Localized Polaron + Mobile electron Two-fluid Model for Doped Manganites

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Plan of the Talk

- The Exotic phenomenology of Manganites
  - Structure and Phase diagram
  - Material trends
  - Metal Insulator transitions and CMR
  - Extra-ordinary sensitivity to perturbations
    - The Isotope effect
    - "Two Phase coexistence"
    - Anomalous Photoemission
- Microscopic Hamiltonian: Interactions at Work (J_H , E_{JT} , U_{dd} , t):

Plan of the Talk

- Degrees of Freedom and Interactions at Work :
  - t_{2g} spins, e_g elctrons and the Hund coupling J_H
  - Phonons and the Jahn-Teller splitting E_{JT} ,
  - The coulomb Interaction U_{dd} ,
  - The eg electron hopping amplitude t
- Previous theories and inadequacies

Plan of the Talk (Continued)

- A new approach and model Hamiltonian
  - Strong Jahn-Teller coupling: Localized (ℓ) and band (b) electrons
  - A new doping dependent ferromagnetic exchange mechanism: "virtual double exchange"
  - New (two-fluid, ℓ - b) model Hamiltonian
- Dynamical mean field theory (DMFT) treatment of the new model

Plan of the Talk (Continued)

- Results and Discussion
  - T = 0 Ferro Insulator to Ferro-metal transition and material trends
  - Thermal M – I transitions and CMR
  - Material Trends
  - Other Properties:
- Role of Long Range Coulomb Interactions
- Explanation of anomalous core-level photo-emission spectra in Manganites
- Inter-site coherence effects
- Concluding Comments

Materials and Structure

Doped Manganites – Chemical Formula:

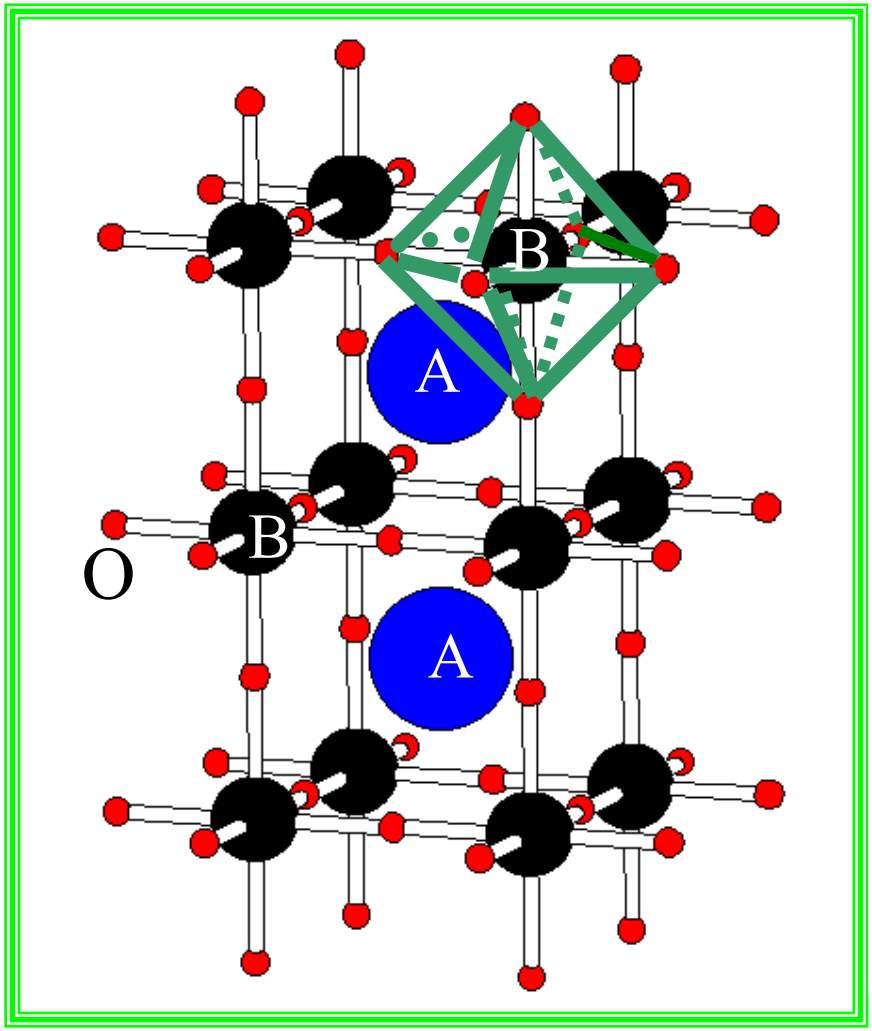
$$R_{1-x}\ A_x\ Mn\ O_3$$

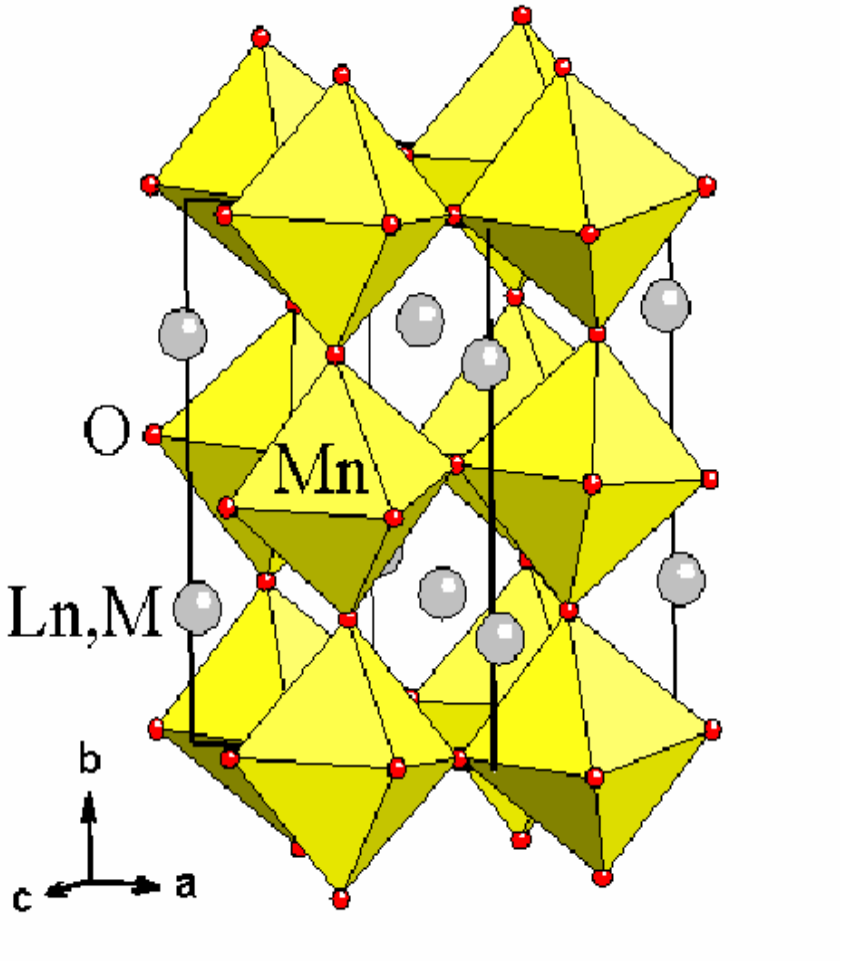
R : 3+ Rare-earth metal ion (La, Nd, Pr, …)
(in $LaMnO_3$, Mn => 3+)

A : 2+ Alkaline-earth ion (Ba, Ca, Sr, …)
(in $CaMnO_3$, Mn => 4+)

Basic Crystal Structure: Cubic Perovskite

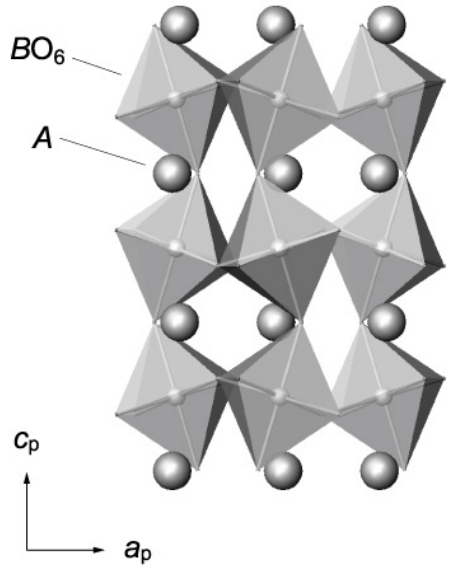
The Cubic Perovskite : ABO_3





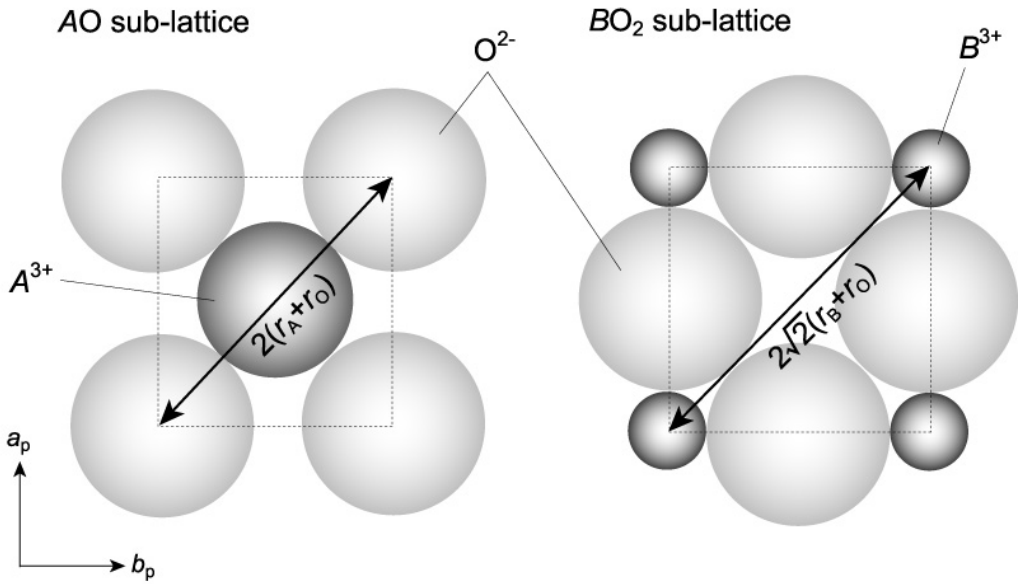
General Concept of Perovskite Structure

(Courtesy Y Ueda)



Crystal structure of perovskite

ABO_3 Perovskite Lattice (~AO-BO_2-AO-BO_2~)

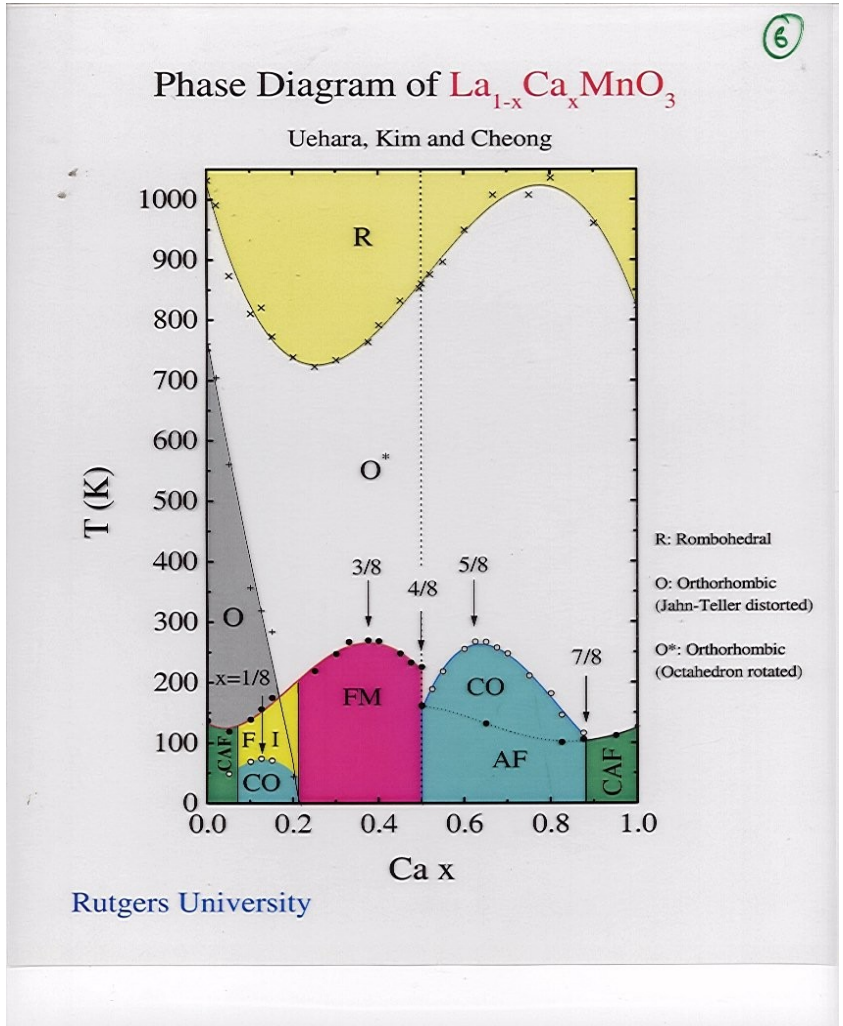


Tolerance factor (f)

$$f=(r_A+r_O)/\sqrt{2}(r_B+r_O)$$

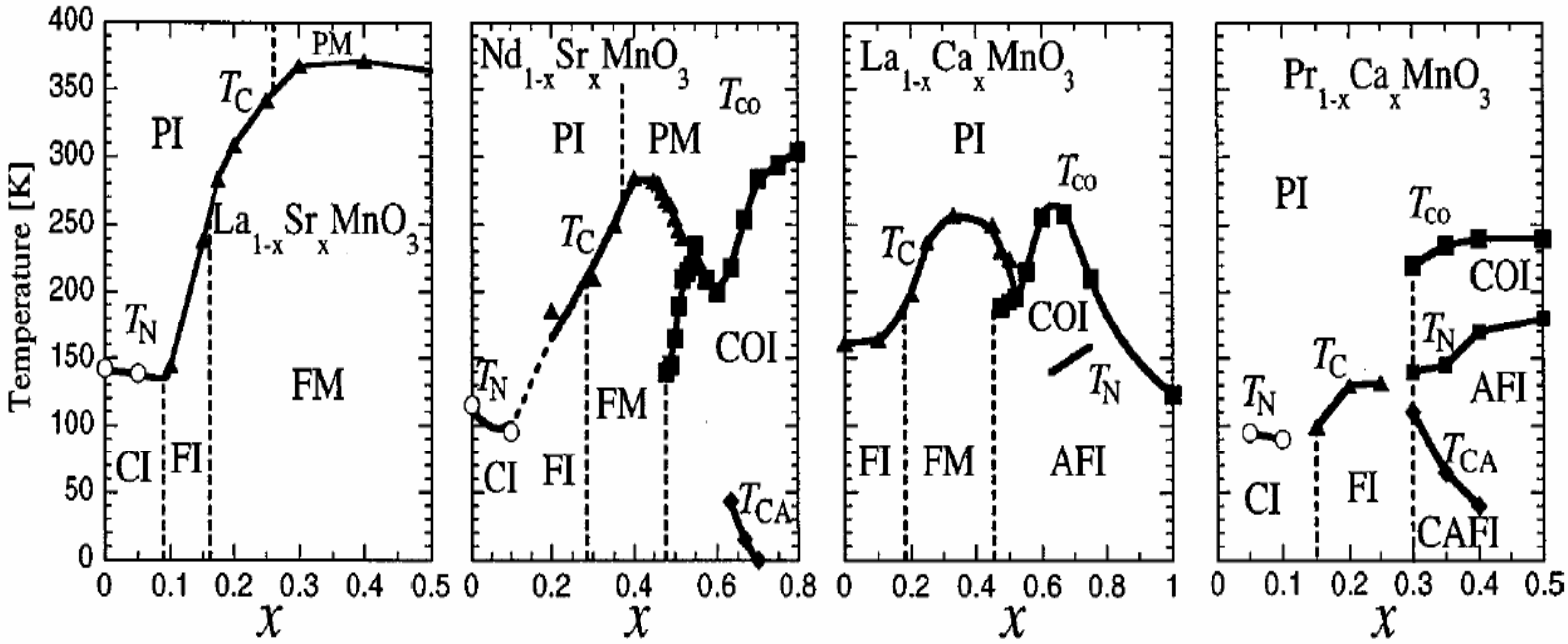
Phase Diagram of La_{1-x} Ca_x Mn O_3

- (C) AF : (Canted) Anti-ferromagnetic Insulator
- FI : Ferromagnetic Insulator
- FM : Ferromagnetic Metal
- PI : Paramagnetic Insulator
- CO : “Charge” ordered Insulator
- O : Orthorhombic (Jahn-Teller Distorted)
- O* : Orthorhombic (octahedron rotated)



Material Trends

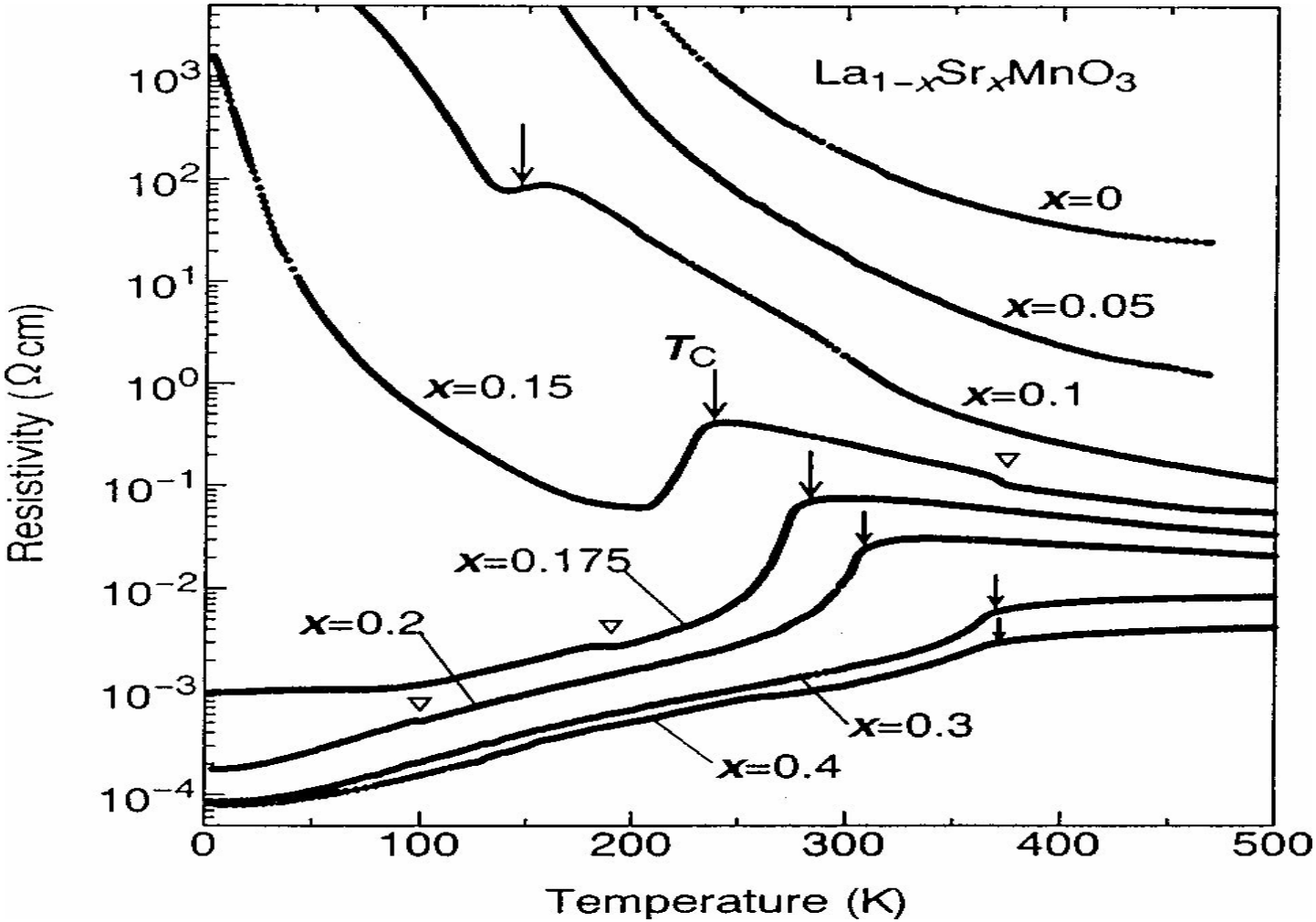
(From M.Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. **70**, 1039 (1998))



- Differences due to changes in cation radius $<r_A>$ causing bending of Mn-O-Mn bonds
- Extreme sensitivity to small changes

Resistive Transitions in the LaSr System

(From Urushibara ,et.. al. 1995, Phys. Rev. B **51**, 14103)



Unusual Aspects of Phase Diagram

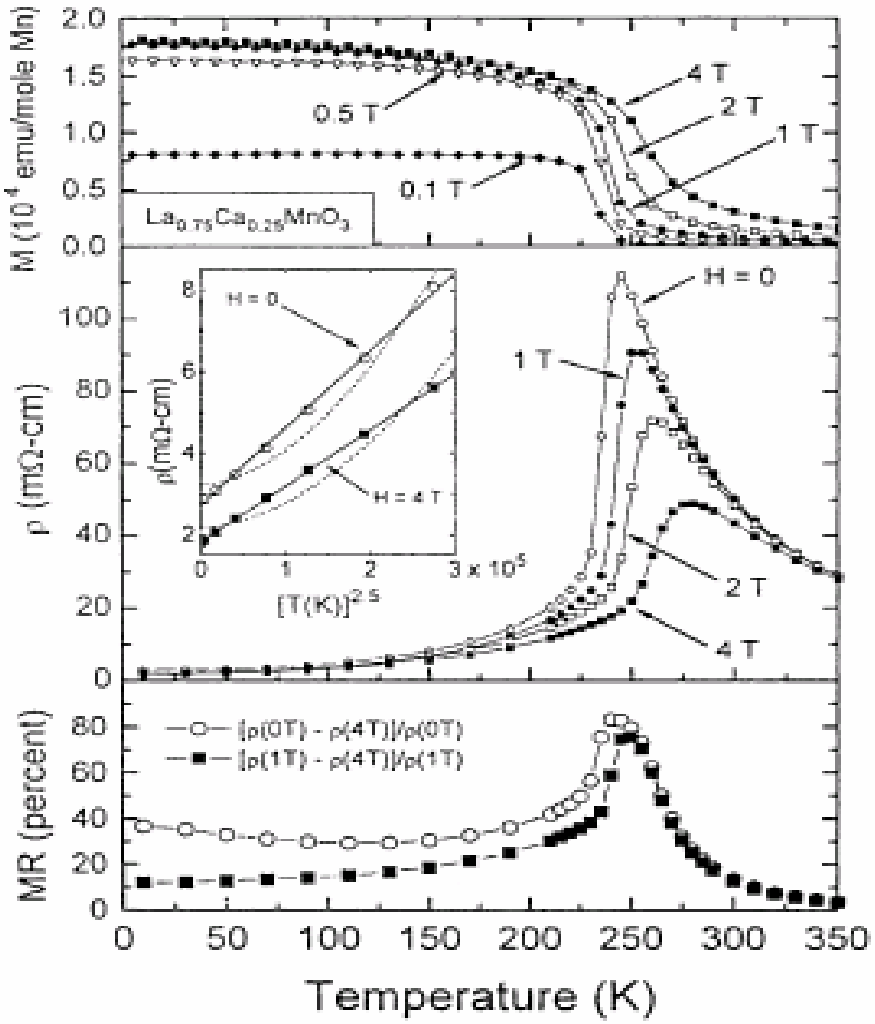
- At low Temperatures:
  - Ferro Insulator (FI) phase for a range of finite hole doping ($x_{c1} < x < x_c$) of a Mott insulator.
  - FI to Ferro Metal (FM) Transition at $x = x_c$.
  - No Metallic phases in some cases (PrCa)
- Thermal Transitions at T_c
  - FI to Para Insulator (PI) Transition for $x < x_c$
  - FM to PI Transition for $x > x_c$
  - For larger x, FM to PM transitions in some systems (LaSr, NdSr)
- Not easy to understand in terms of earlier theories

Colossal Magneto-resistance (CMR)

(From P. Schiffer et al. Phys. Rev. Lett. **75**, 3336, 1995)

- Magnetization, resistivity and magneto-resistance of $La_{.75}Ca_{.25}MnO_3$ vs temperature at various magnetic fields.
- FM to PI transition as T increases past a

  $T_c \sim 230$ K
- Magneto-resistance is about 1000 times larger than that seen in normal metals !



