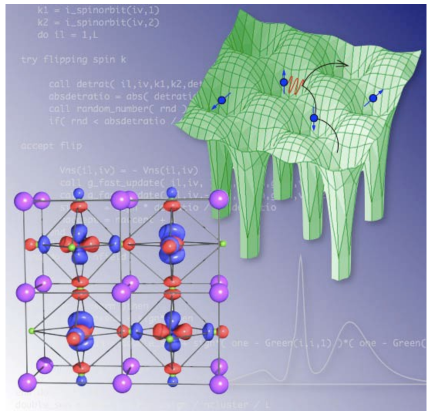
Spin transitions in strongly correlated materials

Jan Kuneš



DFG FOR 1346
Dynamical Mean-Field Approach with Predictive Power for Strongly Correlated Materials
&
GA CR P204/10/0284

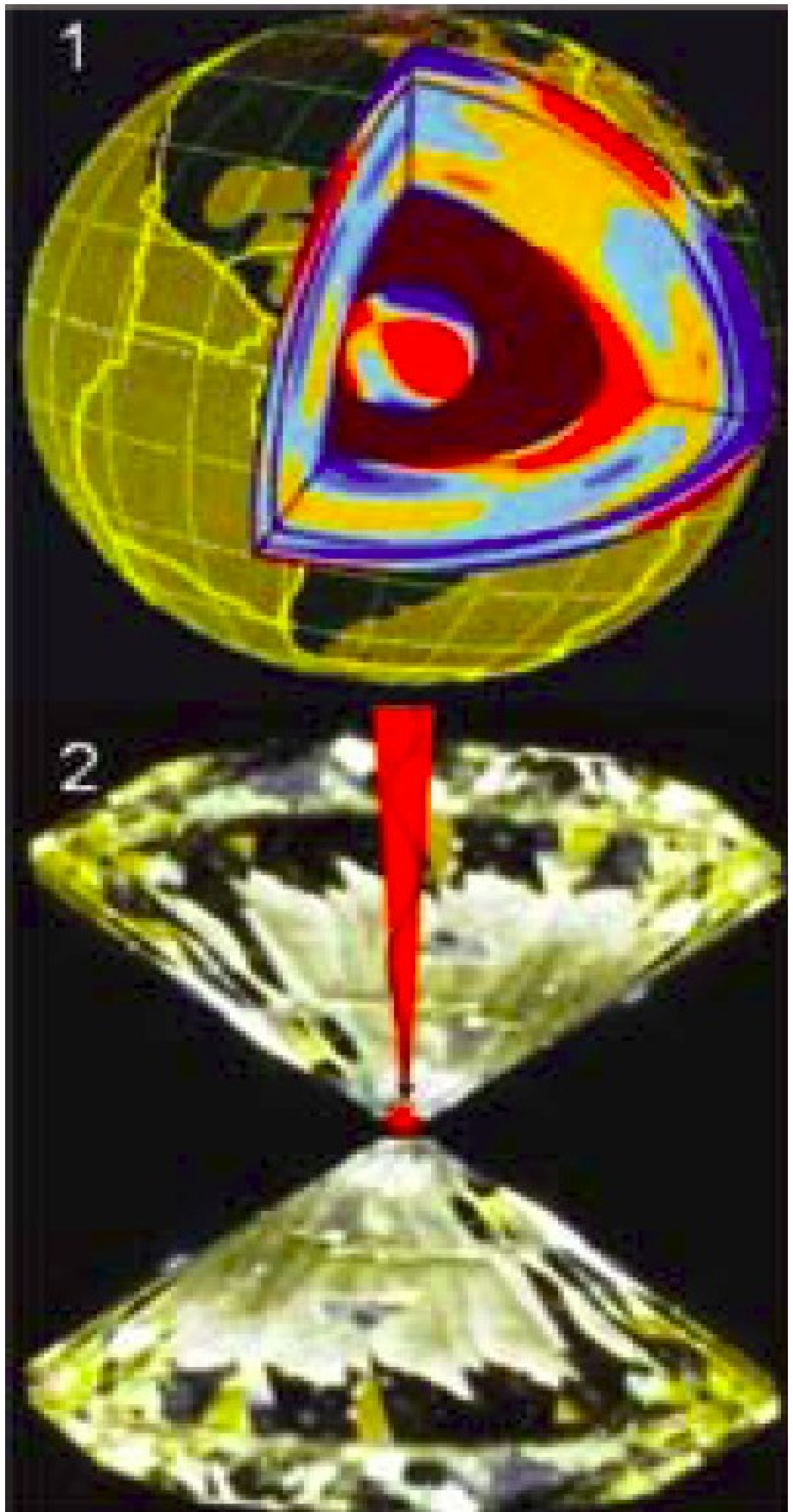
Collaborators

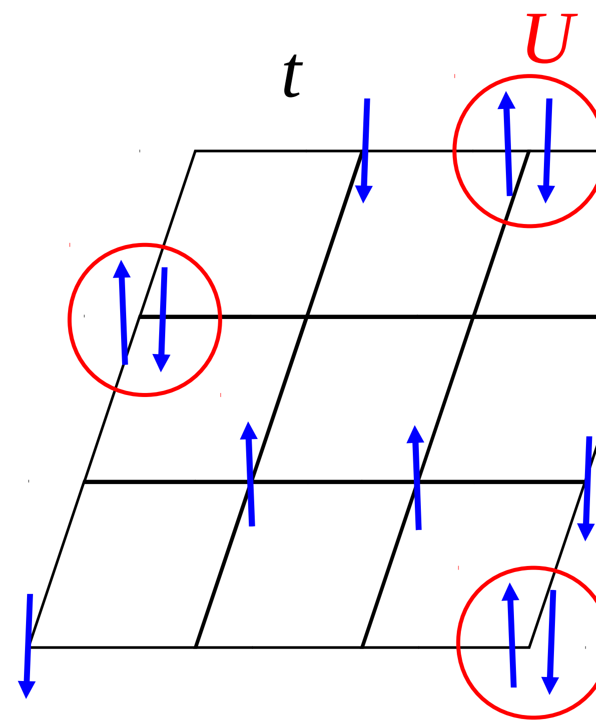
V. Křápek	IoP Prague
V. I. Anisimov, A. V. Lukoyanov, D. M. Korotin, M. A. Korotin	IoMP Yekaterinburg
P. Werner	ETH Zurich
W. E. Pickett, R. T. Scalettar	UC Davis

