K. Huang and F. Rhys, *Proc. Roy. Soc. London Ser. A*, **204** (1950) 406

[14] Our calculations assume an 'orbital liquid', homogeneous ferromagnetic ground state for all x and neglect spatial correlations in $\bar{n}_{\ell i}$, $\bar{n}_{bi}$ and θ_i (the orientation of the local JT distortion). This is reasonable in the metallic phase ($x_c < x \lesssim .5$). The assumption clearly neglects magnetic superexchange and orbital/charge order induced electronic and lattice effects responsible for the observed variety of magnetic and structural phases for $x > .5$. However, since the temperature scales associated with these phase is small ($T_N \sim 200K, T_{co} \sim 250K$), we believe that the overall behavour of the effective b bandwidth $2D$, $\bar{n}_\ell$,$\bar{n}_b$ *etc.* will be close to what we have obtained.

[15] S. Satpathy, Z. S. Popovic, and F.R. Vukajlovic, *Phys. Rev. Lett.*, **76** (1995) 960

[16] A comparison with more detailed calculations with realistic (Koster-Slater) anisotropic hopping, which we have carried out [3,4], shows that the results do not change much if D_0 above is matched with the half bandwidth of the realistic band-structure.

[17] G. V. Pai, *Phys. Rev. B*, **63** (2001) 060402

[18] H. Y. Hwang et .al., *Phys. Rev. Lett.*, **75** (1998) 159

[19] P. Mandal, B. Bandyopadhyay and B. Ghosh, *Phys. Rev. B*, **64** (2001) R180405

[20] Y.Okimoto et. al., *Phys. Rev. B*, **55** (1997) 4206