Other Unusual properties

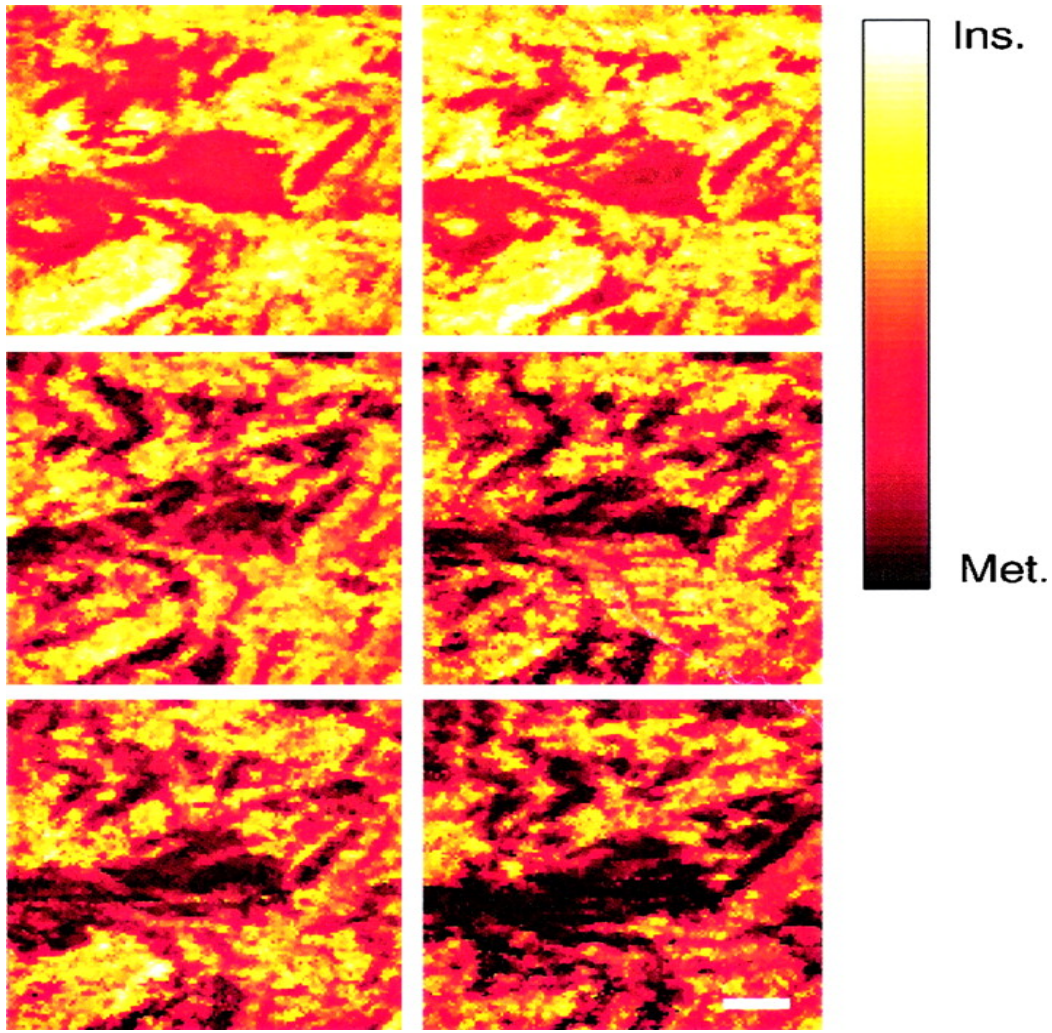
- Extreme sensitivity to small perturbations
  - CMR itself
  - Giant isotope effect on T_c ($\Delta T_c \approx$ 15-20K)

    metal–insulator transition on replacing O^{16} by O^{18} !
  - Large strain, ion size and Pressure effects
- Two phase coexistence
  - coexistence of two types of regions
    - one **insulating, locally lattice distorted**
    - the other **metallic and undistorted**
  - Regions static or dynamic, 100-1000 A

STM Images of $La_{.7}Ca_{.3}MnO_3$ Thin Films

(From M. Fath. Et. Al. Science, **285**, 1540-1542(1999))

- At Temperatures just below Tc
- Size of each frame 0.61 μm x 0.61 μm.
- From left to right and top to bottom: magnetic fields 0, 0.3, 1, 3, 5, and 9 Tesla.
- Light regions: Insulating
- Dark regions: Metallic



Micron-scale Inhomogeneities in $La_{1/4}Pr_{3/8}Ca_{3/8}MnO_3$ from photoemission

(From D. D. Sarma et. al., PRL, **93**, 097202 (2004))

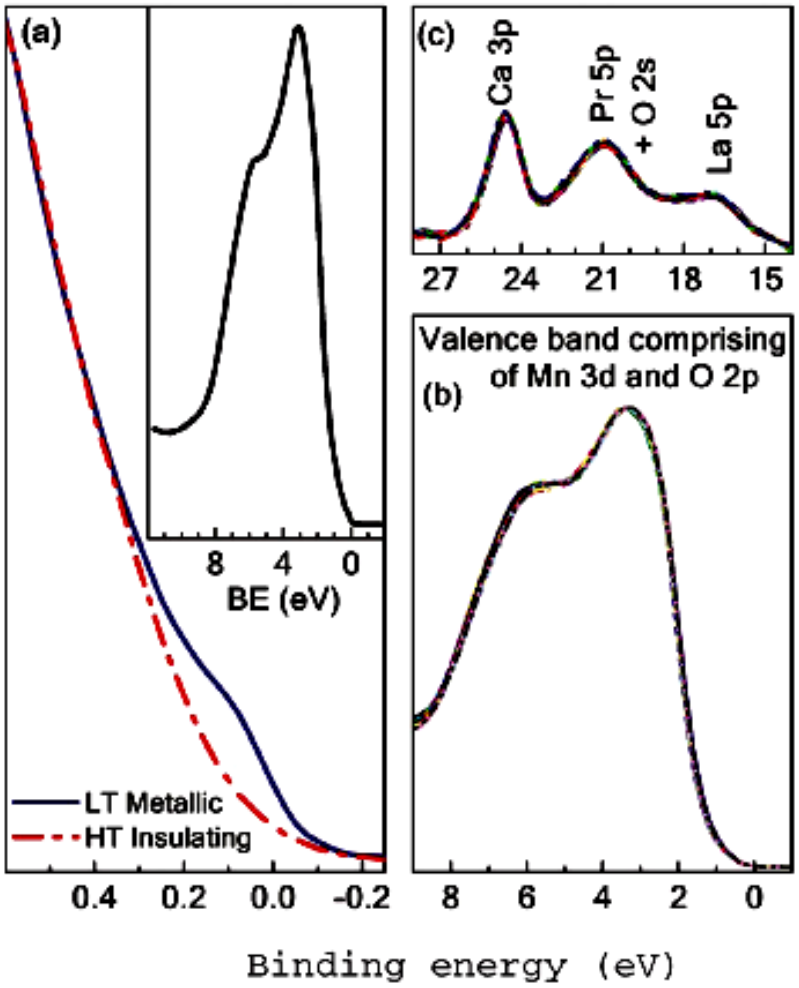


FIG. 2 (color online). . (a) Spectral changes close to the Fermi energy across the metal-insulator transition, exhibiting a finite density of states at E_F in the metallic phase. The inset shows the overall spectral feature over a wide energy range. (b) Superposition of valence band spectra consisting of mainly Mn $3d$ and O $2p$ states recorded with a high spatial resolution (0.5 μm) at 28 different spots on the sample. (c) Superposition of the shallow core level spectra from La, Pr and Ca after a linear background subtraction from the same set of spots as in panel (b).

Micron-scale Inhomogeneities in $La_{1/4}Pr_{3/8}Ca_{3/8}MnO_3$ from photoemission

(From D. D. Sarma et. al., PRL, **93**, 097202 (2004))

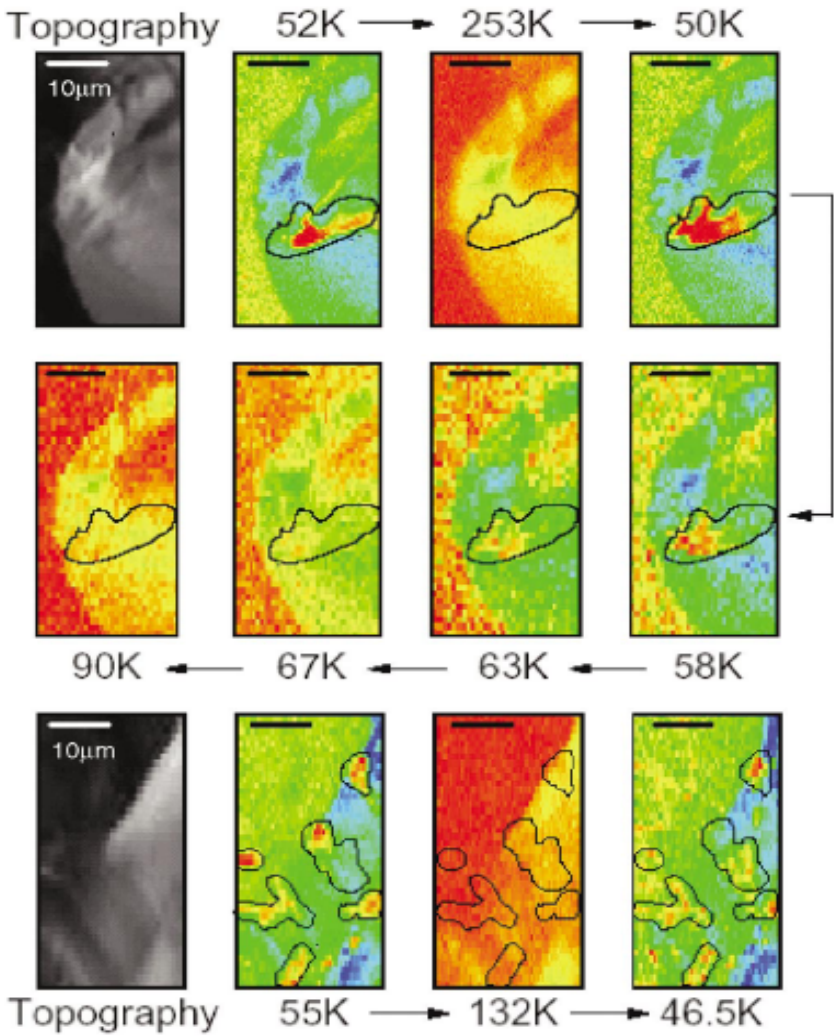
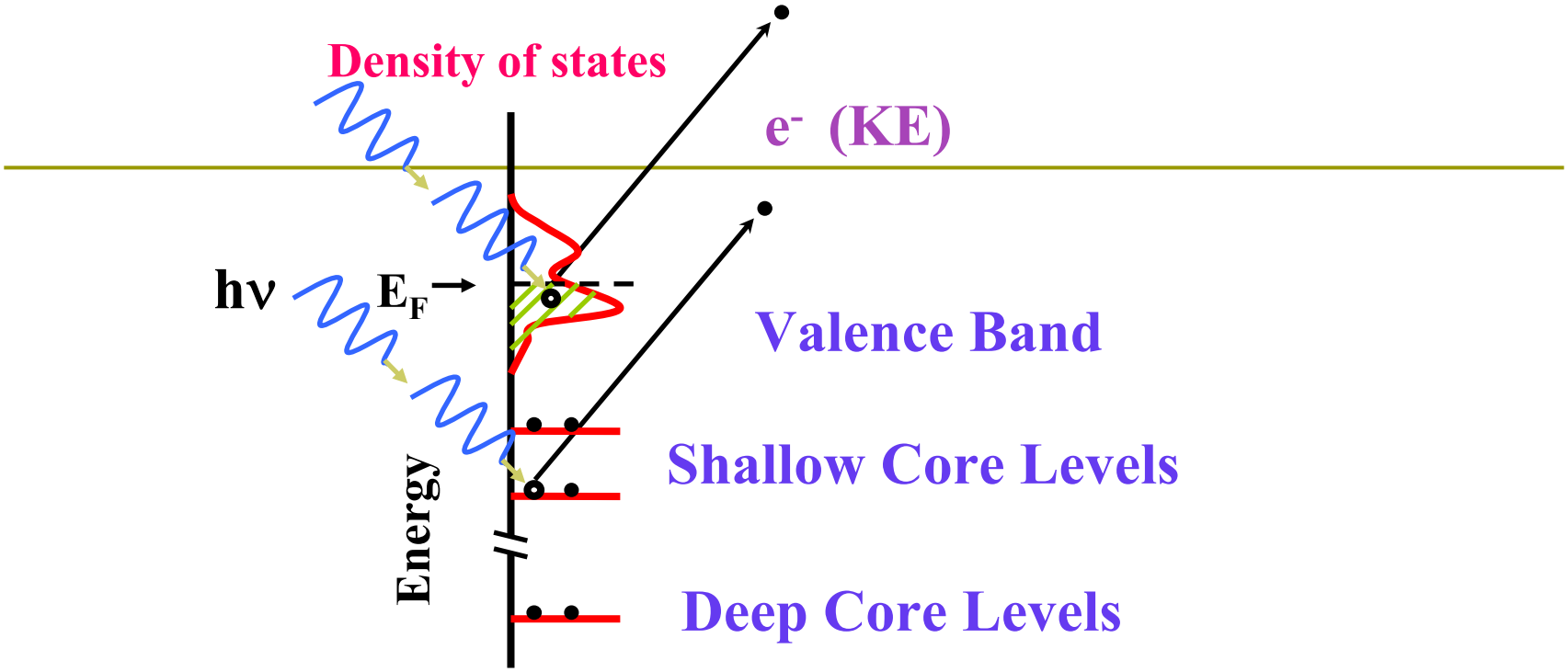


FIG. 3 (color). . Spectromicroscopic images over ~54 × 25 μm^2 areas of the sample surface. The top two rows show images from one region of the sample and the bottom row from another part, with the first panel in each of the two sets represented by gray scale being a topographic image and the rest ratio images. Ratio images at the lowest temperature for each image show emergence of distinct insulating patches (red-yellow) deep within the metallic regime (blue-green), which exhibit memory effects in the formation and morphology on temperature cycling. The color contrast in the ratio images vanishes and the entire sample transforms into the insulating phase as the temperature is increased, converting the system into an electronically homogeneous phase.

PHOTOELECTRON SPECTROSCOPIES



Energy Conservation: $E_i(N) + h\nu = E_f(N-1) + KE$

$h\nu - KE = [E_f(N-1) - E_i(N)]$

known *measure* *"BE"*

Evaluate

[As KE ≥ 0 $\therefore$ BE $\leq h\nu$]

Also as BE ≥ 0 $\therefore$ KE $\leq h\nu$

EXPERIMENTAL CORE LEVEL SPECTRA FOR $La_{(1-x)}Ba_xMnO_3$

(H. Tanaka et. al., *Phys. Rev. B*, **73,** 094403 (2006))

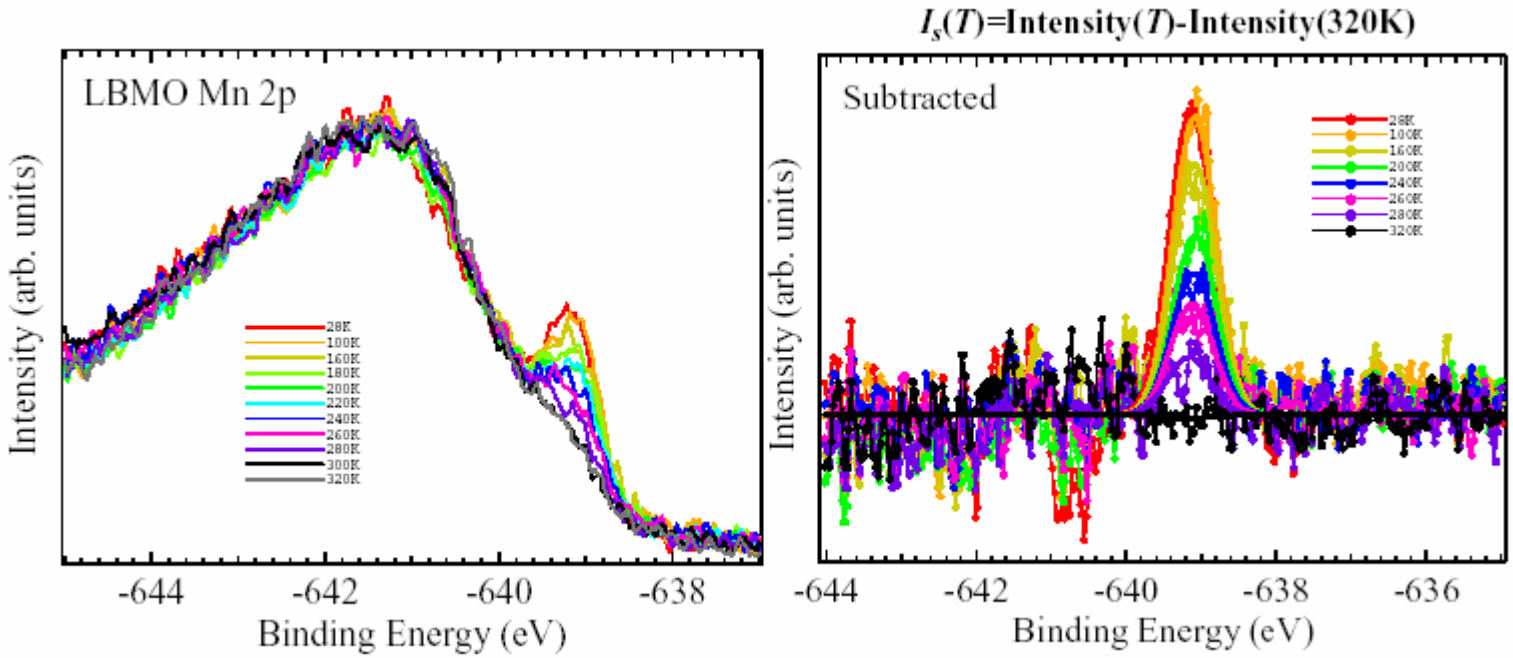
L_3 edge for different temperatures

28K (red) to 320K (black)

(T_C~300K)

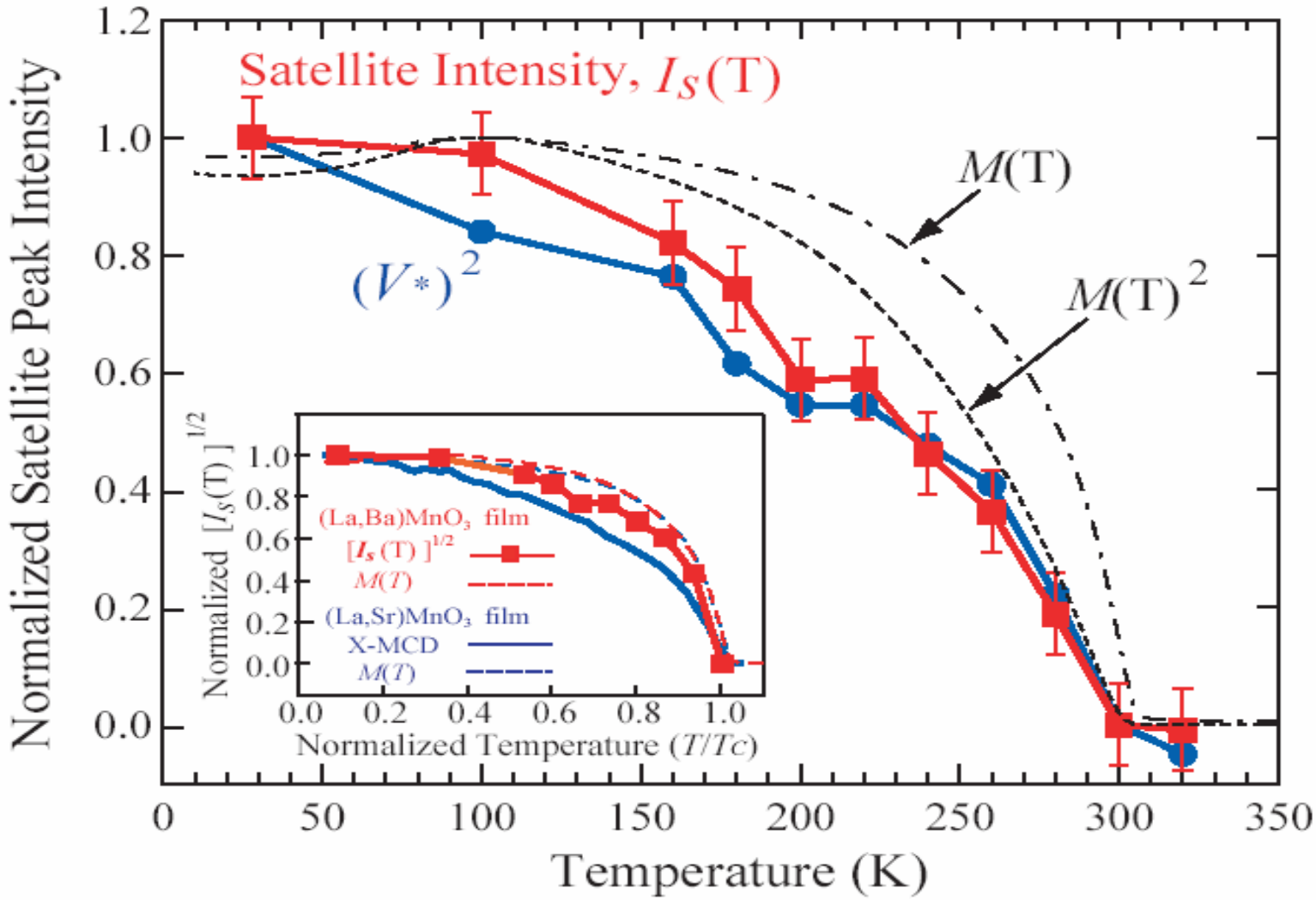
Difference Spectra (T) :

Spectra (T) - Spectra(T_C)



INTEGRATED SHOULDER WEIGHT FROM DIFFERENCE SPECTRA (EXPT.)