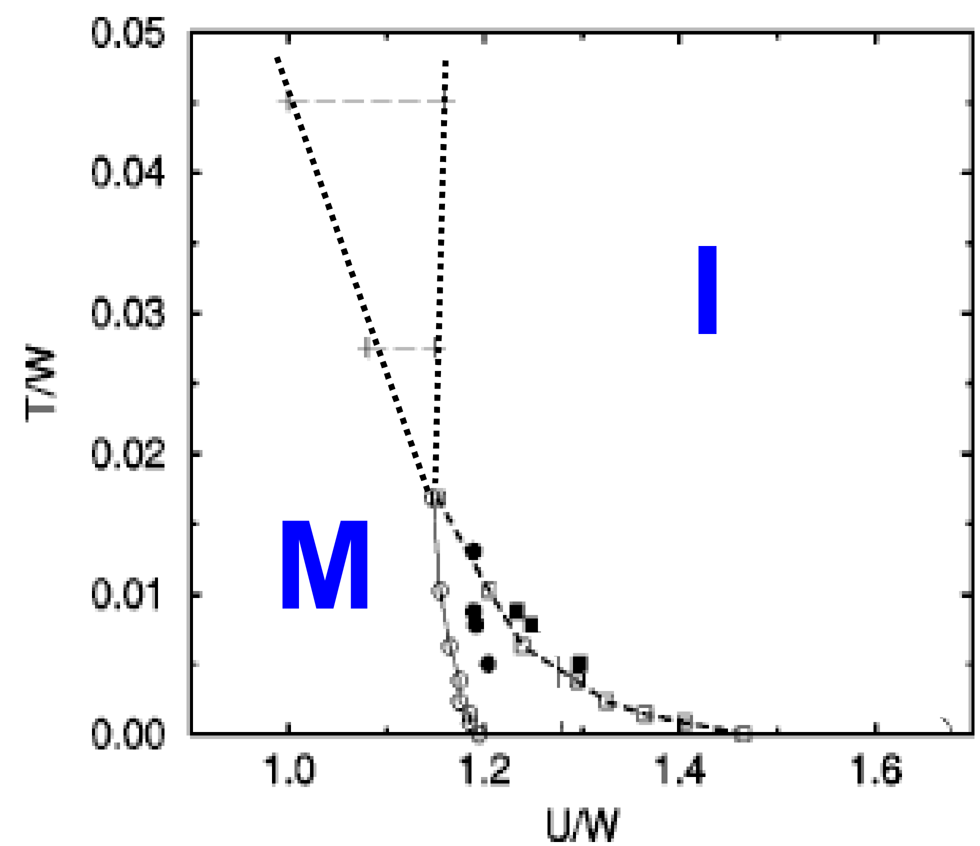
Outline

- HS-LS transitions in models and materials
- Pressure-driven transition: MnO, Fe_2O_3
- HS/LS degeneracy: $LaCoO_3$
- Blume-Emery-Griffiths model in fermionic systems
- From cobaltites to manganites
- Conclusions

Materials ⟷ Models







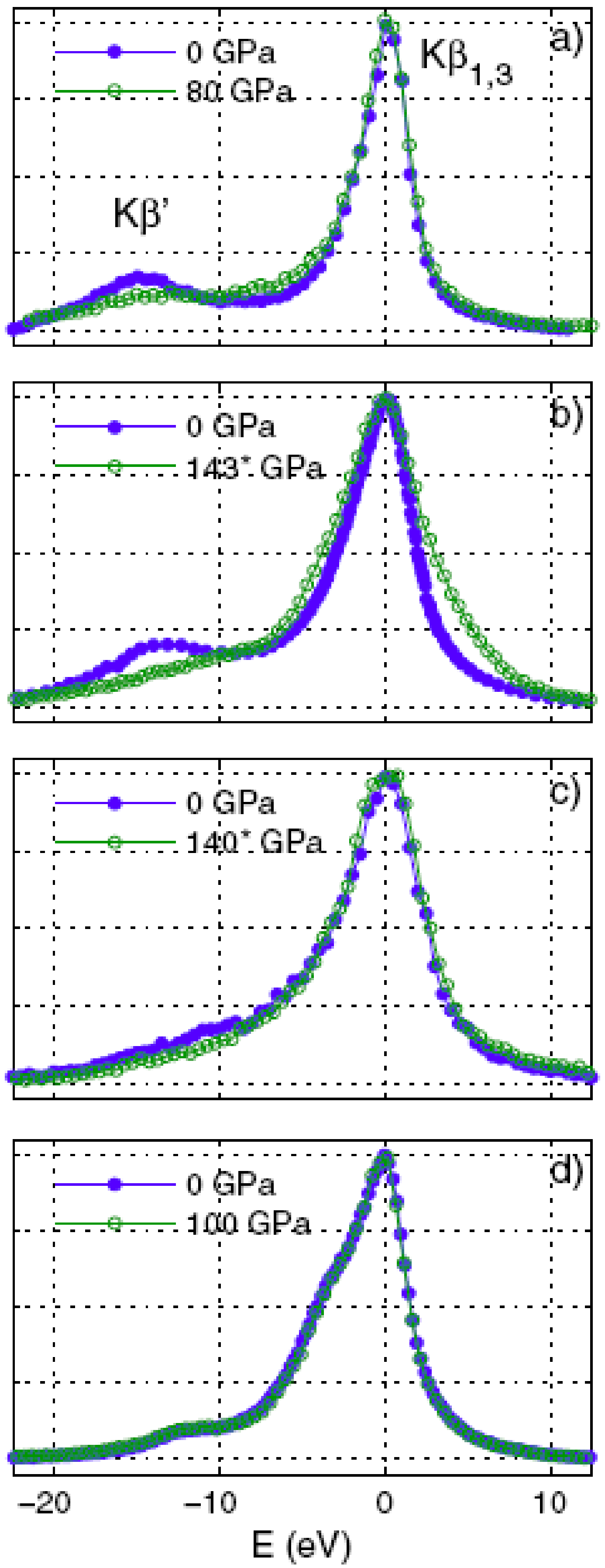
Bulla et al. Phys. Rev. B ***64****, 045103 (2001)*

MnO

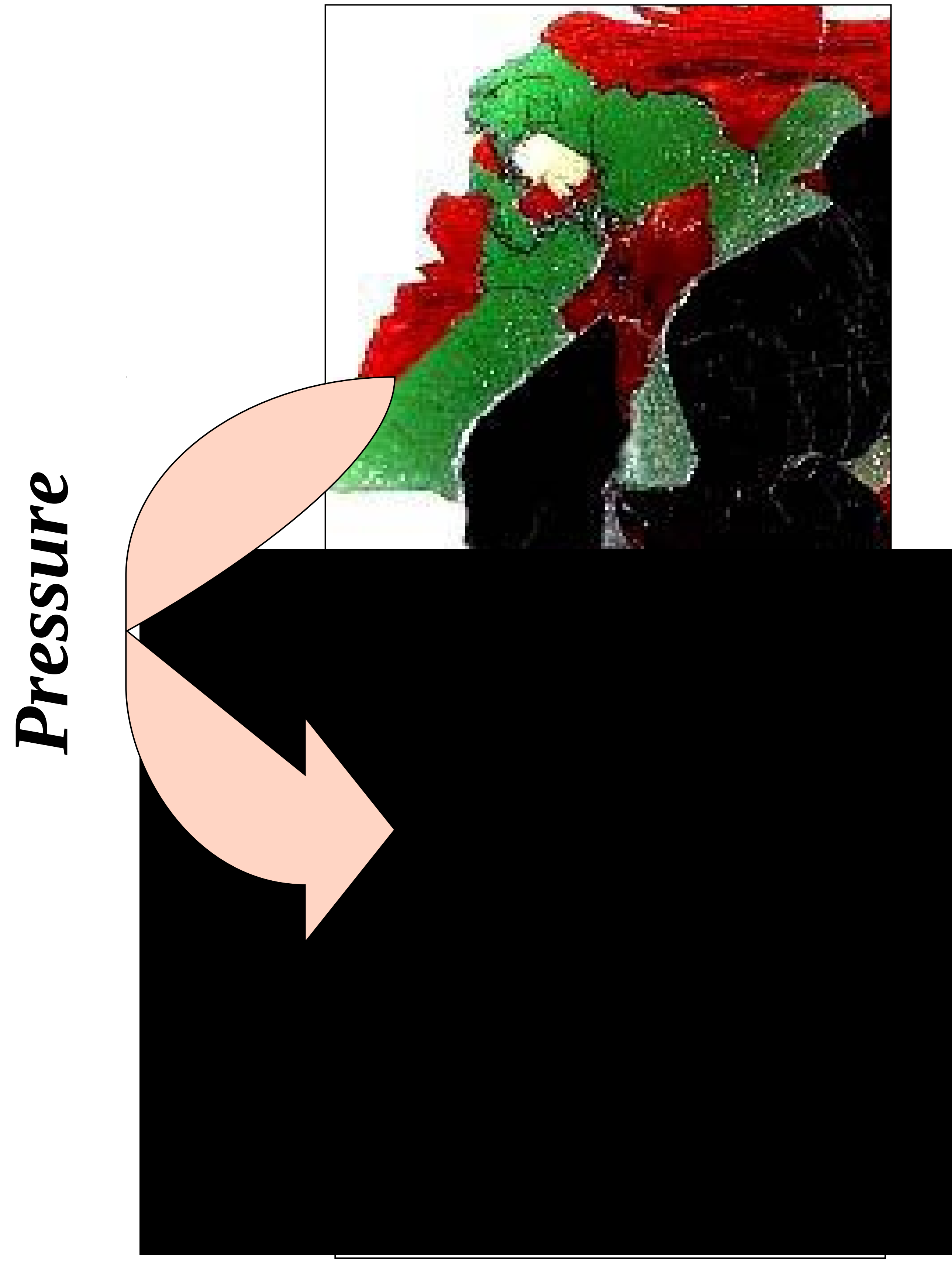
FeO

CoO

NiO



MnO

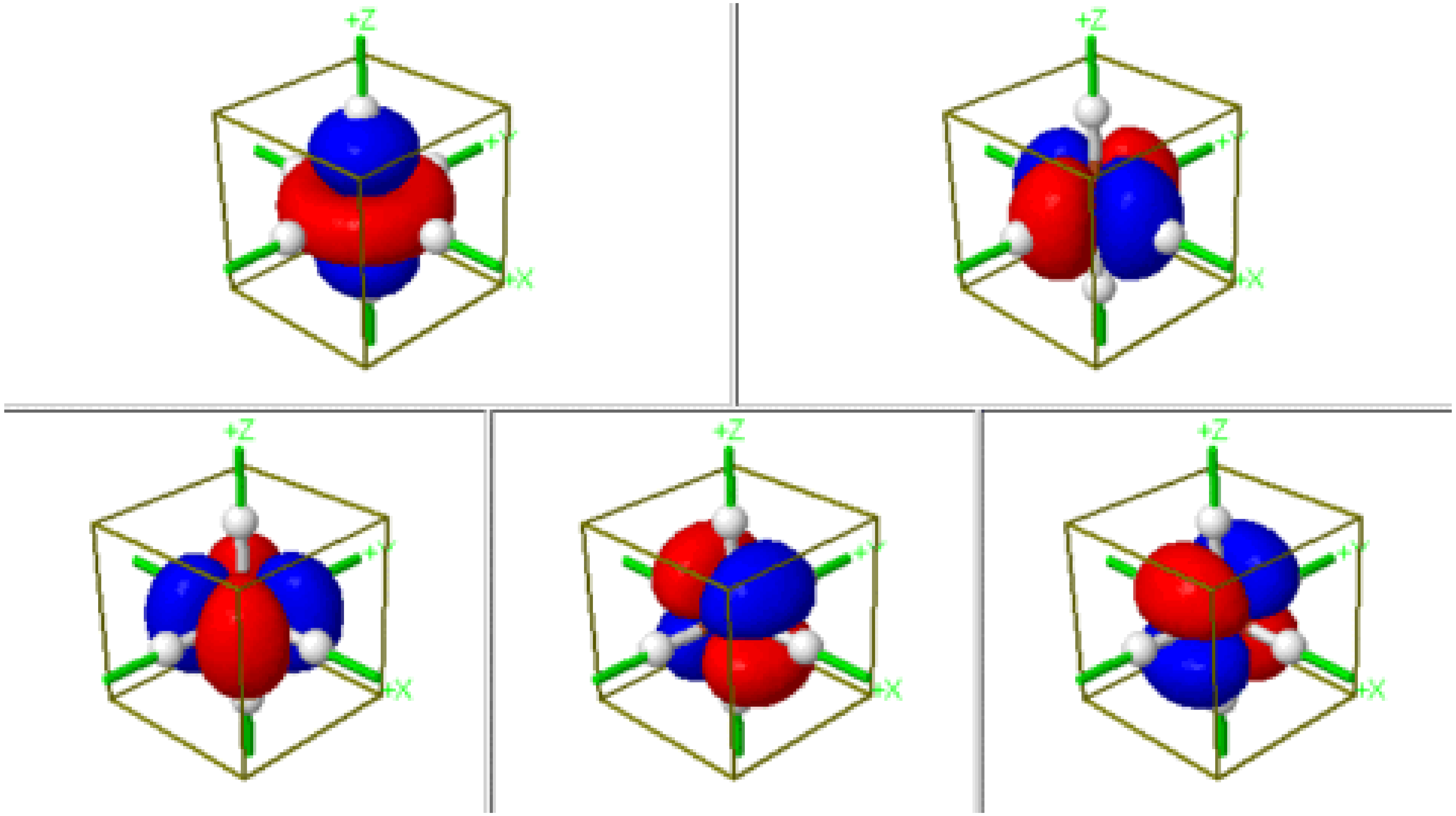