(H. Tanaka et. al., *Phys. Rev. B*, **73,** 094403 (2006))

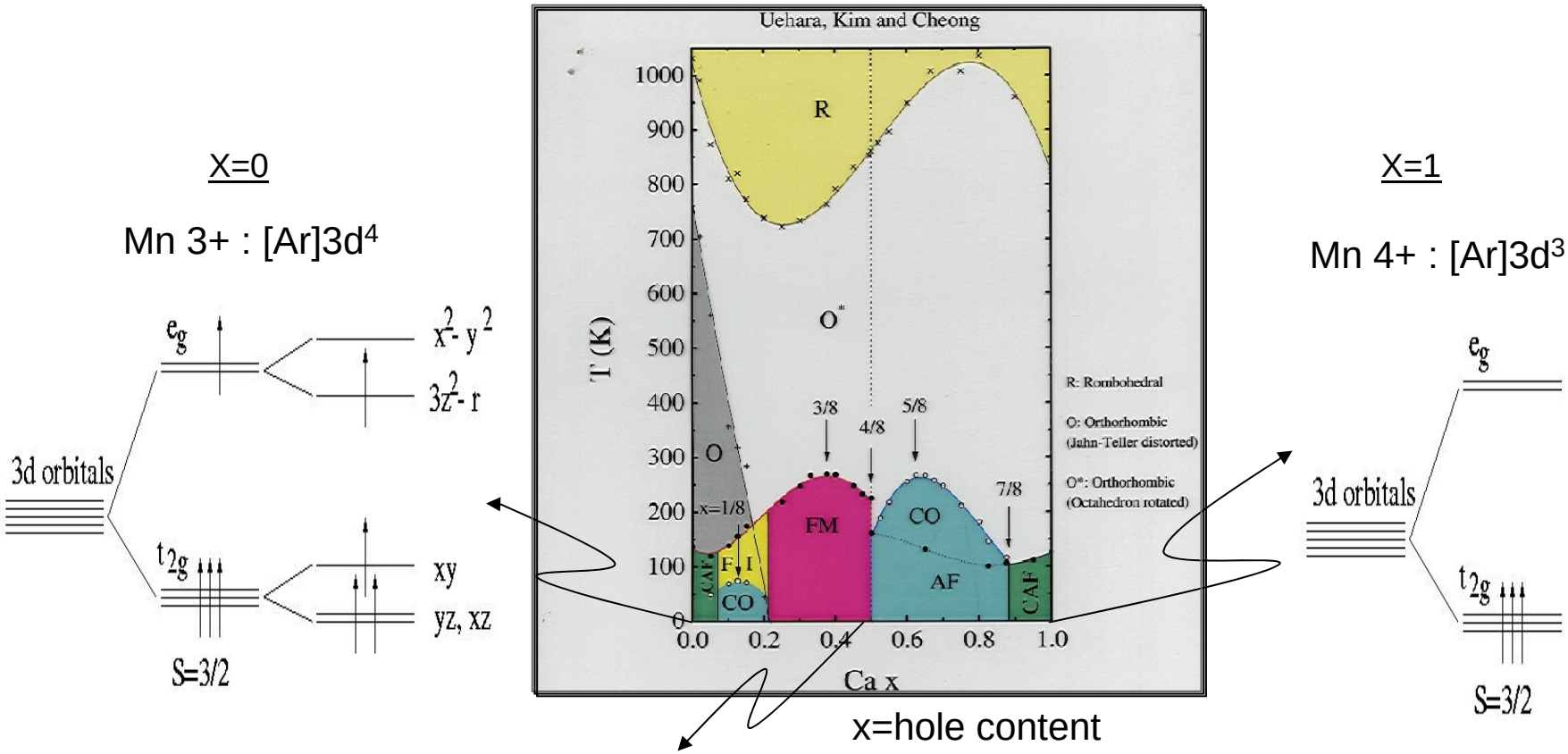


Active Degrees of Freedom and Interactions at Work

Degrees of Freedom responsible and Interactions at work clarified by the pioneering work of many:

- **Zener** (1951), **Anderson** and **Hasegawa** (1955) (Double Exchange)
- **Goodenough** (1955) **Kanamori** (1960) Chemical bonding, Co-operative Jahn-Teller distorsion, magnetic/orbital/charge order
- **de Gennes** (1960) Canting and magnetic polarons
- **Kubo** and **Ohata** (1972) Double exchange Hamiltonian
- More recently, **Millis et. al.**, (JT, exchange Interactions), **Dagotto et. al.**, (Numerical studies of many models, disorder effects), **Khomskii et. al.**, (orbital effects),…
- Many **outstanding experimental studies** over the years

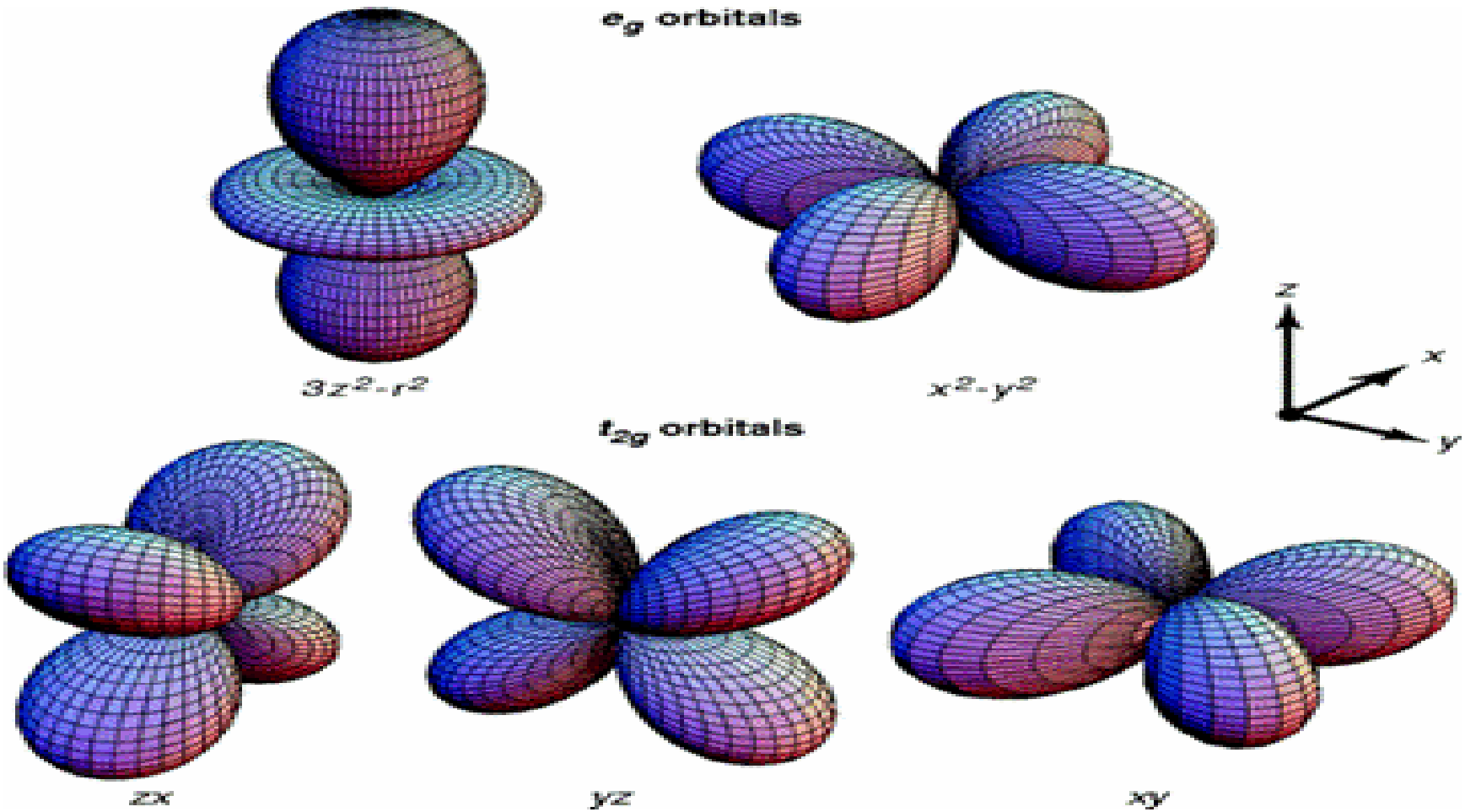
Active Degrees of Freedom and Interactions at Work



x=hole content

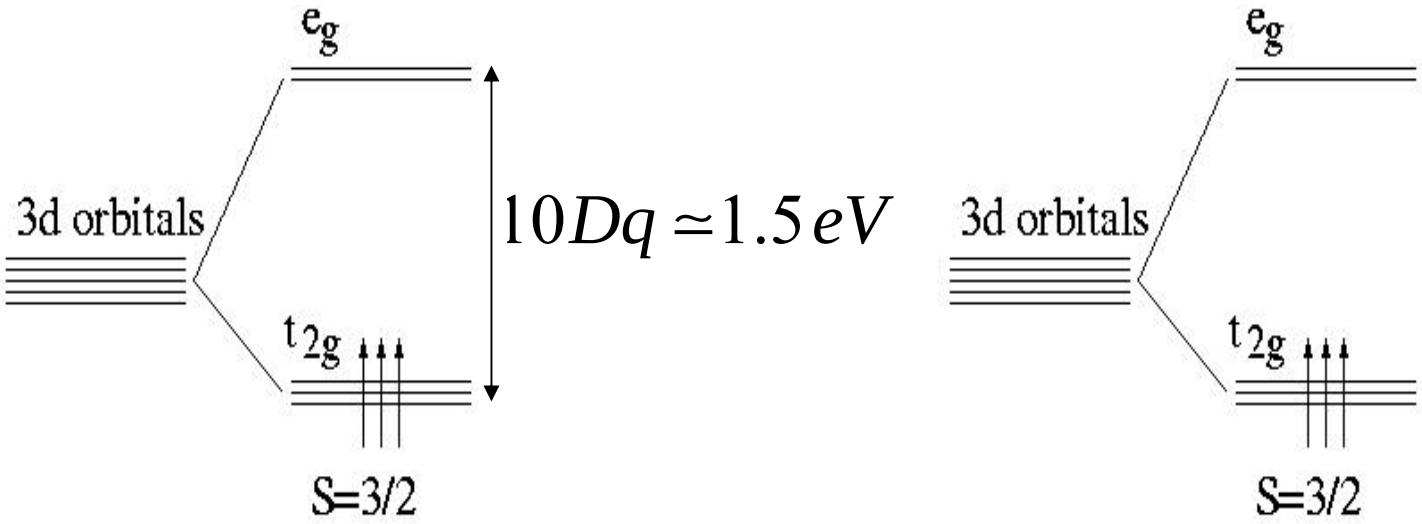
x=1/2 : 1 e_g electron for 2 sites
(equal mixture of Mn 3+ and Mn 4+)

The 3d Orbitals



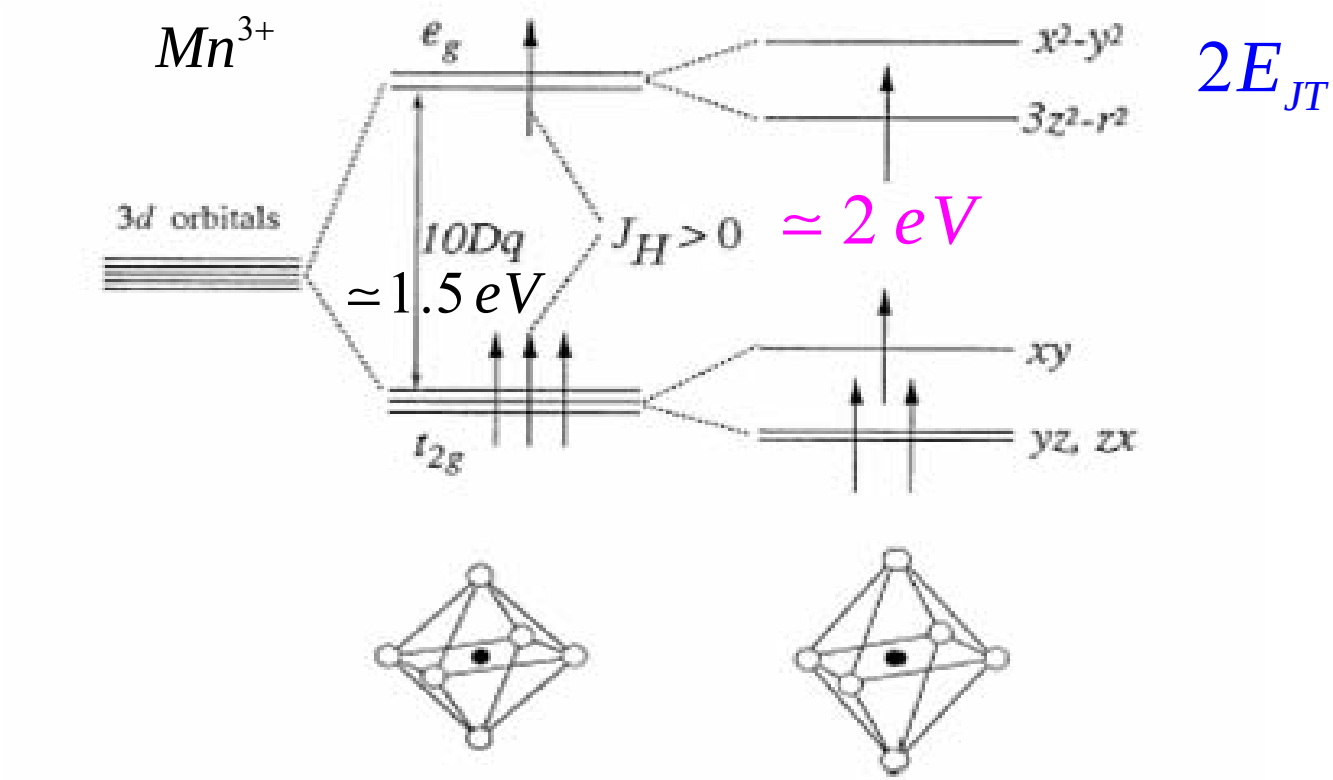
Degrees of Freedom & Interactions at Work:
Cubic Crystal Field Splitting, Hund's Rule, t_{2g} Core-spins and Super-exchange J_{SE}

Mn^{4+} Site *i* Mn^{4+} Site *j*



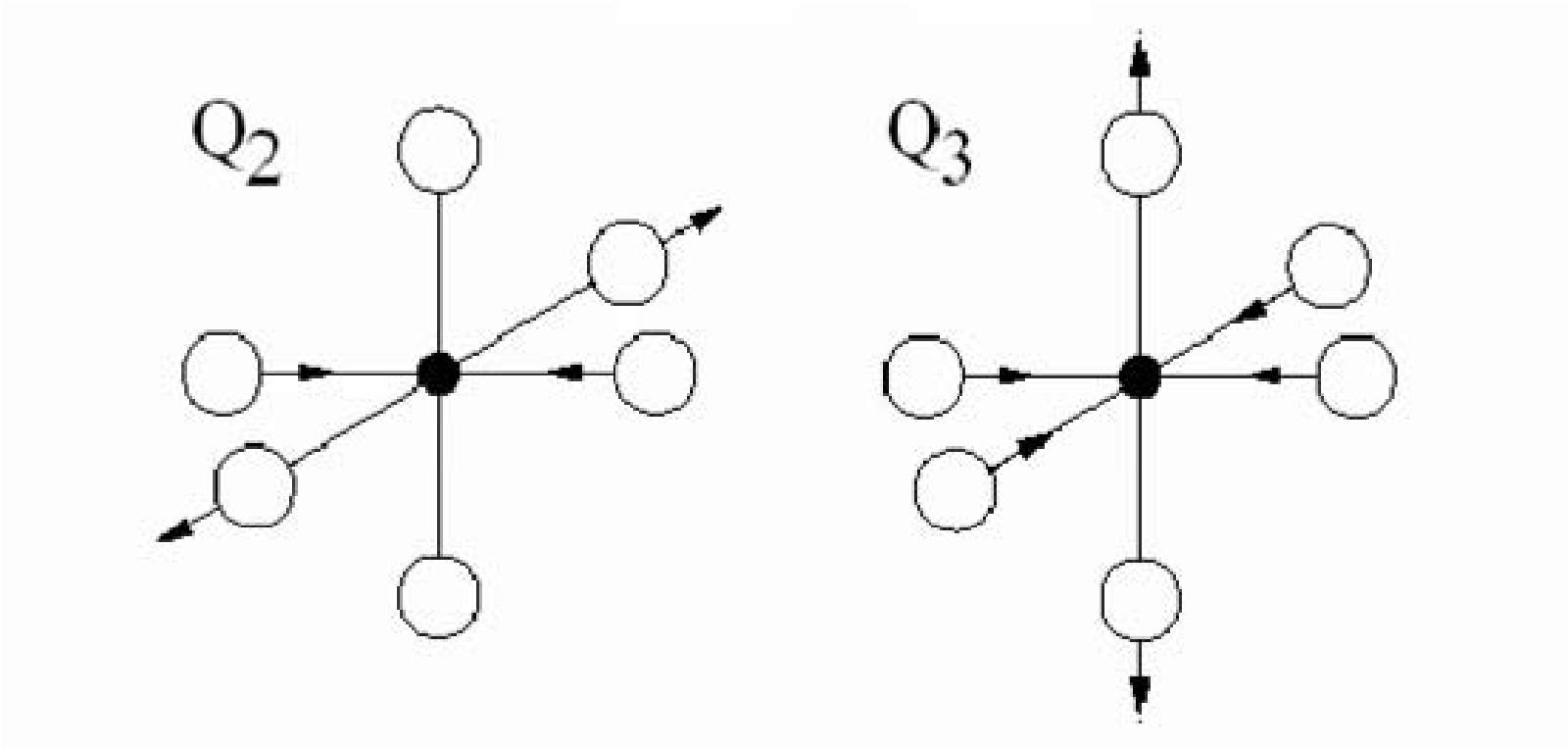
$$H_{SE} = \sum_{ij} J_{SE}^{ij} \vec{S}_i \cdot \vec{S}_j$$

Degrees of Freedom & Interactions at Work: e_g electrons, Hund Coupling J_H and Jahn-Teller Distortion



$$H_{Hund} = -J_H \sum_i (\vec{s}_{1i} + \vec{s}_{2i}) \cdot \vec{S}_i$$

Coupling of e_g electrons to Jahn Teller (JT) phonons ($\hbar\omega_o$, E_{JT})



$$g\,(d_1^{\dagger}d_2 + d_2^{\dagger}d_1)\,Q_2 \qquad g\,(d_1^{\dagger}d_1 - d_2^{\dagger}d_2)\,Q_3$$

Jahn Teller (JT) phonons ($\hbar\omega_o$)

$$\vec{Q}_i \equiv (Q_{2i}, 0, Q_{3i}) \qquad \vec{P}_i \equiv (P_{2i}, 0, P_{3i})$$

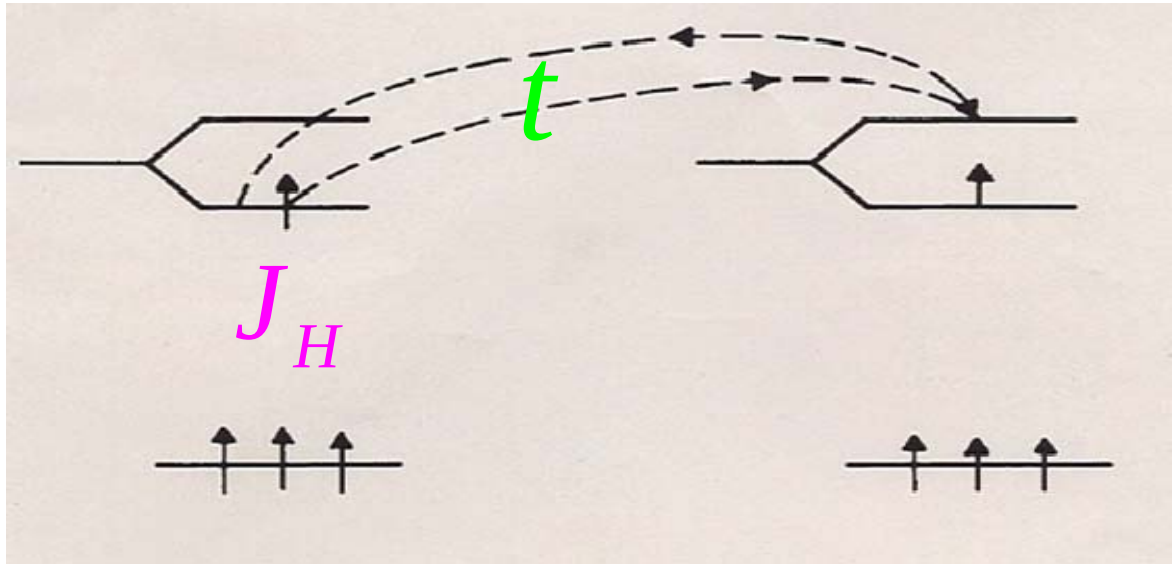
$$H_{lat} = \sum_i \left(\frac{1}{2M} \vec{P}_i^{\,2} + \frac{1}{2} K \vec{Q}_i^{\,2} \right) + \ldots$$

➡ Weakly Dispersing Einstein or Optical Phonons

$$\hbar\omega_o = \sqrt{\frac{K}{M}} \simeq 0.05 eV$$

$$H_{JT} = g \sum_i (d_{i\alpha}{}^{\dagger} \vec{\tau}_{\alpha\beta} d_{i\beta}) \cdot \vec{Q}_i \qquad E_{JT} = \frac{g^2}{2K} \simeq 0.5 eV$$

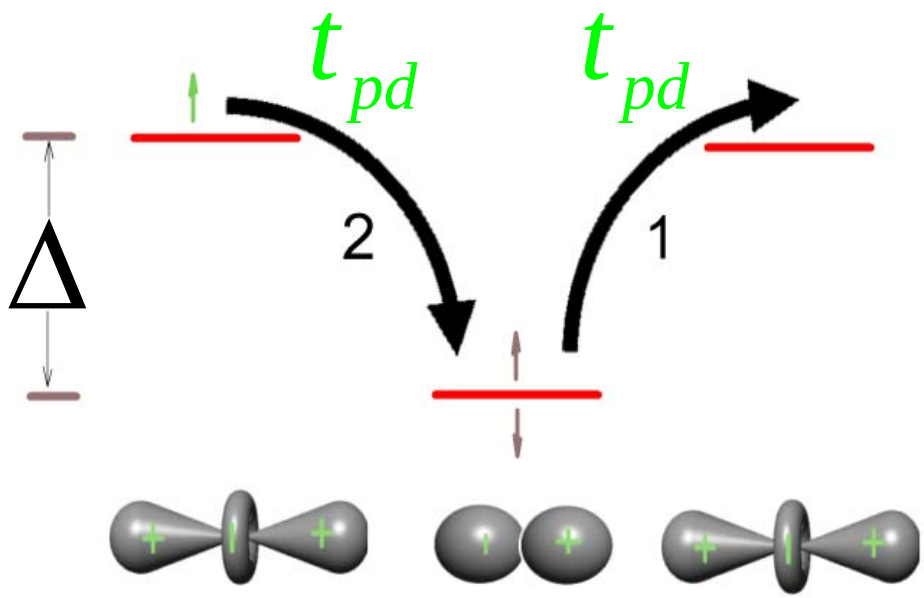
Interactions at Work : e_g electron hopping t



$$H_K = -\sum_{<ij>} (\mathbf{t}_{<ij>})^{a\beta} d_{i\alpha}{}^{\dagger} d_{j\beta}$$