Mattila et al. Phys. Rev. Lett. ***98,*** *196404 (2007)*

d-electron in octahedral environment

e_g

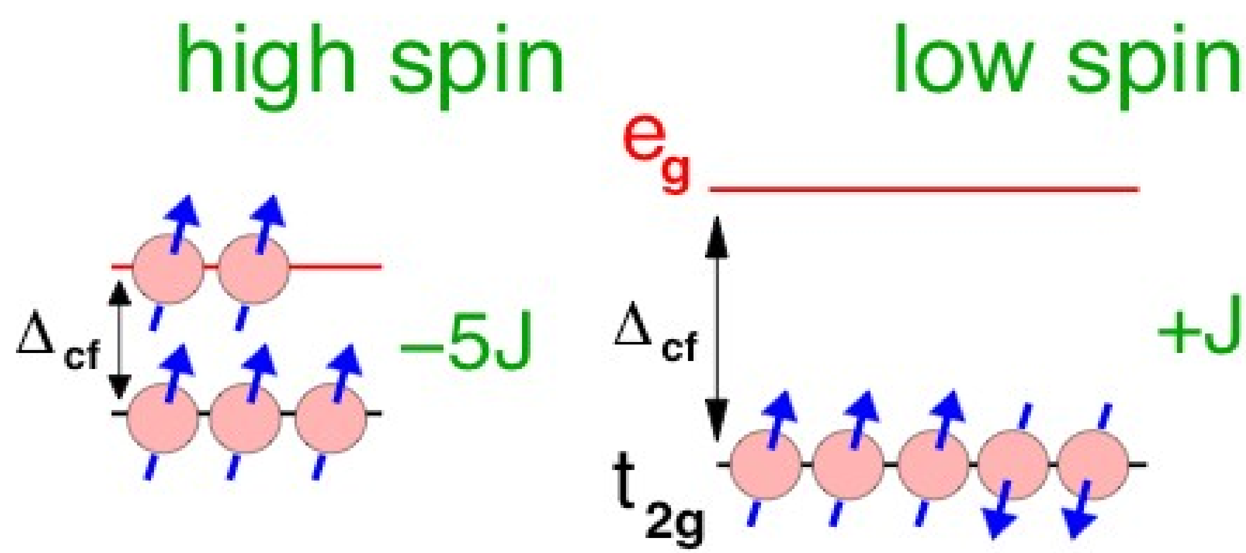
t_{2g}

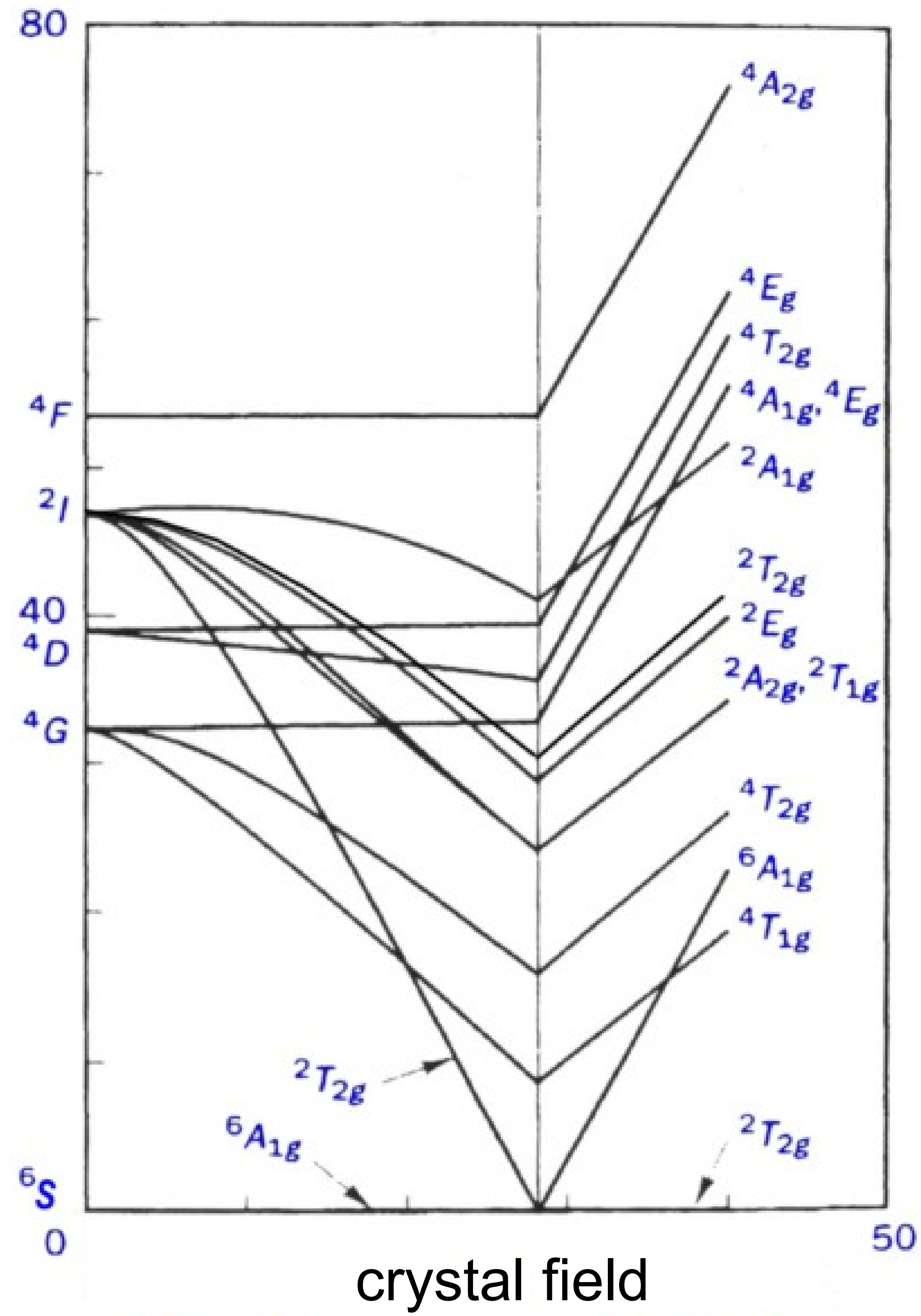


Crystal-field splitting: electrostatic forces
hybridization (band repulsion)