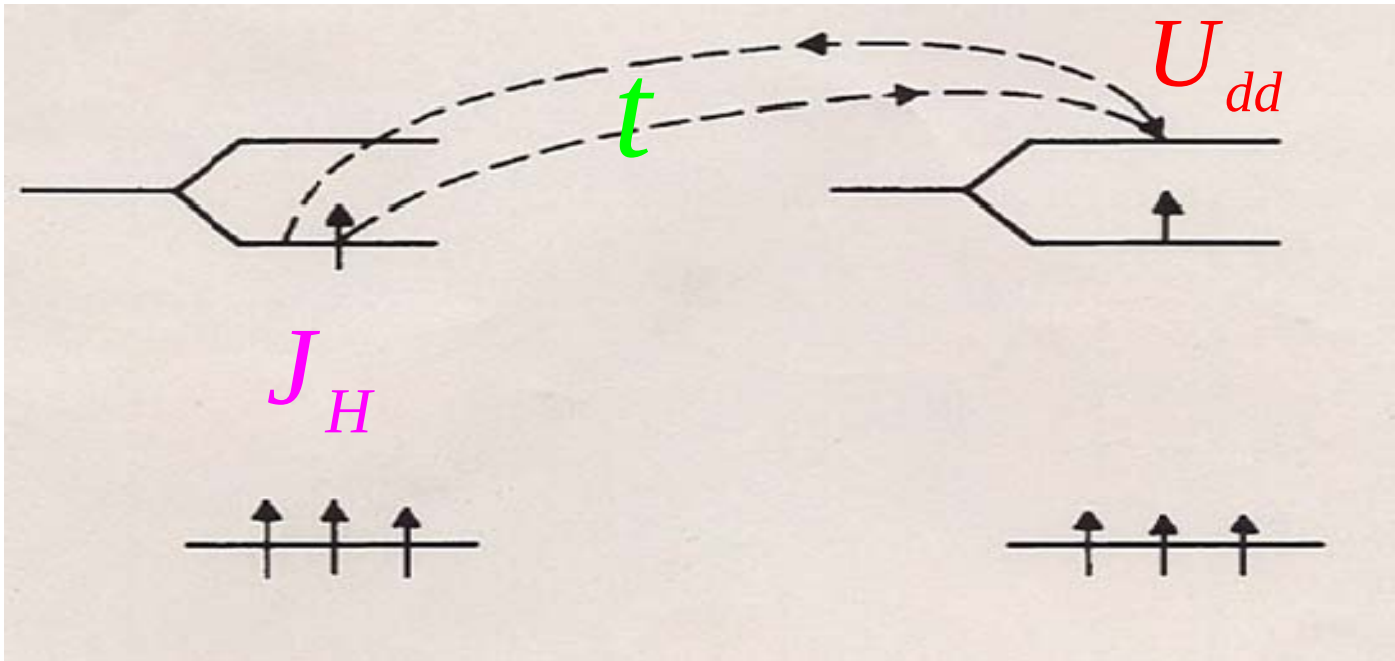
$$\mathbf{t}_x = t \begin{pmatrix} \frac{3}{4} & -\frac{\sqrt{3}}{4} \\ -\frac{\sqrt{3}}{4} & \frac{1}{4} \end{pmatrix}, \quad \mathbf{t}_y = t \begin{pmatrix} \frac{3}{4} & \frac{\sqrt{3}}{4} \\ \frac{\sqrt{3}}{4} & \frac{1}{4} \end{pmatrix}, \quad \mathbf{t}_z = t \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$$

Interactions at Work :
e_g electron hopping t comes via t_{pd}



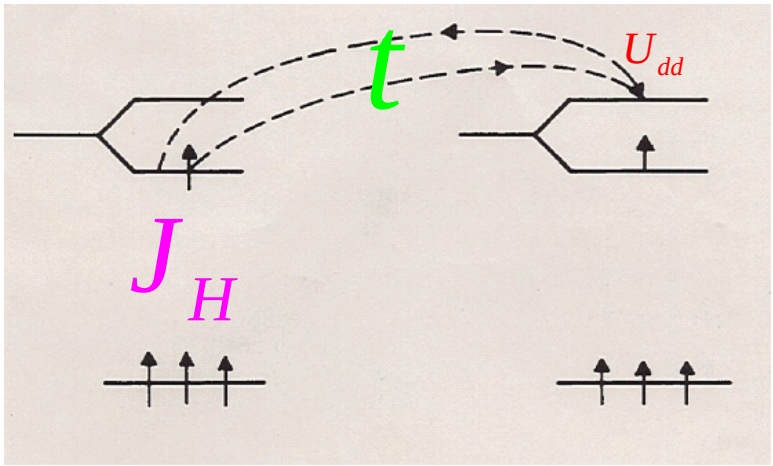
$$t = (t_{pd})^2 / \Delta \simeq 0.2\ eV$$

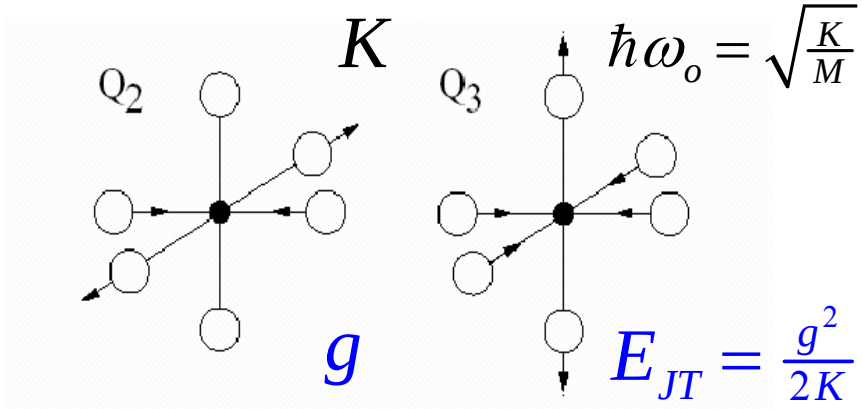
Interactions at Work : Coulomb repulsion U_{dd}



$$H_U = U_{dd} \sum_i n_i (n_i - 1)$$

Interactions at Work and Scales : J_H , t , U_{dd}, E_{JT} , $\hbar\omega_o$, J_{SE}

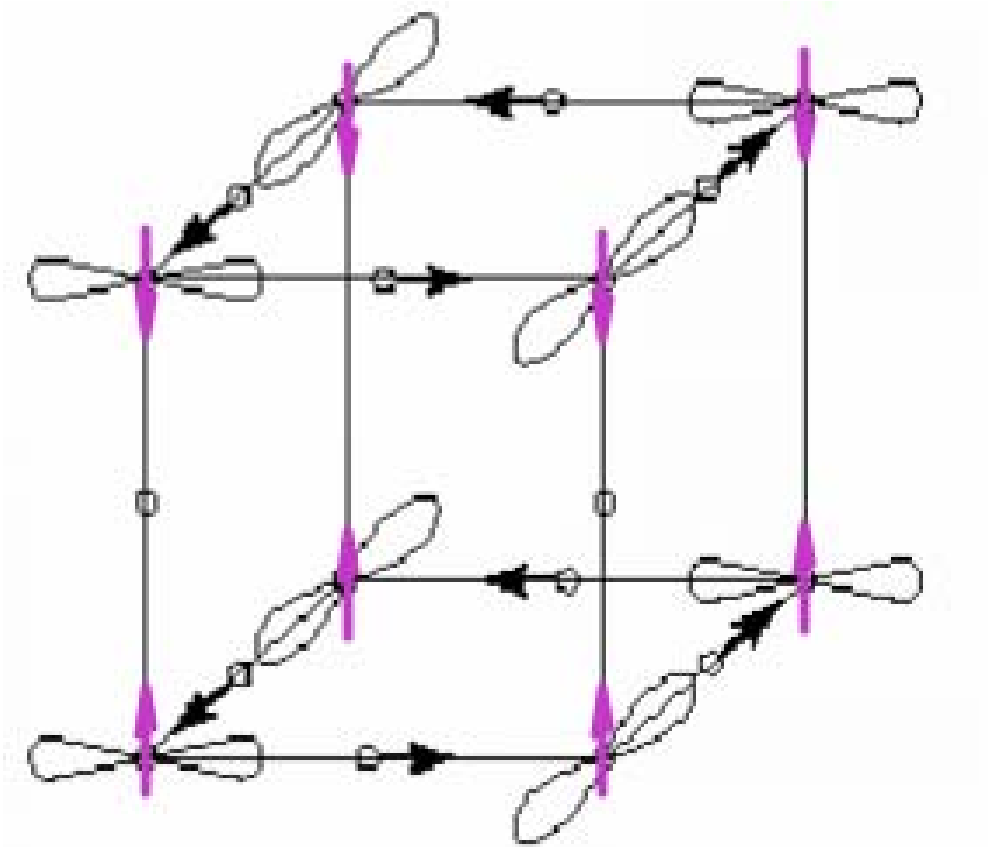




Hund Coupling J_H	~ 2 eV		
Hopping energy t	~.2 eV		
Coulomb energy U_{dd}	~ 5 eV		
Jahn-Teller Energy E_{JT}	~.5 eV		
JT phonon energy $\hbar\omega_o$	~.05 eV		
Super-exchange energy J_{SE}	~.008 eV		

La Mn O3 : Mott Insulator with Orbital and A-type Anti-ferromagnetic order

- At high T, no orbital or magnetic order, but still (Mott) insulator
- (Anti-ferro distortive) Orbital order below 740K
- A type AFM order below 140K



Doped Manganites
Earlier Theoretical Efforts

- Earliest theoretical efforts commonly referred to as double exchange theories

  (eg. recent DMFT treatment by N Furukawa 1995)
  - Consider solely the Hund coupling J_H and hopping t
  - Only a metallic state can be obtained
- Theory due to Millis, Mueller and Shraiman (1996)

  includes JT coupling *g*, but
  - Treats the JT modes classically, as annealed static disorder
  - Neglects *U*.
  - Polaronic insulating phase also occurs now for large enough *g*
  - But the predicted results do not resemble experiments
    - At nonzero x , one finds only metal-metal or insulator-insulator Curie transitions, unlike the commonly observed metal-insulator transition.
    - Magnetoresistance large but not colossal
    - There is no isotope effect.

DMFT Results from

A. J. MILLIS, R. MUELLER, AND BORIS I. SHRAIMAN
PHYSICAL REVIEW B 54, 5405 (1996)

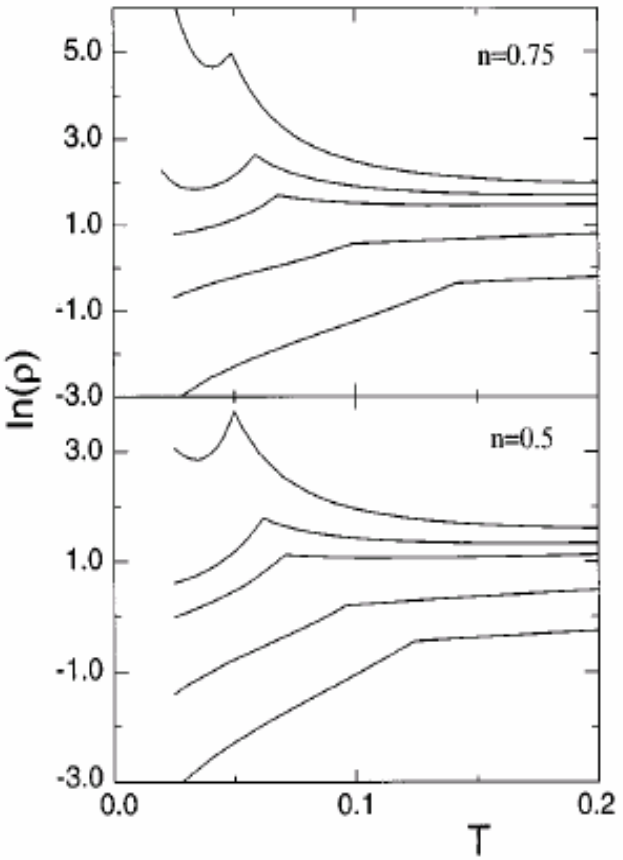


FIG. 8. Resistivity (ρ) vs temperture (T) for $n = 0.75$ (upper panel) and $n = 0.5$ (lower panel) and couplings $\lambda = 0.71$ (lowest), 1.12, 1.41, 1.49, and 1.58 (highest).

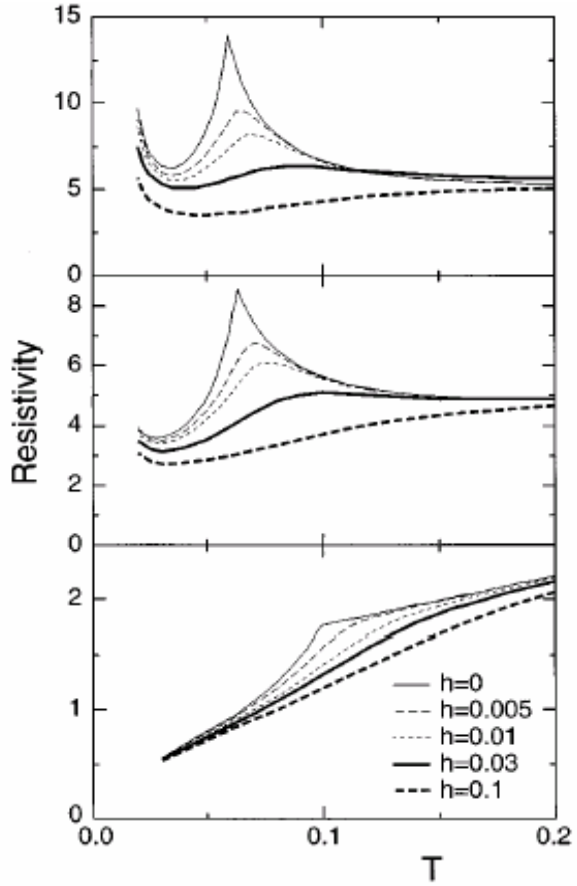


FIG. 9. Magnetic field dependence of resistivity for $n = 0.75$ and $\lambda = 1.12$ (lower panel), $\lambda = 1.46$ (middle panel), and $\lambda = 1.49$ (upper panel).

Doped Manganites
Earlier Theoretical Efforts

- Work of Dagotto, Moreo and co-workers
  - Monte-carlo simulations and exact diagonalization studies of small systems with core spins and phonons treated classically, but including effects of disorder
  - See lots of instances of "phase separation"
  - Attribute properties entirely to this (eg transport and CMR due to tunneling between differently oriented metallic regions surrounded by filamentary insulating regions)

Doped Manganites
Earlier Theoretical Efforts

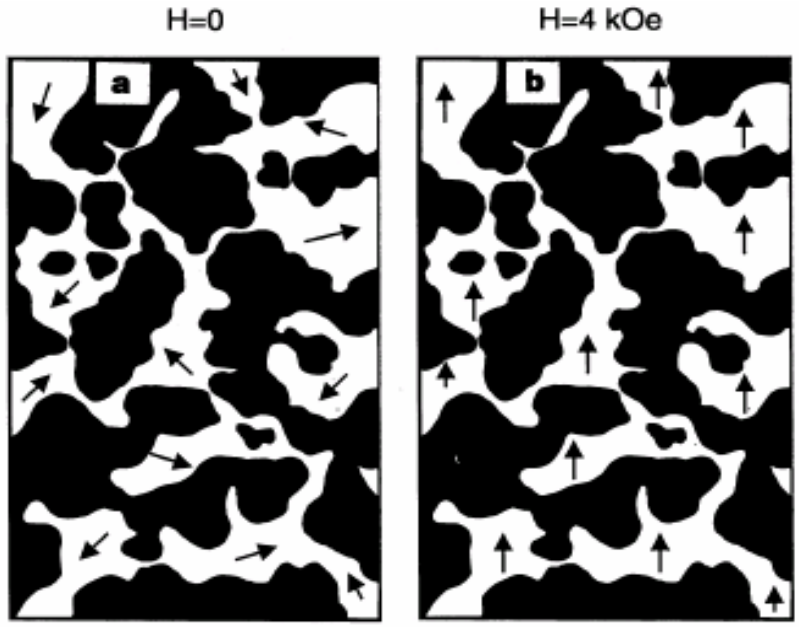


Figure 4 Schematic illustration of the sub-micrometre-scale coexistence of the $x = 1/2$-type CO insulating (dark area) and FM metallic (white area) domains. The typical size of domains is ~0.5 μm. In zero field (**a**), the magnetizations of FM domains are random, but all magnetizations of FM domains can be aligned by applying field of about 4 kOe (**b**). With the variation of y (that is, the abundance of CO domains), the residual ρ_0 follows $\rho_0 \propto (y_c - y)^P$ with $P \approx -6.9$ and $P \approx -2.6$ **a** and **b**, respectively.

- Many other models designed to address specific effects (eg. Khomskii and collaborators on Orbital ordering effects at special values of doping, etc.,)

New 2-Fluid (Localized Polaron+ band electron) Model for Manganites

Key ideas:

- **Two types of e_g electronic states spontaneously arise in doped manganites** (due to strong JT coupling, strong U_{dd}, filling conditions, …):
  - $l^{\dagger}_{i\sigma}$: Localized Polarons, trapped at JT distorted sites, do not hop
  - $b^{\dagger}_{j\sigma}$: Mobile band electrons that hop around on undistorted sites
- Interactions:
  - Old: strong repulsion U_{dd} between e_g electrons, strong J_H with core spins, super-exchange between core spins
  - **new : "Virtual Double exchange" ℓ occupancy dependent Ferromagnetic interaction.**

$$H_{VDE} \approx -\frac{\overline{t}^{2}}{2E_{JT}S^{2}}[1+\vec{S}_i\cdot\vec{S}_j][\hat{n}_{li}(1-\hat{n}_j)+\hat{n}_{lj}(1-\hat{n}_i)]$$

Localized (ℓ) Polarons: Bound states of e_g electrons and local lattice distortions

- JT Polaron Binding Energy

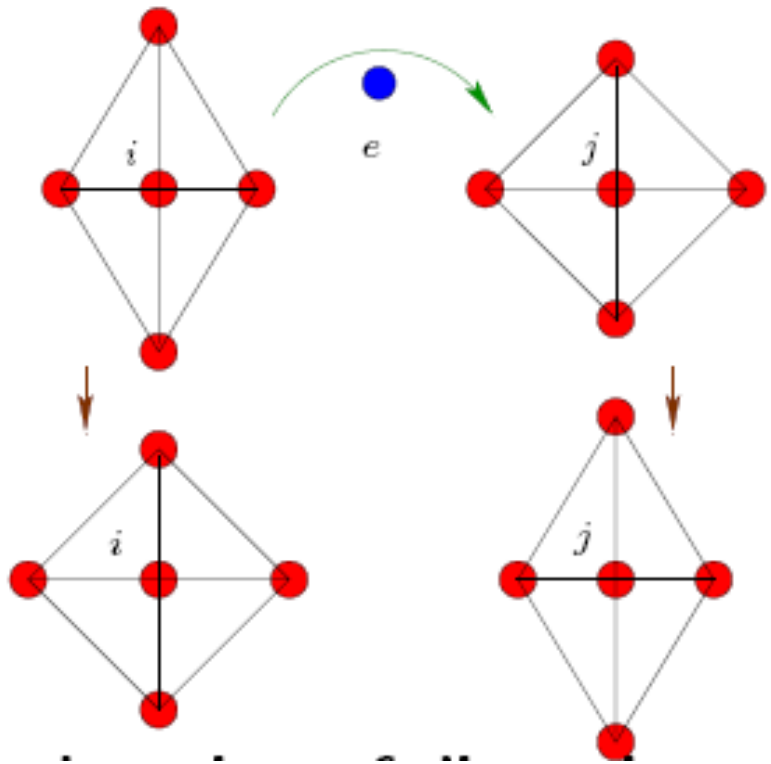
$$E_{JT} = g^2 / 2K$$

- JT polaronic displacement

$$|\vec{Q}_i|^{JT} = g / K$$

- Intersite hopping of the ℓ polaron requires relaxation of distortion at site i and build up of distortion at site j =>suppressed amplitude

$t^* = t\,\eta \approx t\ exp(-E_{JT}/\hbar\omega_o)$
$\approx (t/200) \approx 0$!



New doping dependent ferromagnetic exchange mechanism: "virtual double exchange"

- ℓ electron can take part in fast (adiabatic) virtual hopping processes to neighbouring sites, i.e., ***leaving the local lattice distortion unrelaxed***
- Energy cost in the intermediate state $E_I \approx 2E_{JT}$.
- For **large** U_{dd}, happens only if neighboring state is empty (Otherwise E_I more by U_{dd} *!*)
- for **large** J_H only if t_{2g} spins on the two sites are parallel. (Otherwise E_I more by J_H*)*

- Effective Hamiltonian in second order Perturbation theory (ignoring the orbital angle dependence, etc)

$$H_{VDE} \approx -\frac{\overline{t}^2}{2E_{JT}S^2}[1+\vec{S}_i\cdot\vec{S}_j][n_{li}(1-n_j)+n_{lj}(1-n_i)]$$

- New, occupancy dependent, ferromagnetic coupling between the t_{2g} core spins
- In homogeneous orbital liquid approximation

.

$$J_F \approx \frac{\overline{t}^2}{2E_{JT}S^2}\,x(1-x)$$

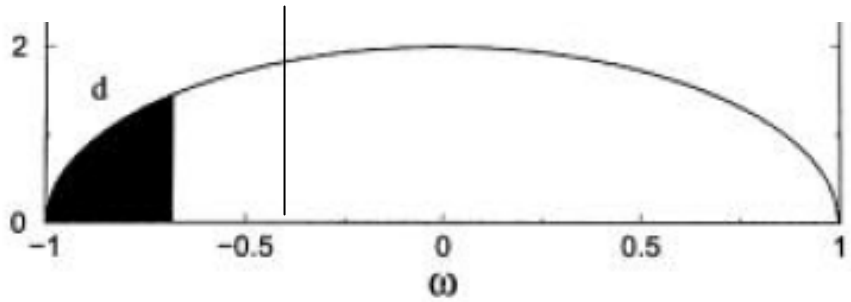
Mobile band electron States

- If an e_g electron is completely free to move around on undistorted sites, the preferred low energy states are Mobile band electronic states created by

$$b^{\dagger}_{\vec{k}\sigma} = \sum_j \exp(i\vec{k}\cdot\vec{r}_j) b^{\dagger}_{j\sigma}$$

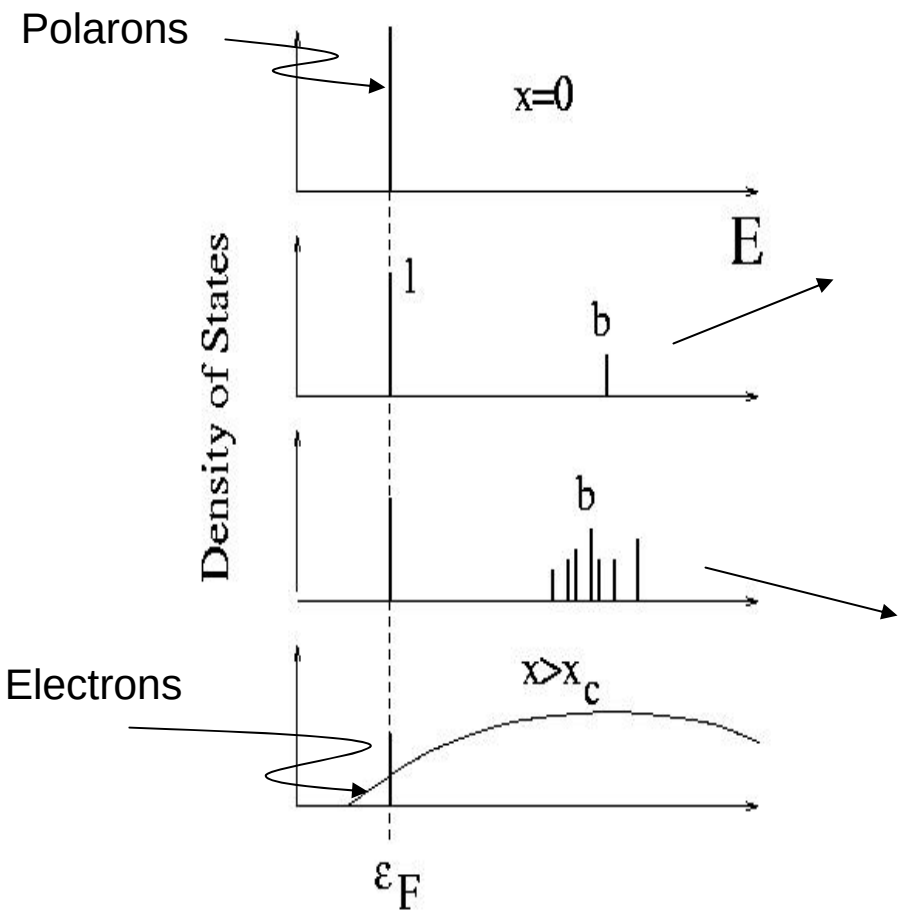
- With energies

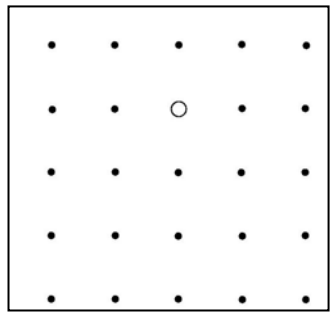
$$-6t < \varepsilon_{\vec{k}} < 6t$$

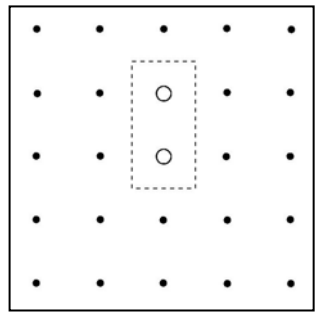


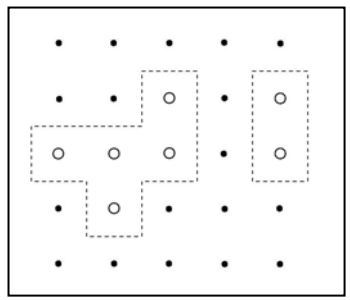
- **But all the other interactions** (U_{dd}, g, J_{SE} and J_H) and **filling constraints inhibit this lowering of the Kinetic energy, and lead to polaron formation to make the most of the JT interaction => two fluid formation**

Picturizing the Ferro-insulator to ferro-metal transition in terms of the 2-fluid Model









- ● = polaron
- ○ = empty site, no lattice distortion

2-Fluid [Localized (ℓ) + band electron (b)] Model for Doped Manganites in the Orbital Liquid regime

- In orbital liquid regime, ignoring **ℓ-b coherence** :

$$H_{lb} = -E_{JT}\sum_{i\sigma} l^{\dagger}_{i\sigma} l_{i\sigma} - \bar{t} \sum_{<ij>\sigma} b^{\dagger}_{i\sigma} b_{j\sigma}$$

$$-\mu\sum_{i\sigma}(n_{\ell i\sigma} + n_{bi\sigma}) + U_{dd} \sum_{i\sigma} n_{\ell i\sigma} n_{bi\sigma}$$

$$-J_H \sum_i (\vec{s}_{\ell i} + \vec{s}_{bi})\cdot\vec{S}_i - J_F \sum_{<ij>} \vec{S}_i \cdot \vec{S}_j - \vec{h}\cdot\sum_i \vec{S}_i$$

- Falicov-Kimball like Model, can be solved exactly in Dynamical Meanfield Theory (DMFT)

T V Ramakrishnan, HRK, SRH and VP,
Cond-Matt / 0308376, *Phys. Rev. Lett.* 92, 157203 (2004)
Also Cond-Matt / 0308396.

Dynamical Mean Field Theory (DMFT) of Localized +band electron Model

- Single site , Dynamical, self consistent effective medium theory
  - Pick one typical site of the lattice, replace all other sites by an effective medium
  - Solve the single site problem
  - Make the effective medium self consistent
- Replace t_{2g} core spin $\vec{S}_i$ by a classical spin $S\hat{\Omega}_i$
- Treat ferromagnetic coupling between the core spins in molecular field approximation
- Exact in the limit of infinite dimensions. Good approximation in d=3!
- Ref: A. Georges et. al. Rev. Mod. Phys. 68, 13 (1996)

Dynamical Mean Field Theory (DMFT) of Localized +band electron Model

- Only the variables $b^{\dagger}_{i\sigma}$ and $\hat{\Omega}_i$ see the effective medium
  - $b^{\dagger}_{i\sigma}$ sees an electron bath with which it hybridizes
  - $\hat{\Omega}_i$ sees a local "molecular" field which adds to the external magnetic field

$$H_{DMFT} = -E_{JT}\, n_{\ell} - \sum_{k\sigma} V_{\sigma}(\varepsilon_k)[b^{\dagger}{}_{\sigma} c_{k\sigma} + c^{\dagger}{}_{k\sigma} b_{\sigma}]$$

$$+\sum_{k\sigma} \varepsilon_k\, c^{\dagger}{}_{k\sigma} c_{k\sigma} - \mu\,(n_{\ell} + n_b) + U_{dd} \sum_{\sigma} n_{\ell\sigma}\, n_{b\sigma}$$

$$-J_H\, S(\vec{s}_{\ell} + \vec{s}_b)\cdot\hat{\Omega} - (J_F\, z\, S^2\, \vec{m} + \vec{h}\, S)\cdot\hat{\Omega}$$

Dynamical Mean Field Theory (DMFT) of Localized +band electron Model

- Material parameters: E_{JT}, $D_o (= z\,\bar{t})$, J_F, x, $U(\to \infty)$, $J_H(\to \infty)$
- Effective Medium parameters (to be self consistently determined): μ, m, $V(\varepsilon)$
- From solving single site problem get
  - Annealed probabilities $P(n_l)$, $P(\hat{\Omega})$
  - b elctron self energy $\Sigma(\omega^+)$
  - b electron local propagator

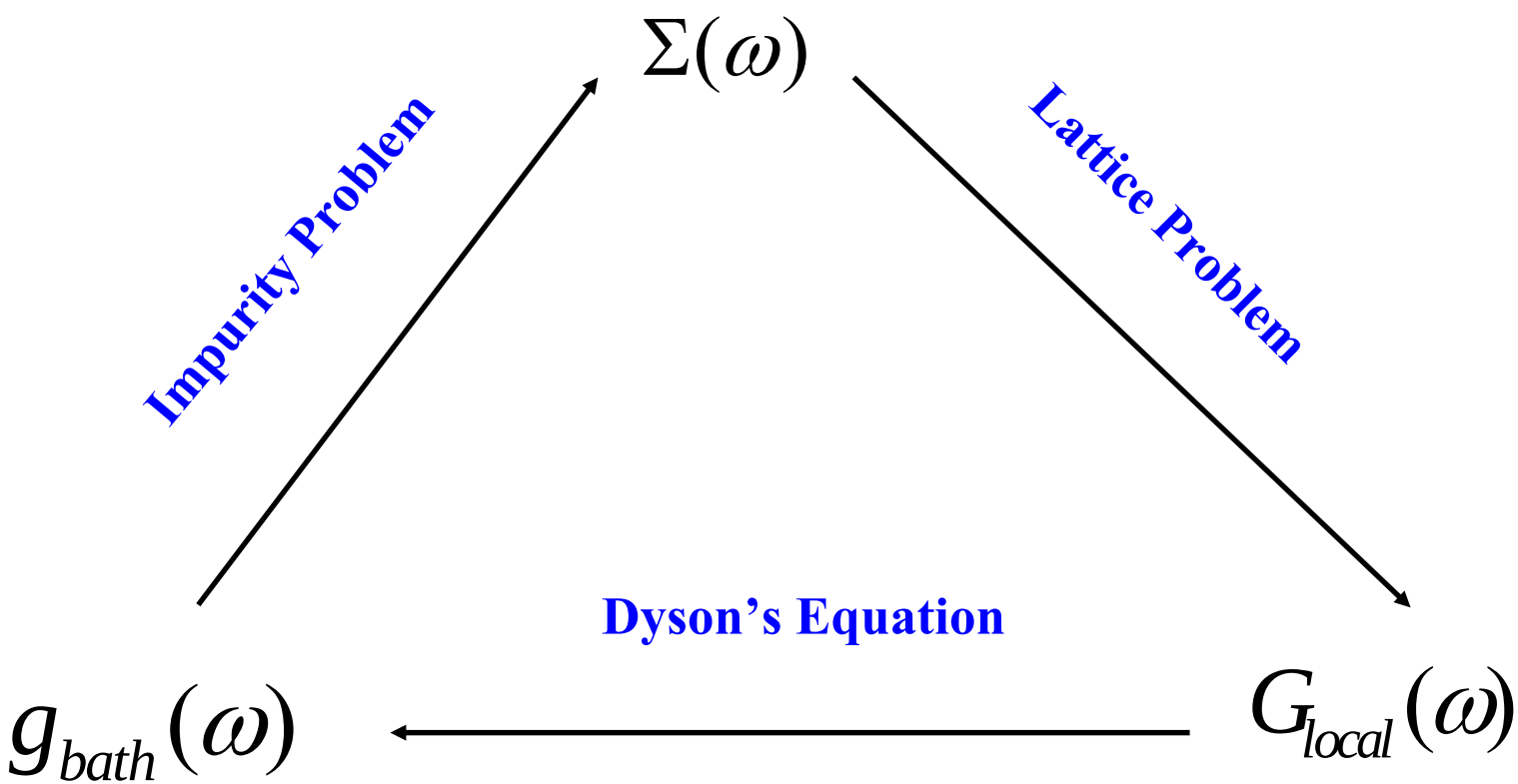
$$G_{loc}(\omega^+) = [\,\omega^+ + \mu - \int d\varepsilon \frac{[V(\varepsilon)]^2}{\omega^+ - \varepsilon} - \Sigma(\omega^+)\,]^{-1} = [(g_{bath}(\omega))^{-1} - \Sigma(\omega^+)\,]^{-1}$$

- DMFT self consistency requires

$$m = <\hat{\Omega}> \qquad <n_\ell> + <n_b> = 1 - x$$

$$G_{loc}(\omega^+) = \sum_{\mathbf{k}} \frac{1}{\omega^+ + \mu - \varepsilon_{\mathbf{k}} - \Sigma(\omega^+)}$$

Dynamical Mean-Field Theory
Triangle of self consistency

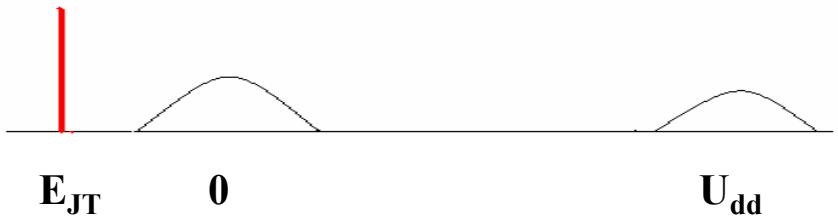


T = 0 Ferro-Insulator to Ferro-Metal Transition with Doping

(G. Venketeswara Pai, SRH, HRK and TVR, *Europhysics Letters* 64, 696 (2003))

- **x=0:** All electrons are in 'l' state. One at each site.→ Only UHB with energy U_{dd} available for 'b' states → **insulator**

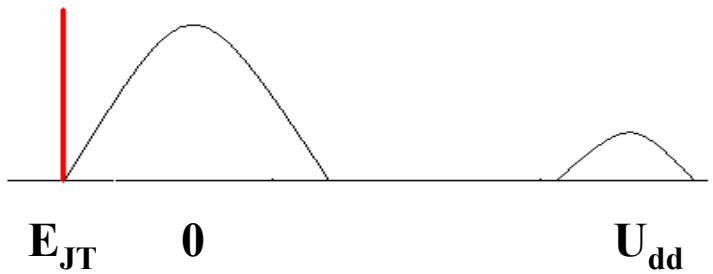
- For small x , Few hole sites → small LHB for b develops, with bandwidth (2D) strongly suppressed due to U
  - b band fully above ℓ levels
  - All electrons still in ℓ levels
  - System is (Ferro) **insulator**



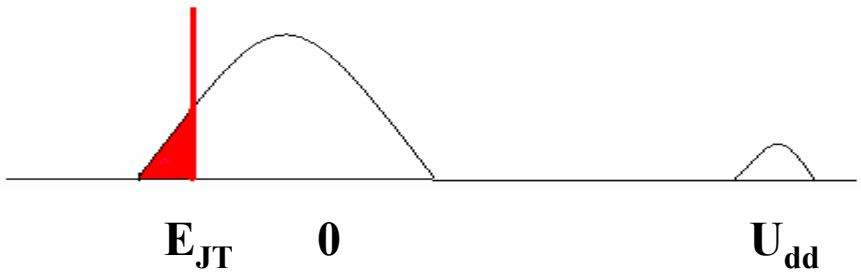
T = 0 Ferro-Insulator to Ferro-Metal Transition with Doping

(G. Venketeswara Pai, SRH, HRK and TVR, *Europhysics Letters* 64, 696 (2003))

- As x increases, b-LHB bandwidth grows as $D \sim D_0\sqrt{x}$
- At a critical $x_c \sim (E_{JT}/D_0)^2$, $D=E_{JT}$
  → Insulator-Metal Transition!



- For $x>x_c$, partial (small) occupancy of b-(LHB) band. System is (Ferro) Metal



T = 0 Band Edges and Insulating Gap

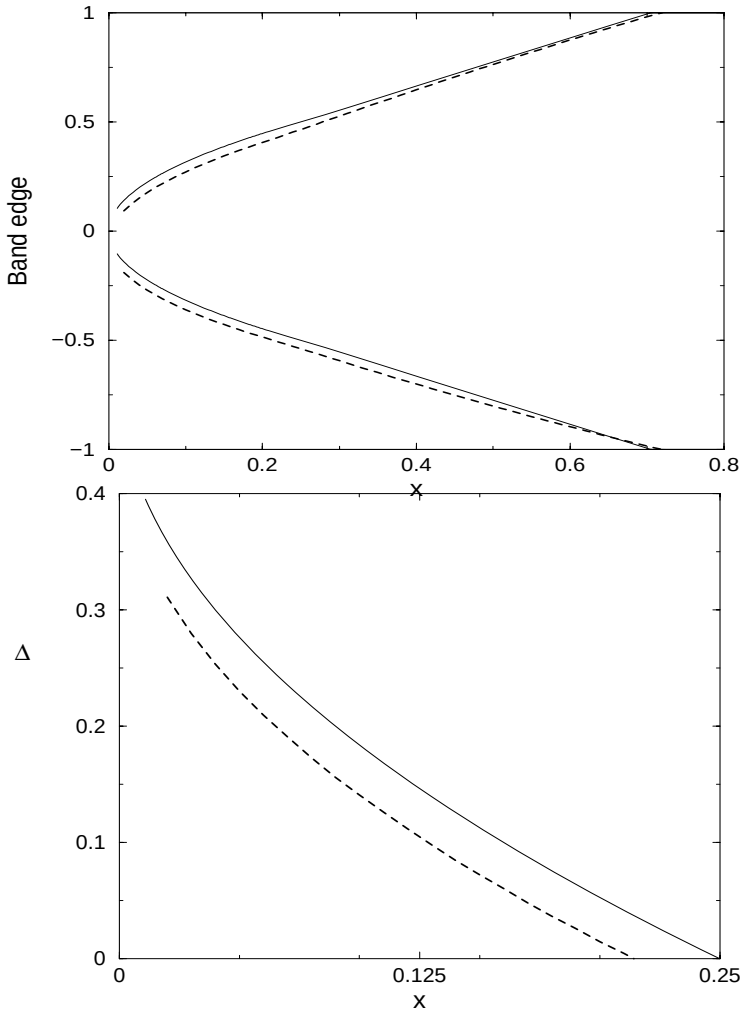
(G. Venketeswara Pai, SRH, HRK and TVR, *Europhysics Letters* 64, 696 (2003))

- Decrease of b band-edges with doping x. For U=∞

$$D = D_o \sqrt{x}$$

- Decrease of Δ with doping x shown like what is seen in (LaCa). For U=∞

$$\Delta = E_{JT} - D_o \sqrt{x}$$



(E_{JT} =0.5 eV; full line : U = ∞; dashed line : U = 5 eV)

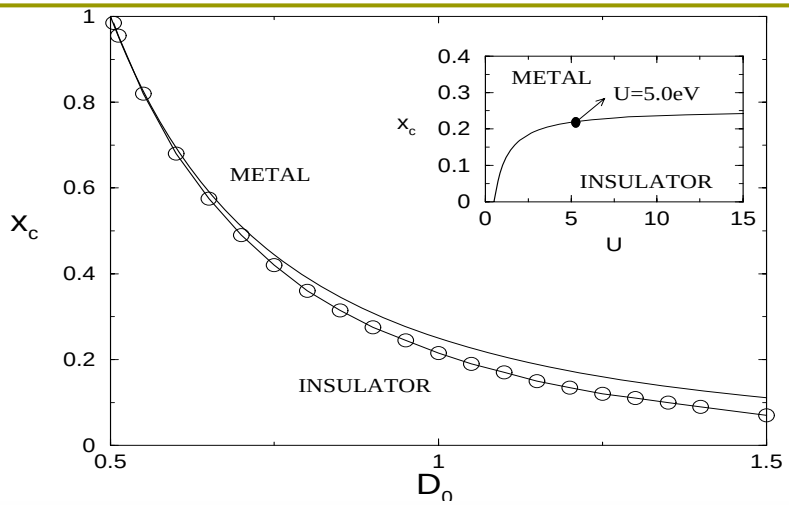
T = 0 Phase Diagram and carrier Density

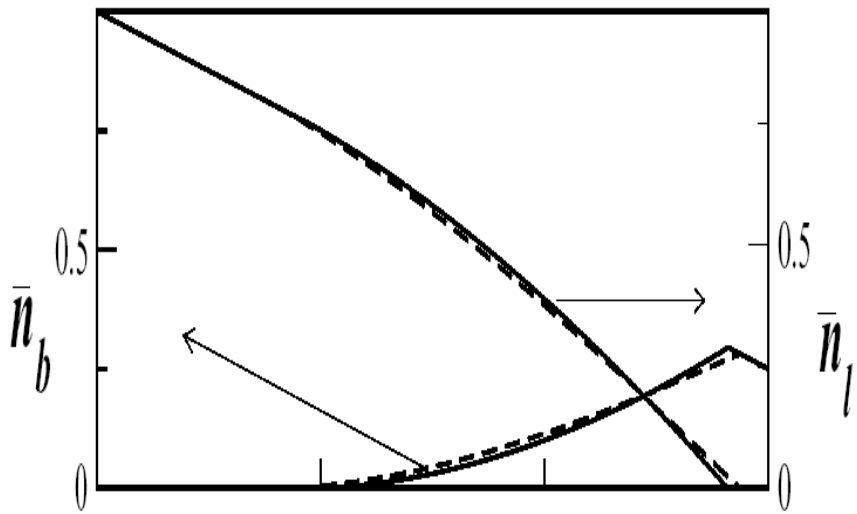
(G. Venketeswara Pai, SRH, HRK and TVR, *Europhysics Letters* 64, 696 (2003))

- For U=∞ $x_c = (E_{JT} / D_o)^2$
- Reduction of x_c with increasing D_o agrees with experimental trends: x_c(LaSr) = 0.16 > x_c(LaCa) = 0.18 > x_c(NdSr) (> 0.28)
- (PrSr) has no metallic phase for x < 0.4 , or 0.5; accounted for if $(E_{JT} / D_o) \geq 0.7$ for (PrSr) ; i.e., for E_{JT} 0.5 eV, bandwidth $2D_o$ < 1.4 eV.
- carrier density in metallic regime (x ~ 0.3) very small :

$$\overline{n}_b \equiv < n_b > \simeq 0.05$$

Agrees with anomalously small values inferred from optical conductivity

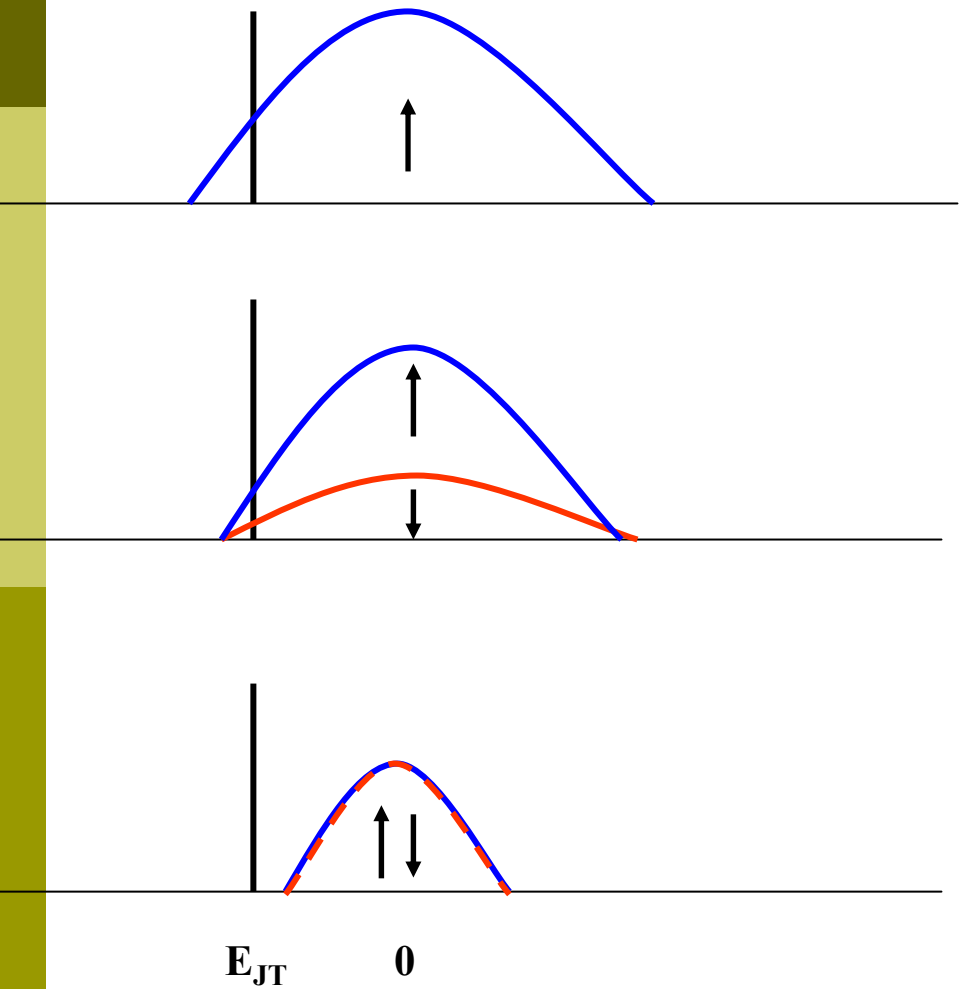




(EJT =0.5 eV; full line : U = ∞; dashed line : U = 5 eV)

Thermal Ferro-Metal to Para-Insulator Transition

(TVR, HRK, SRH and GVP, *Phys. Rev. Lett.* 92, 157203 (2004))



T=0 : All core spins up due to VDE → only up-spin b-LHB states at low energies (down-spin b-LHB states J_H above) → **FERRO-METAL (FM)**

Small T>0: Core spins disorder → Small number of low energy down spin (minority spin) b-LHB states appear. Average hopping by double-exchange reduces due to spin-mismatch at different sites: LHB Bandwidth reduces.

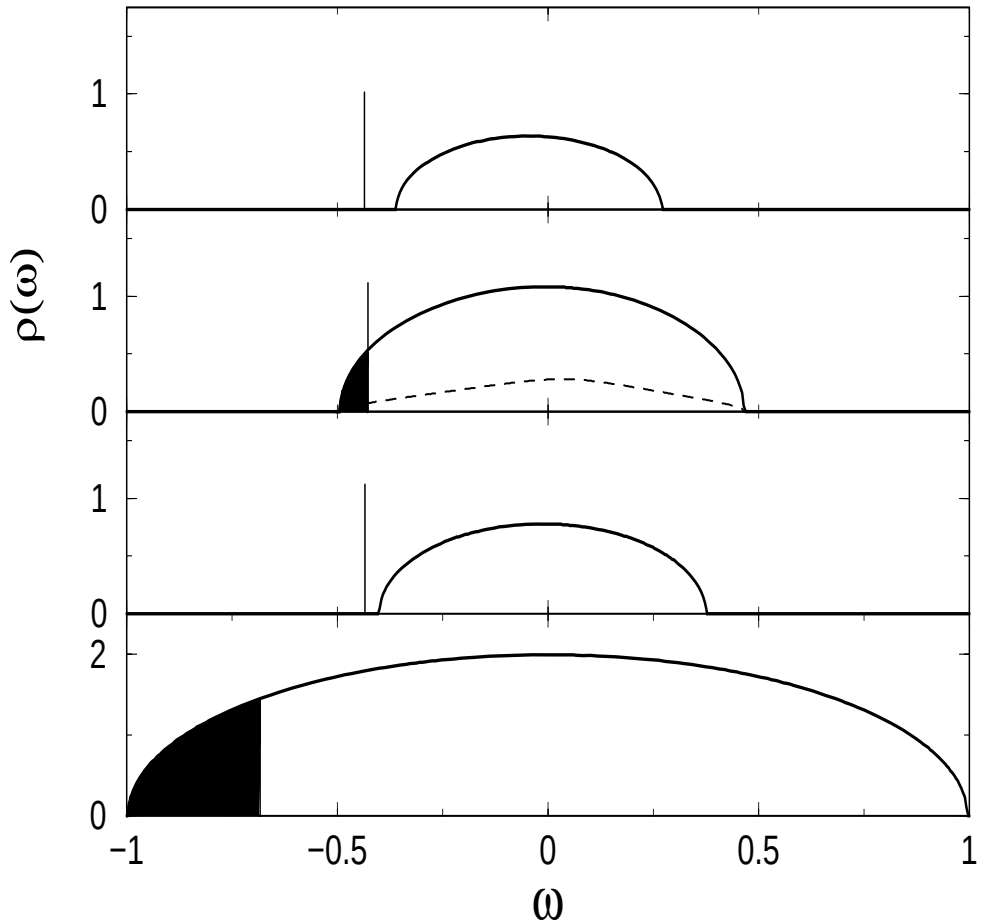
$T>T_C$: Down spins DOS becomes equal to up spin DOS, lower edge of LHB for both spins go above 'l'-level: → **PARA-INSULATOR (PI)**

Only b-LHB is shown

Thermal Ferro-Metal to Para-Insulator Transition

TVR, HRK, SRH and VP, *Phys. Rev. Lett.* 92, 157203 (2004)

- **up-spin : full line**
  down-spin: dashed line.
  occupied states :
  thick line (ℓ) or
  black shading (*b*)
- **(a) $x = 0{:}1$, $T = 0$; ferromagnetic insulator.**
- **(b) $x = 0{:}3$, $T = 180K$; ferromagnetic metal.**
- **(c) $x = 0{:}3$, $T = 350K$ ($> T_c = 240K$); paramagnetic insulator.**
- **(d) $x = 0{:}8$ (electron doped), $T = 230K$; paramagnetic metal.**

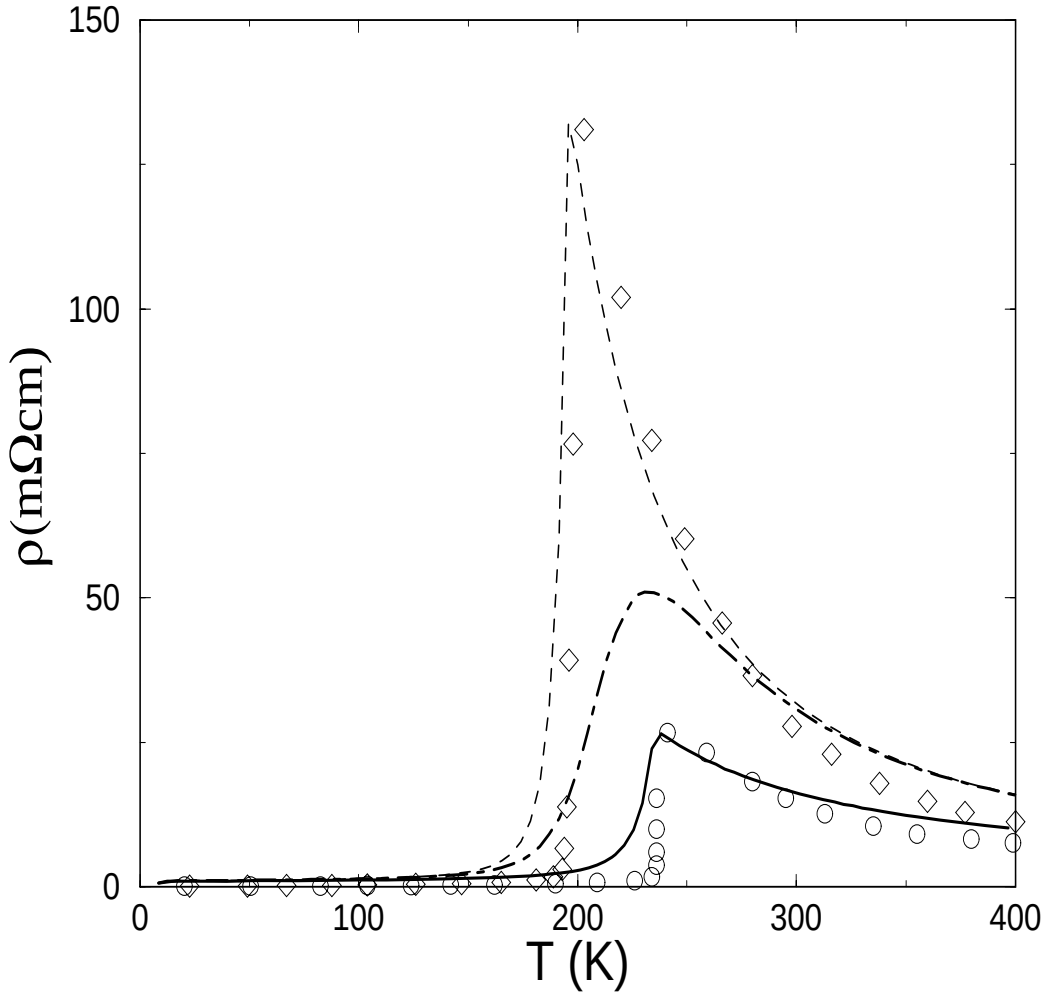


DOS of ℓ & *b* electrons for various x and T
($E_{JT} = 0.5\ eV$, $D_o = 1.2\ eV$, $U = 5.0\ eV$ and $J_F = 2.23\ meV$)

Thermal M-I Transition and CMR

TVR, HRK, SRH and VP, *Phys. Rev. Lett.* 92, 157203 (2004)

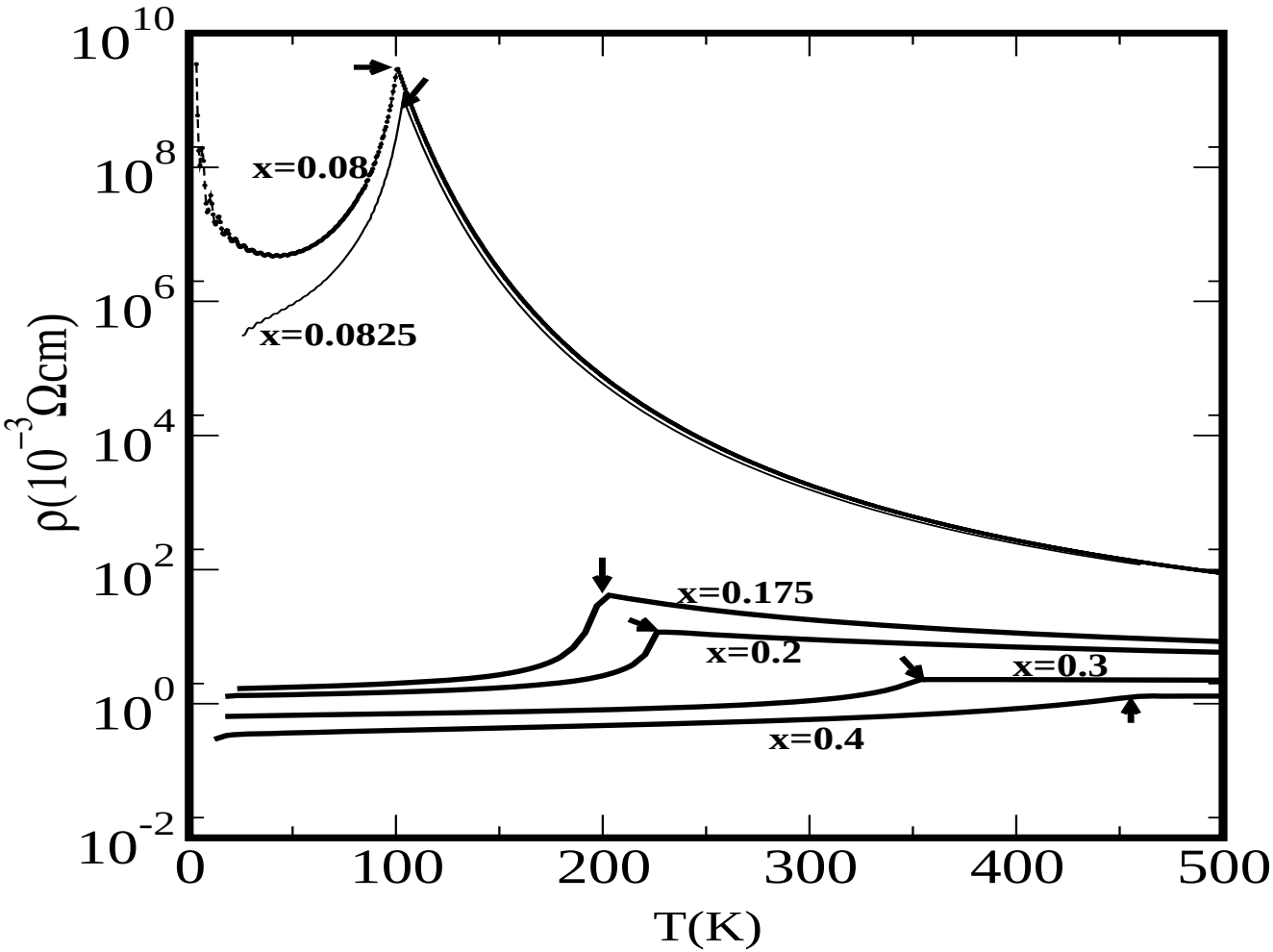
- Full line: theory - LaCa **(D_o =1.05 eV, J_F = 1.95 meV)**
- Circle (o) : experiment – LaCa
- Dashed line: theory - NdSr **(D_o = 1.15 eV, J_F = 2.23 meV)**
- Diamond (◇) : experiment - NdSr.
- (dash-dotted line) : Calculated ρ(T) at H = 7 Tesla for NdSr



(E_{JT} = 0.5 *eV* , *U = 5 eV* and *x = 0.3*)

Calculated Resistivity vs T for various x (parameters chosen to correspond to LaSr system)

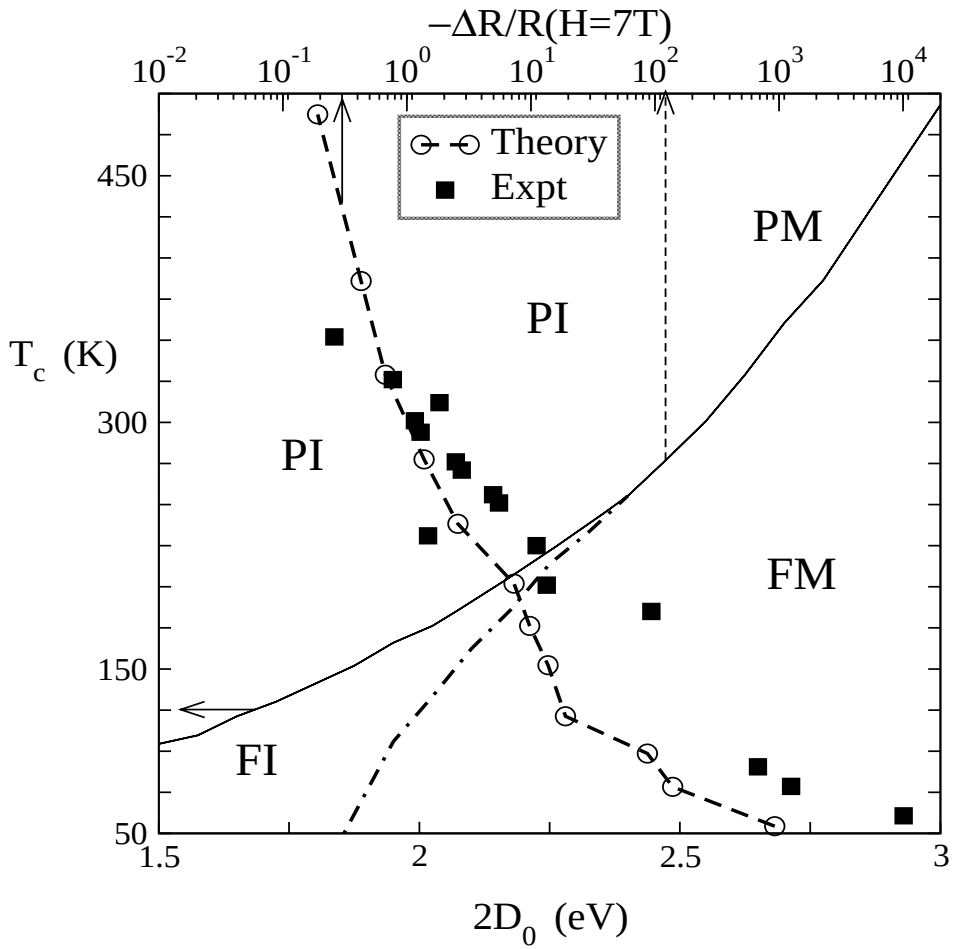
(S. R. Hassan, Thesis (IISc, 2003) Unpublished)



Material (varying D_o) Systematics

TVR, HRK, SRH and VP, *Phys. Rev. Lett.* 92, 157203 (2004)

- full line :ferromagnetic T_c vs D_o ;
  - Small D_o , Curie transition from Para Insulator to Ferro Insulator;
  - Intermediate D_o, from Para Insulator to Ferro metal,
  - for large D_o , from Para metal to Ferro Metal
- Broken line : calculated fractional magneto-resistance ($\Delta R(H)/R(H)$) at T_c for H = 7 Tesla compared with experimental points (▪) from Khazai.



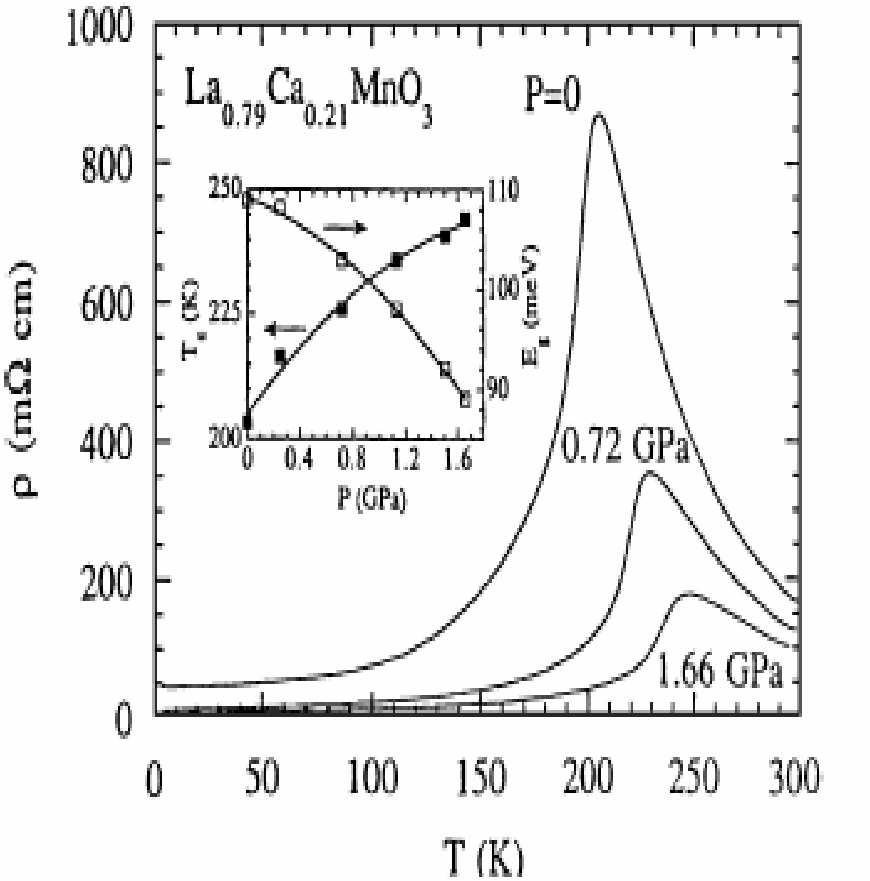
(For fixed E_{JT} = 0.5 eV , U = 5 eV, $J_F \sim (D_o)^2$)

Pressure Dependence of ρ and Tc

(From J. J. Neumeier et. Al. Phys. Rev. B **52**, R7006 (1995))

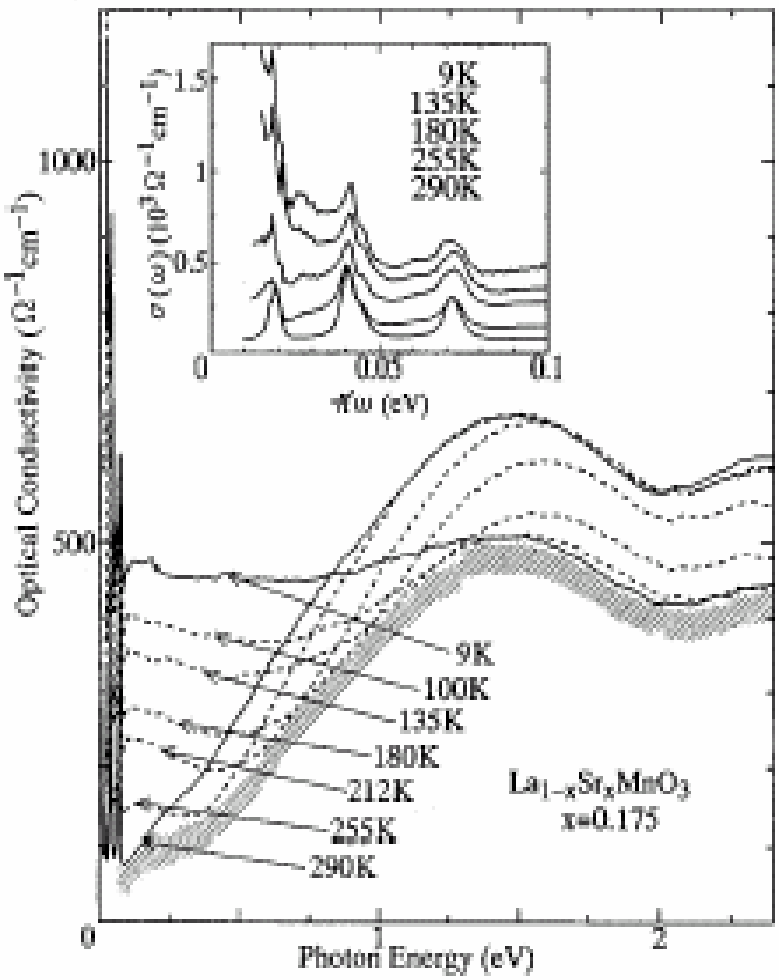
- ρ vs. T at three hydrostatic pressures for LaCa system
- Inset: T_c and activation energy vs. P
- Consistent with our theory if

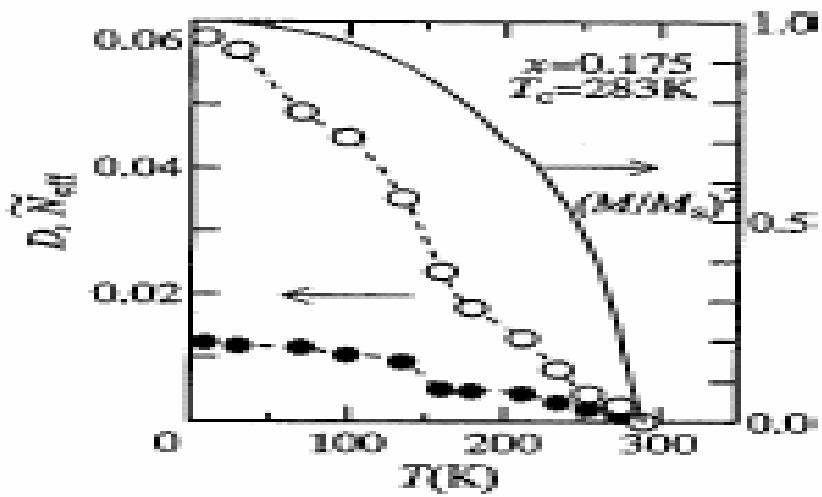
$$dD_o / dP \cong .01eV / Kbar$$

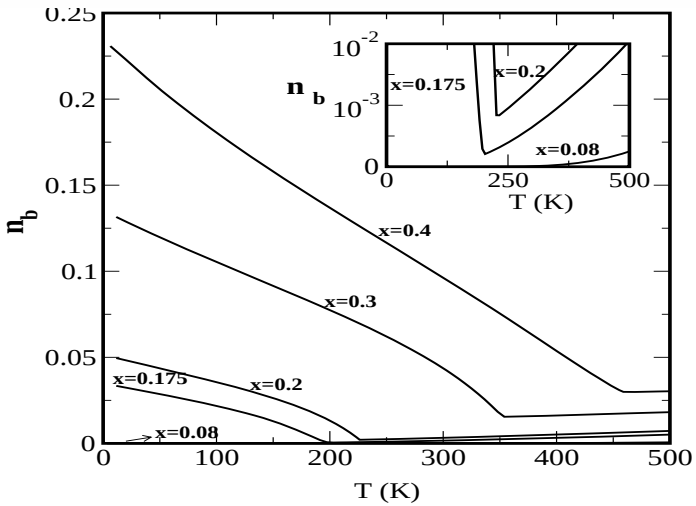


Optical conductivity and Low N_{eff}

(from Y.Okimoto et. al.1995a, Phys. Rev. Lett. **75**, 109)







Plasmon Excitations in Electronic Raman Scattering of $La_{1-x}Sr_xMnO_3$ (Bjornsson et.al. PRB 61, 1193 (2000))

- Broad peak around 750 cm^{-1} interpreted as due to plasmons, fit by

$$I(\omega) \sim \frac{\omega_P^2 \Gamma}{(\omega^2 - \omega_P^2)^2 + \Gamma^2}$$

$$\omega_P = \sqrt{4\pi n e^2/m}$$

$$x = 0.35,\ \omega_P^{calc} \sim 0.5 \text{ to } 1\,eV$$

$$\omega_P^{obs} \sim 0.1\,eV$$

- Consistent with our theory

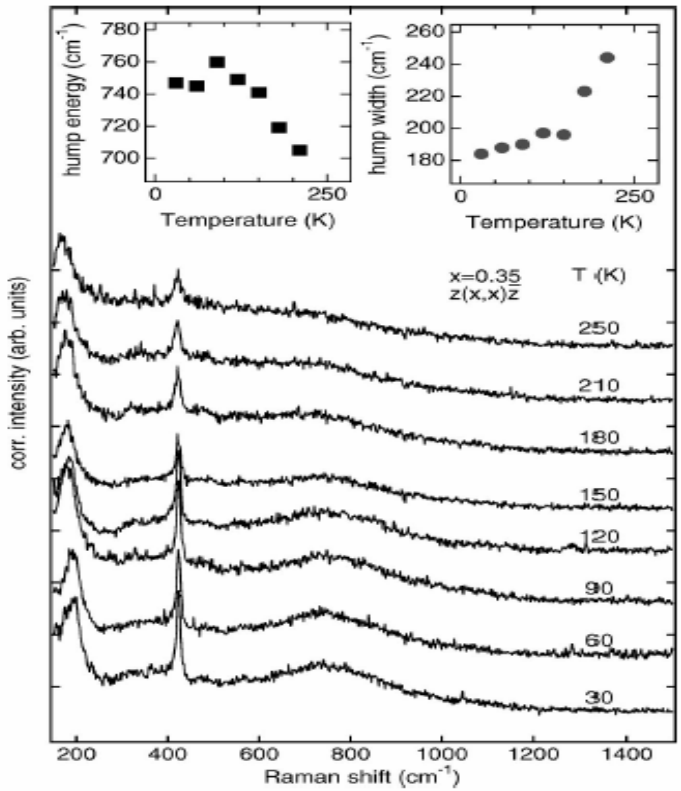


FIG. 4. Raman spectra taken with a laser excitation energy of 2.41 eV for a doping level of $x = 0.35$ displaying the temperature dependence of the hump. Temperatures and base lines are indicated. The insets give the hump energy and width derived from a fit as described in the text. Error bars are indicated by the symbol size.

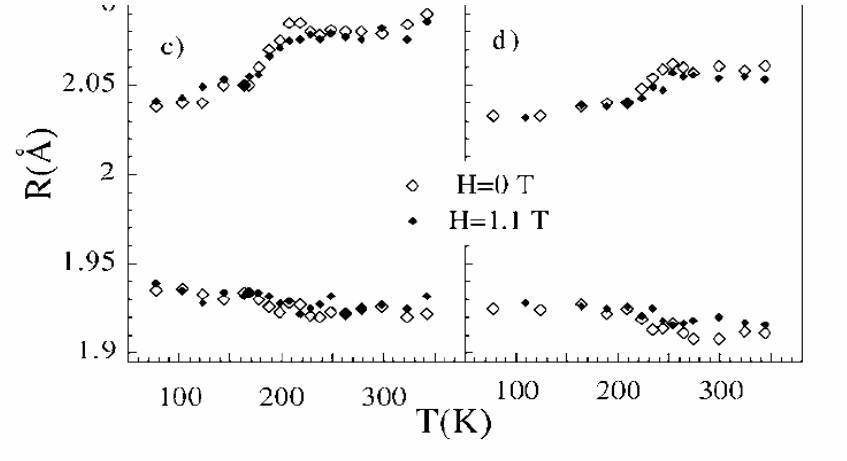
Asymmetry between Over(electron) Doping ($x >> 0.5$) vs. Under(hole) doping ($x << 0.5$)

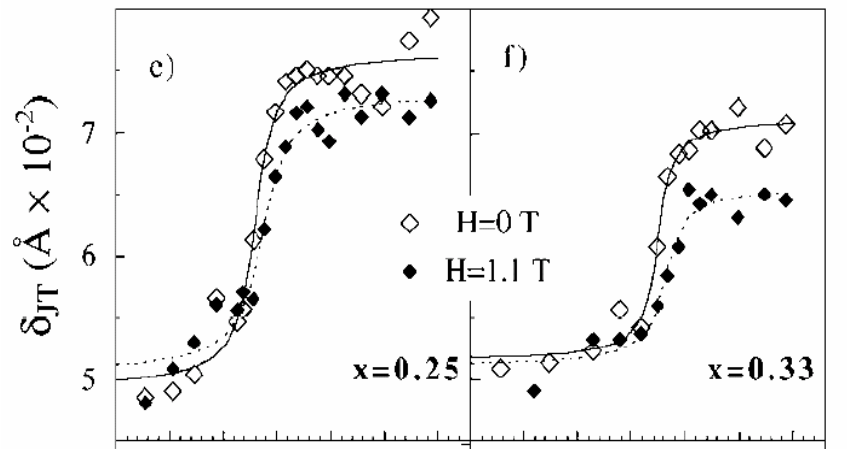
- Electronic and magnetic properties of under (hole) doped ($x << 0.5$) and over (”electron”) doped” ($x >> 0.5$) manganites very different:
  - Latter much more metallic than former in paramagnetic phase
  - (AF or charge ordered phases insulating for other reasons).
- Behaviour unexpected in
  - one orbital strong coupling polaron model (For low e_g carrier density the dilute small polaron assembly should form an insulator)
  - in pure Double Exchange models , where there is electron hole symmetry.
- But natural in our theory where for large x
  - *There are no polarons* as the ℓ states are unoccupied
  - *E*ffectively uncorrelated *b* electrons form a wide band with bottom occupied by the small number of e_g electrons,,
- Also explains why pure band models are fairly successful in describing the magnetic ground states in over-doped limit.

Evidence for JT Distortions in doped manganites

(C. Menenghini et. Al., J. Phys. Cond. Matt. **14** , 1967 (2002))

- Persistence of large local *JT* lattice distortion into the doped regimes seen in EXAFS [LaCa, x=.25 (ins) and .33 (met)]
- $\delta_{JT}(x) \approx \delta_{JT}(0)\,(1-x)$ as if every Mn 3+ site is distorted
- Completely consistent with our picture





Evidence for JT Distortions in doped manganites

(D. Loucca et. Al., Phys. Rev. B. **56** , R8465 (1997))

- Persistence of large local *JT* lattice distortion into the doped regimes seen in Pulsed neutron Diffraction [LaSr system]
- Fraction of JT distorted sites decreases with doping, and with decreasing temperature!
- Completely consistent with our picture

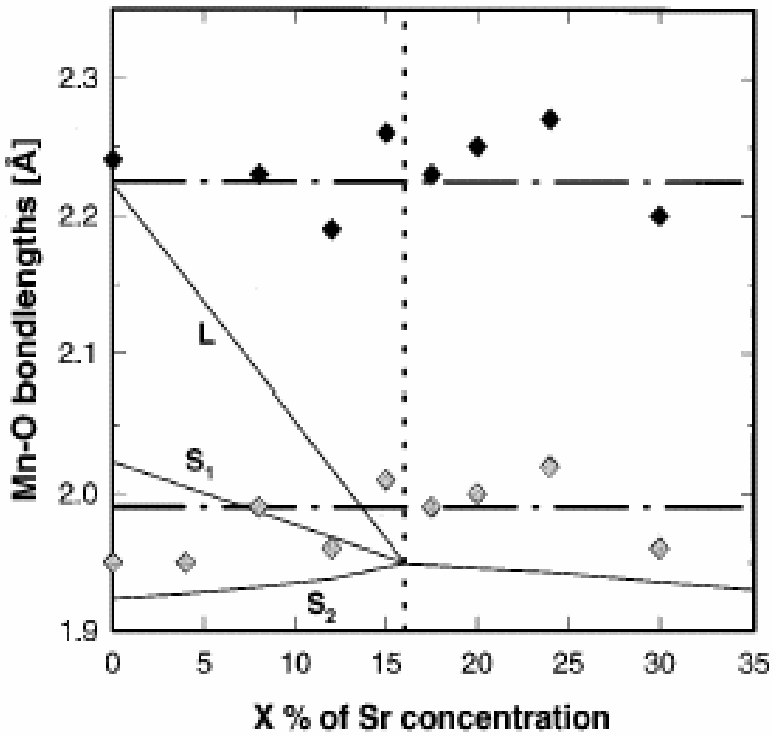


FIG. 4. The Mn-O bond lengths as determined from the PDF (triangles) compared to those deduced from the lattice constants of the crystal structure (solid lines L, S_1, and S_2) (Ref. 26). Note that the local JT distortion is present even in the rhombohedral phase.

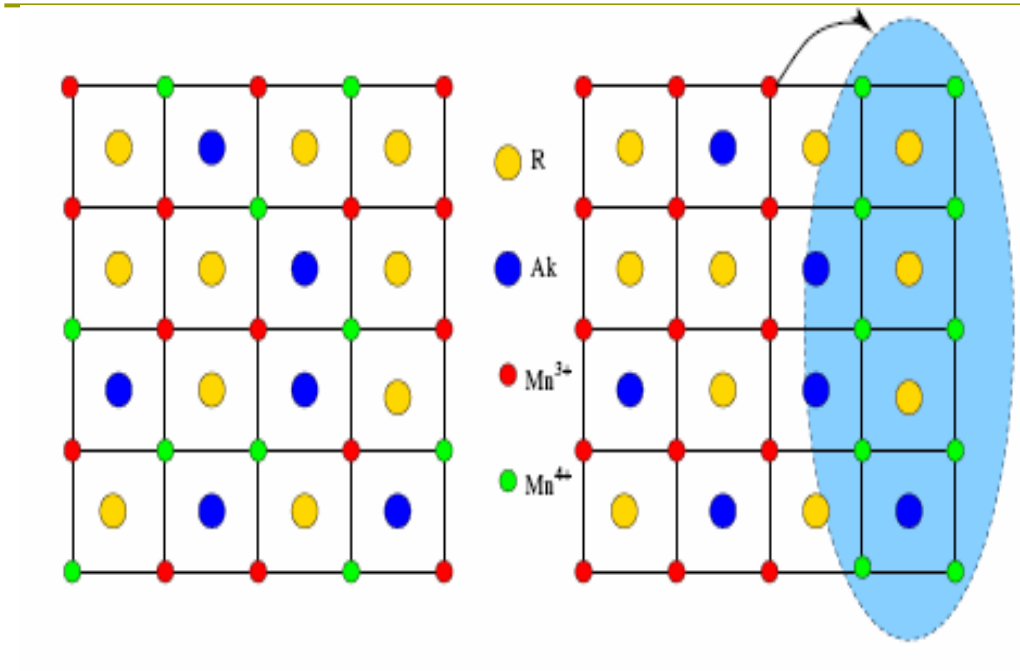
ℓ - *b* model including the effects of Long Range Coulomb Interactions and Doping

(Vijay B Shenoy, TG, HRK and TVR, Phys. Rev. Lett. **98**, 097201 (2007) & TBP)

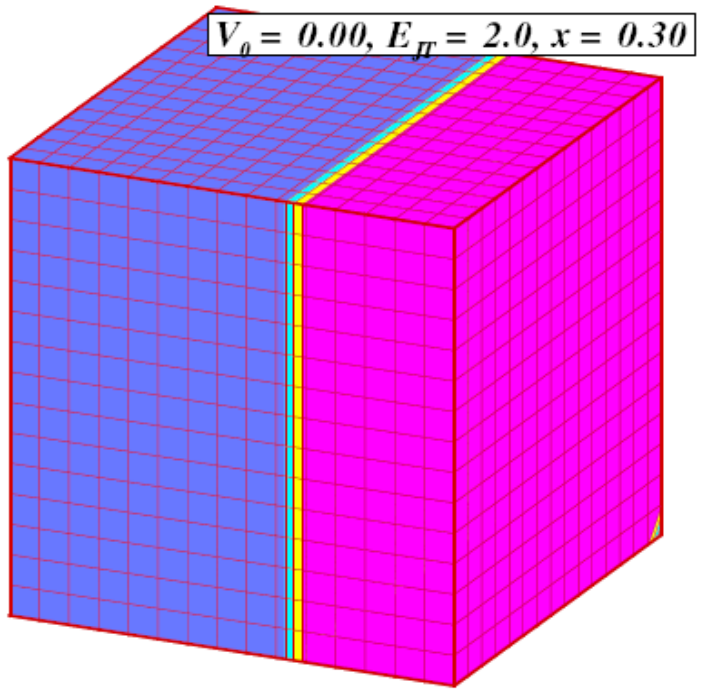
- H_{lb} by itself gives rise to macroscopic phase separation of ℓ and *b* electrons.
- Homogeneous solution stabilized in More realistic model which includes long range coulomb interactions with strength V_0, with
  - Repulsion between ℓ - ℓ , ℓ - *b* and *b* - *b* electrons (treated in Hartree Approximation)
  - Attraction between ℓ and *b* electrons and (quench-disordered) dopant ions.
- Simulation results on finite lattices, upto 20x20x20
- Threshold for occupancy of *b* staes amazingly similar to DMFT results

Macroscopic Phase separation in a simple ℓ - b model

(Vijay B Shenoy, TG, HRK and TVR, Phys. Rev. Lett. **98**, 097201 (2007) & TBP)

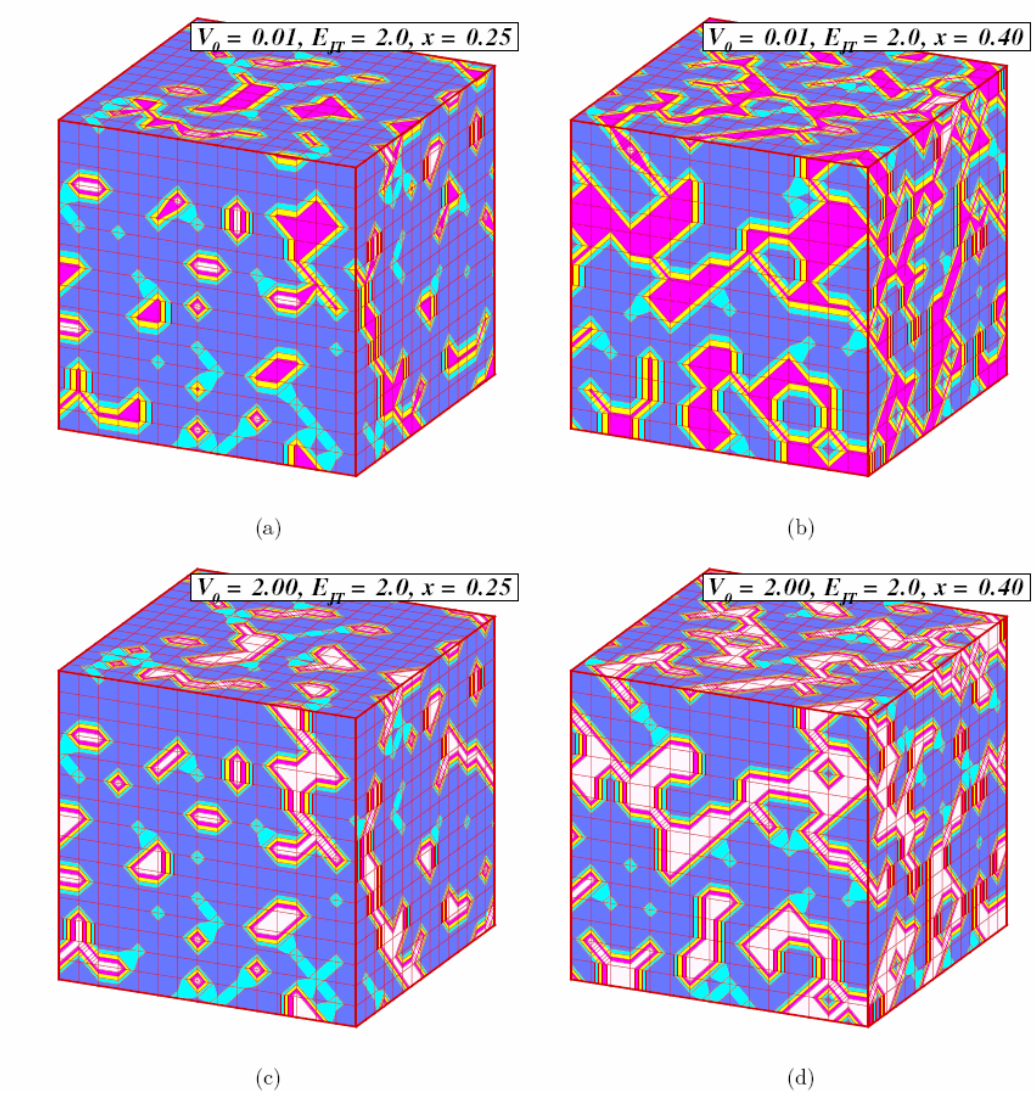


Prevented by Long Range Coulomb Interactions !



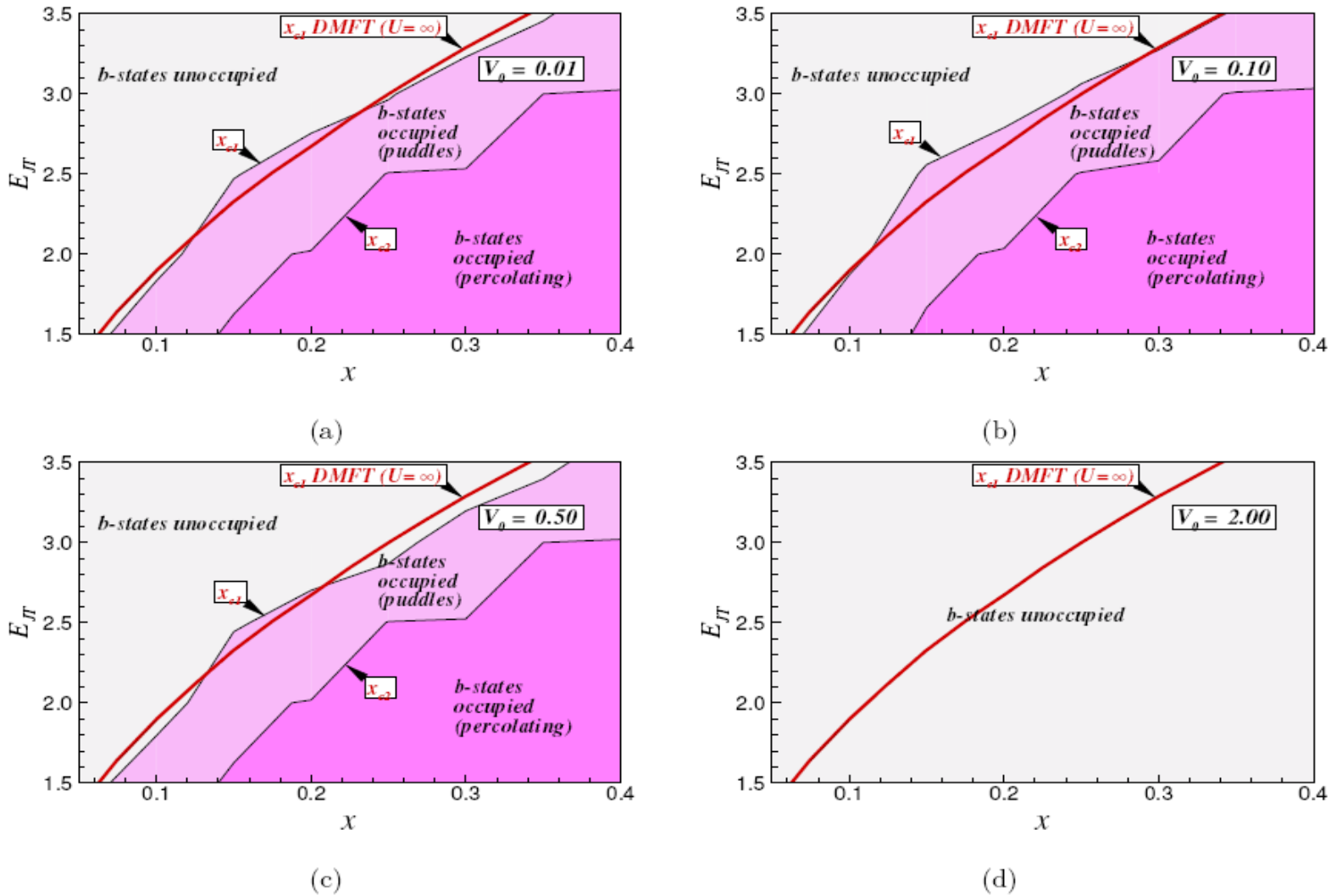
Real Space Structure in the Extended ℓ - b model (with Long Range Coulomb Interactions)

(Vijay B Shenoy, TG, HRK and TVR, Phys. Rev. Lett. **98**, 097201 (2007) & TBP)



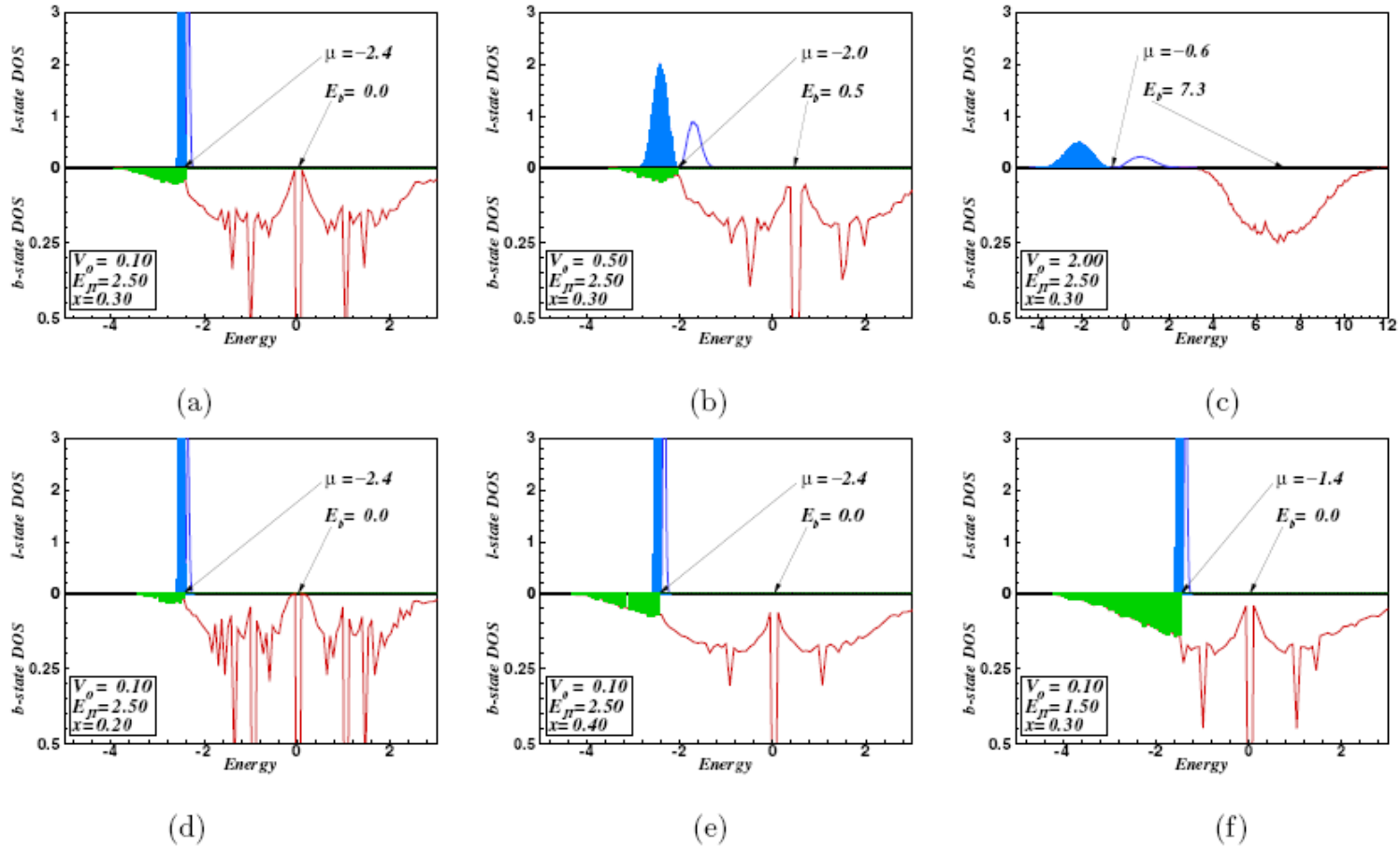
Critical Doping Values from simulations of Extended ℓ - *b* model (with Long Range Coulomb Interactions)

(Vijay B Shenoy, TG, HRK and TVR, Phys. Rev. Lett. **98**, 097201 (2007) & TBP)



DOS of ℓ polarons and *b electrons*

(Vijay B Shenoy, TG, HRK and TVR, Phys. Rev. Lett. **98**, 097201 (2007) & TBP)



CORE-LEVEL PHOTOEMISSION using EXTENSION of ℓ-b MODEL and DMFT

(Prabuddha Sanyal et al., **arXiv:0704.3923** (April 2007) & TBP)

We model the site at which core-level photo-emission takes place using the "impurity Hamiltonian"

$$H = H_{DMFT} + H_{core-level}$$

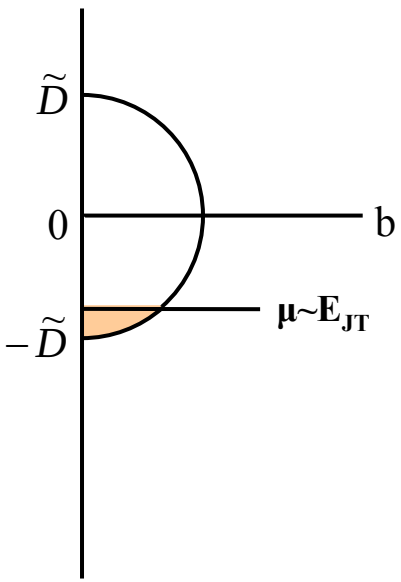
$$H_{core-level} = (\varepsilon_c - \mu)\hat{n}_c + U_{pd}\hat{n}_c(b^{\dagger}b + \hat{n}_l)$$

- ε_c = site energy of core-level
- U_{pd}= attractive interaction between core-hole and the '*l*' and '*b*' electrons.

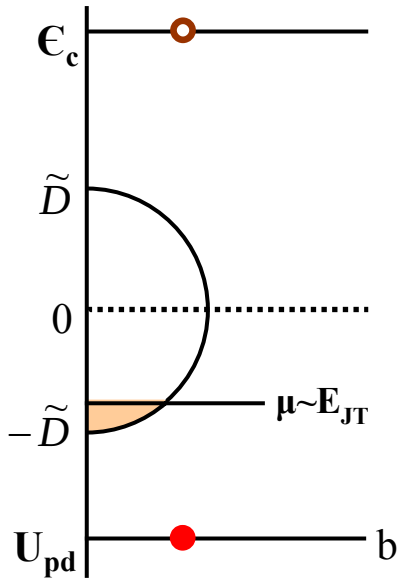
Transitions in the $n_l = 0$ Sector

(Prabuddha Sanyal et al., **arXiv:0704.3923** (April 2007) & TBP)

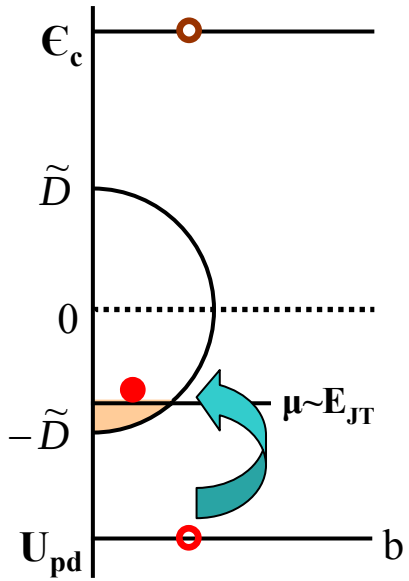
Initial ($n_c = 0$)



Final ($n_c = 1$)
'b' occupied



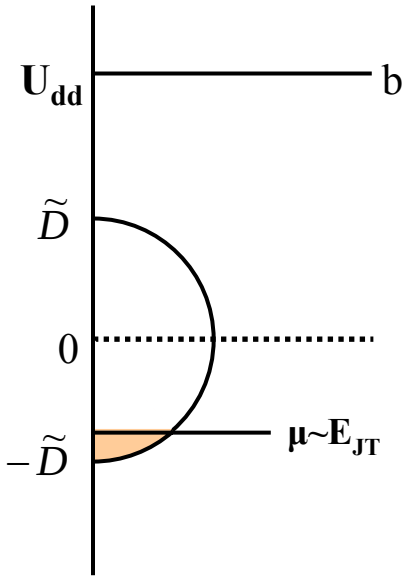
Final ($n_c = 1$)
'b' unoccupied



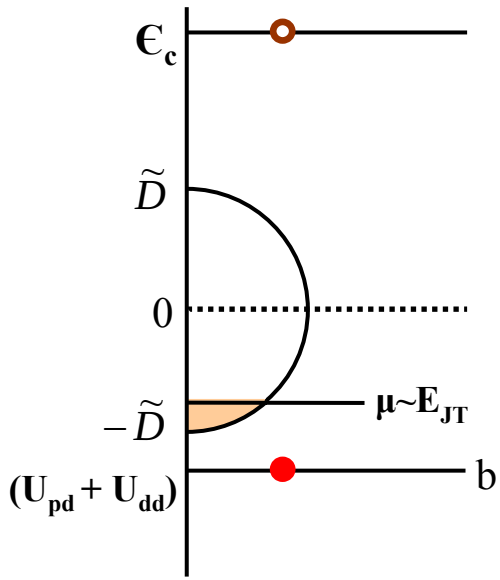
Transitions in the $n_l = 1$ Sector

(Prabuddha Sanyal et al., **arXiv:0704.3923** (April 2007) & TBP)

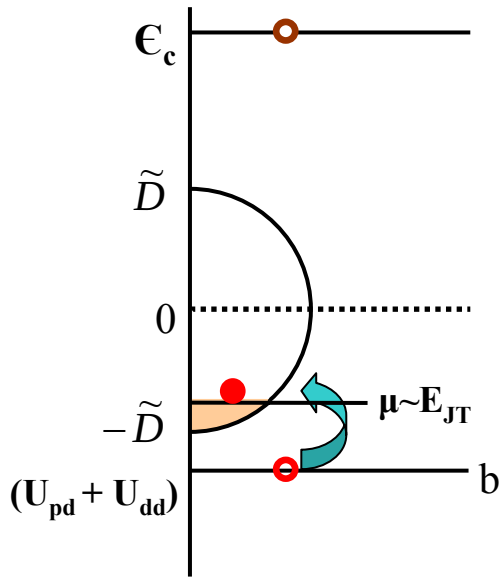
Initial ($n_c = 0$)



Final ($n_c = 1$)
'b' occupied

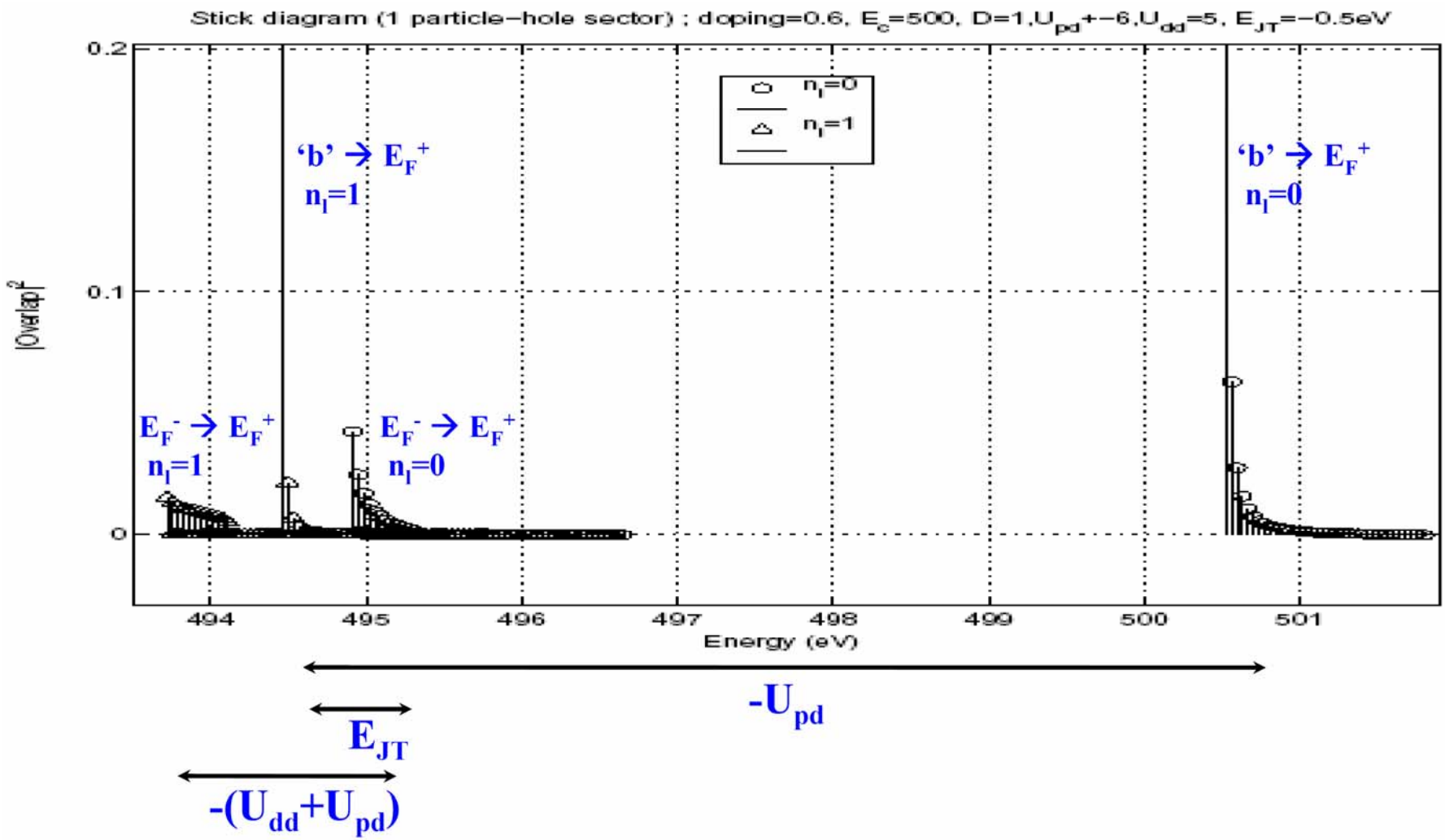


Final ($n_c = 1$)
'b' unoccupied



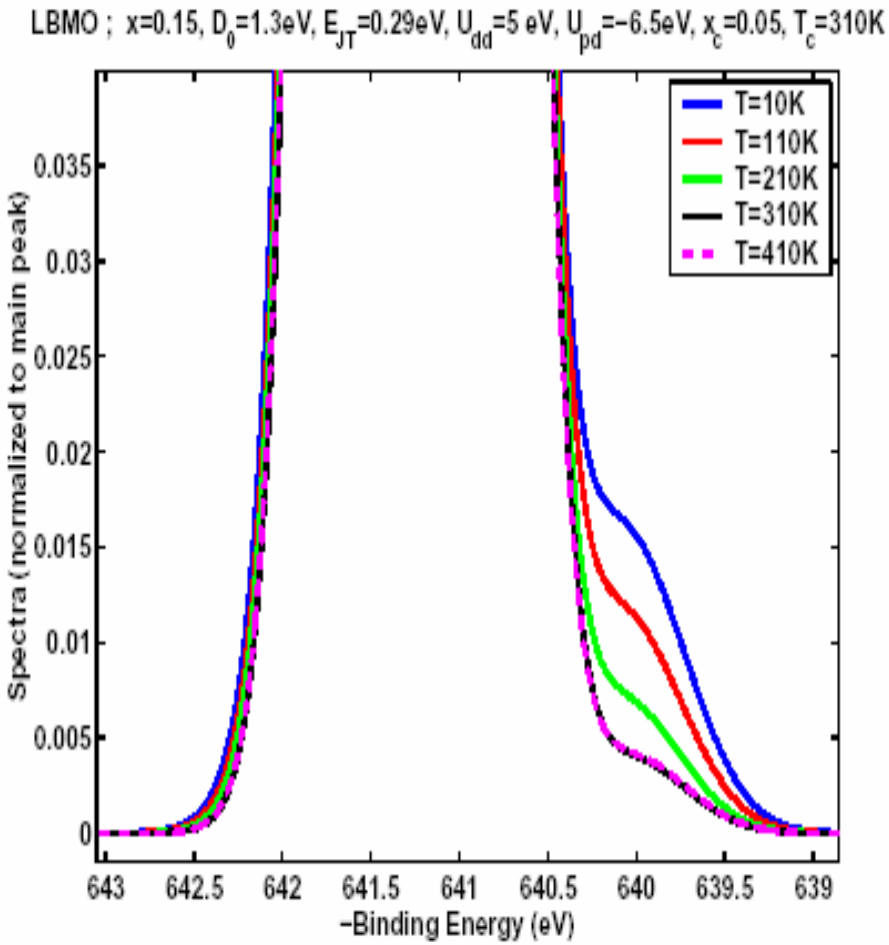
The four edge singularities : Two in each n_l sector

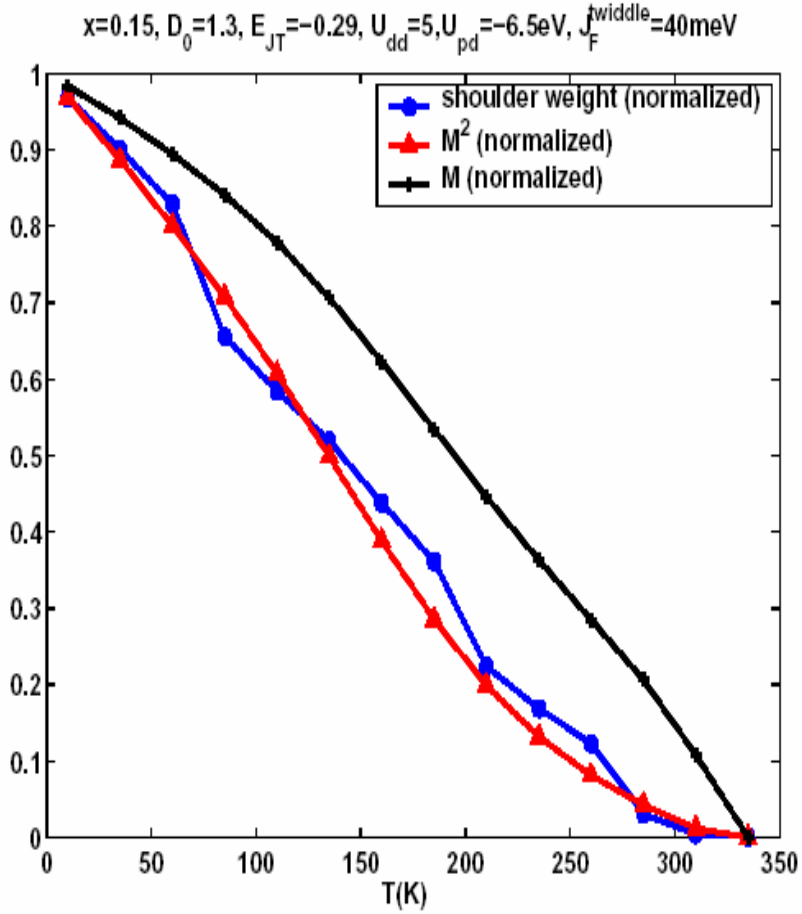
(Prabuddha Sanyal et al., **arXiv:0704.3923** (April 2007) & TBP)



THEORETICAL SPECTRA FOR LBMO

(Prabuddha Sanyal et al., **arXiv:0704.3923** (April 2007) & TBP)





Effects of Intersite ℓ-b coherence

- Intersite ℓ-*b* coherence arises from the term

$$-t_2\eta^2\sum_{i\sigma} l^\dagger_{i\sigma} l_{i\sigma} \;-\; t_1\eta \sum_{<ij>\sigma} (b^\dagger_{i\sigma} l_{j\sigma} + l^\dagger_{j\sigma} b_{i\sigma})$$

with $t_1 \approx t_2 \approx \overline{t}$ If we add the term to our model, then

  - ℓ polarons can form a band of narrow width of order $2D^* = 2zt_1\eta = k_B T^*$ with $T^* \approx 150K$.
  - accounts for the drop in resistivity seen in experiments from ρ($T < Tc$) ≈ 1 *or* 2 *mΩ cm* to about 50 *μΩ cm* well below *Tc*.
  - For $T < T^*$, since ℓ polarons hop, the JT effect becomes dynamic, as seen by many probes (unless there is long range orbital order).
  - Can account for the giant isotope effect !
    - ℓ polaron coherent hopping can make a double exchange contribution $T_{c\ell} \approx k_B D^*(1 - x)$ to the ferromagnetic T_c.
    - Depends exponentially on $\sqrt{M_o}$
    - estimate for $T_c = T_c(O^{16}) - T_c(O^{18})$ close to what is observed.

Effects of Intersite ℓ-b coherence

- Can account for changes of sign of Hall coefficient with temperature
- …

- ℓ - *b* hybridization strongest in a metal because the states are degenerate in energy
  - broadens the ℓ band => reduces the polaronic distortion ρ^{JT} => broadens the ℓ band further by increasing η.
  - Because of this feedback, possible that *JT* polarons weaken and disappear deep in the metallic phase rather than becoming merely dynamic.

Harder Theoretical challenges

- Extension of theory to describe short or long range charge/ orbital order not complete
- For this one needs to study the dependence of properties on local degrees of freedom *eg.* orbital angles θ_i , average occupancies $n_{\ell i}$, n_{bi} and their spatial correlations.
- As lattice distortions, strain, disorder, long range coulomb interactions, an-harmonicities, breathing modes etc. also couple to the above, such terms may need to be added as necessary.
- Yet to obtain microscopic theory of structure and dynamics of nano/meso-scale phase separation

Summary and Concluding Remarks

- **Have argued that two types of electronic states**
  - **ℓ , JT distorted (polaronic), localised, and**
  - ***b* , *undistorted, extended***

  with well separated time scales coexist in doped manganites.
- **Proposed a new '2-fluid 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**

Summary and Concluding Remarks

- **Extensions of theory including long range coulomb interactions, inter-site ℓ-b coherence effects, charge and orbital ordering, etc., in progress, with some promise of providing a complete theory of manganite physics**
- **Does similar 'two fluid physics' with two types of low energy electronic states with exponentially separated timescales appear in other contexts?**
  - **Other oxides, organic solids and molecules, with degenerate orbitals and strong symmetry breaking JT coupling?**
  - **Holstein-Hubbard model?**
  - **…**

Some References and Weblinks

- A New Theory of Doped **Manganites** Exhibiting Colossal Magnetoresistance
  HR Krishnamurthy - **Pramana** Journal of Physics, **64**, 1063 (2005)
  (Invited Talk, Proceedings of STATPHYS 22)
- Unusual doping and temperature dependence of photoemission spectra from manganites
  Prabuddha Sanyal, Subhra Sen Gupta, Nandan Pakhira, H. R. Krishnamurthy, D. D. Sarma and T. V. Ramakrishnan **arXiv:0704.3923** (April 2007)
- Coulomb Interactions and Nanoscale Electronic Inhomogeneities in Manganites
  Vijay B. Shenoy, Tribikram Gupta, H. R. Krishnamurthy and T. V. Ramakrishnan
  Phys. Rev. Lett. **98**, 097201 (2007) **cond-mat/0606660** (June 2006)
- Instabilities and Insulator-Metal transitions in Half-Doped Manganites induced by Magnetic-Field and Doping
  O. Cepas, H. R. Krishnamurthy and T. V. Ramakrishnan
  Phys. Rev. B **73**, 035218 (2006) **cond-mat/0601469** (January 2006)
- Doping and Field-Induced Insulator-Metal Transitions in Half-Doped Manganites
  O. Cepas, H. R. Krishnamurthy and T. V. Ramakrishnan
  Phys. Rev. Lett. **94**, 247207 (2005) **cond-mat/0412651** (December 2004)
- Zero Temperature Insulator-Metal Transition in Doped ManganitesG. Venketeswara Pai, S. R. Hassan, H. R. Krishnamurthy and T. V. Ramakrishnan
  Europhysics Letters **64,** 696 (2003) **cond-mat/0309493** (September 2003)
- Theory of Manganites Exhibiting Colossal MagnetoresistanceT. V. Ramakrishnan, H. R. Krishnamurthy, S. R. Hassan and G. Venketeswara Pai
  cond-mat/0308396.
- Theory of Insulator Metal Transition and Colossal Magnetoresistance in Doped ManganitesT. V. Ramakrishnan, H. R. Krishnamurthy, S. R. Hassan and G. V. Pai
  Phys. Rev. Lett. **92**, 157203 (2004); **cond-mat/0308376** (August 2003)

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Other Interaction

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