d-multiplets in octahedral field

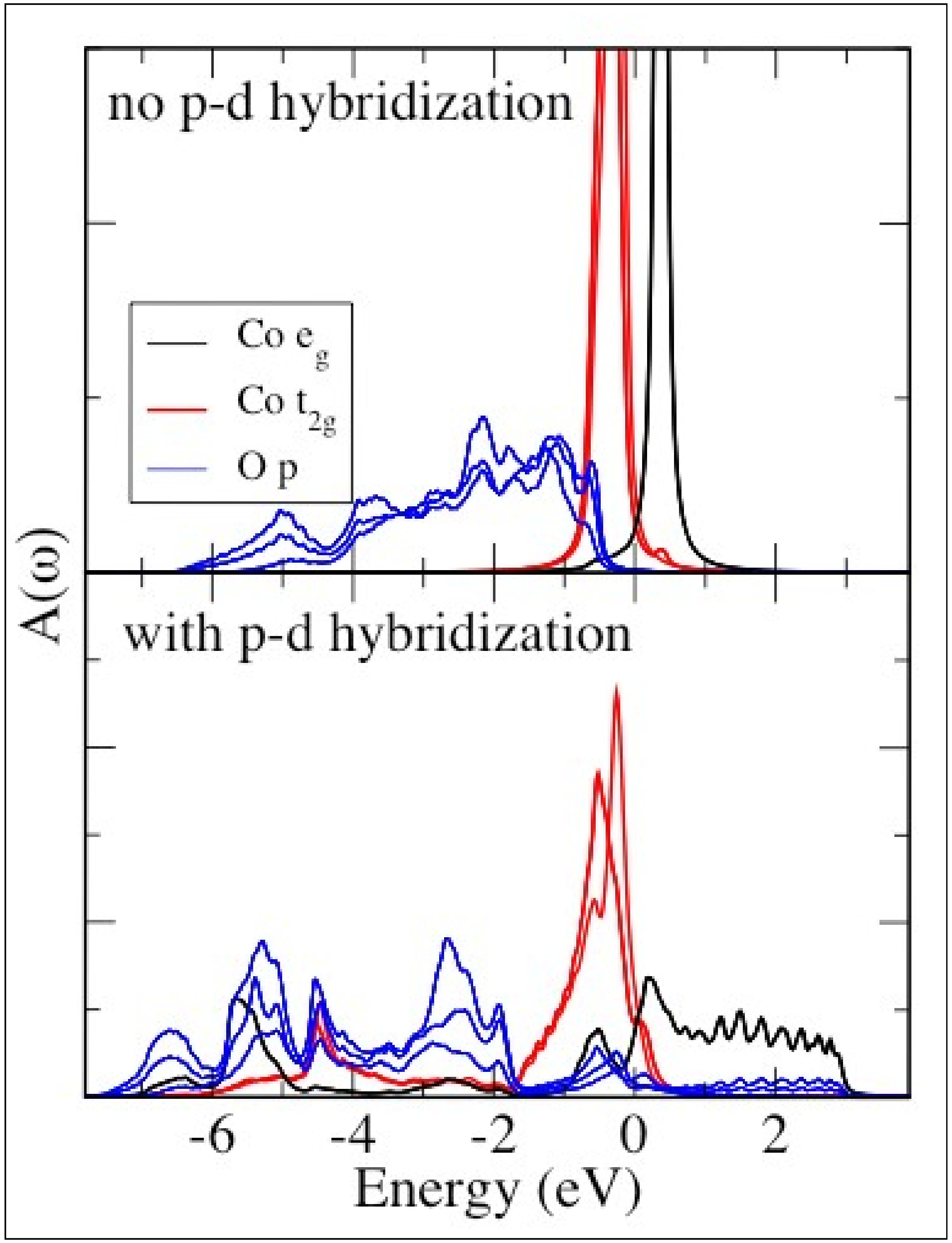
Tanabe-Sugano diagram for d^5





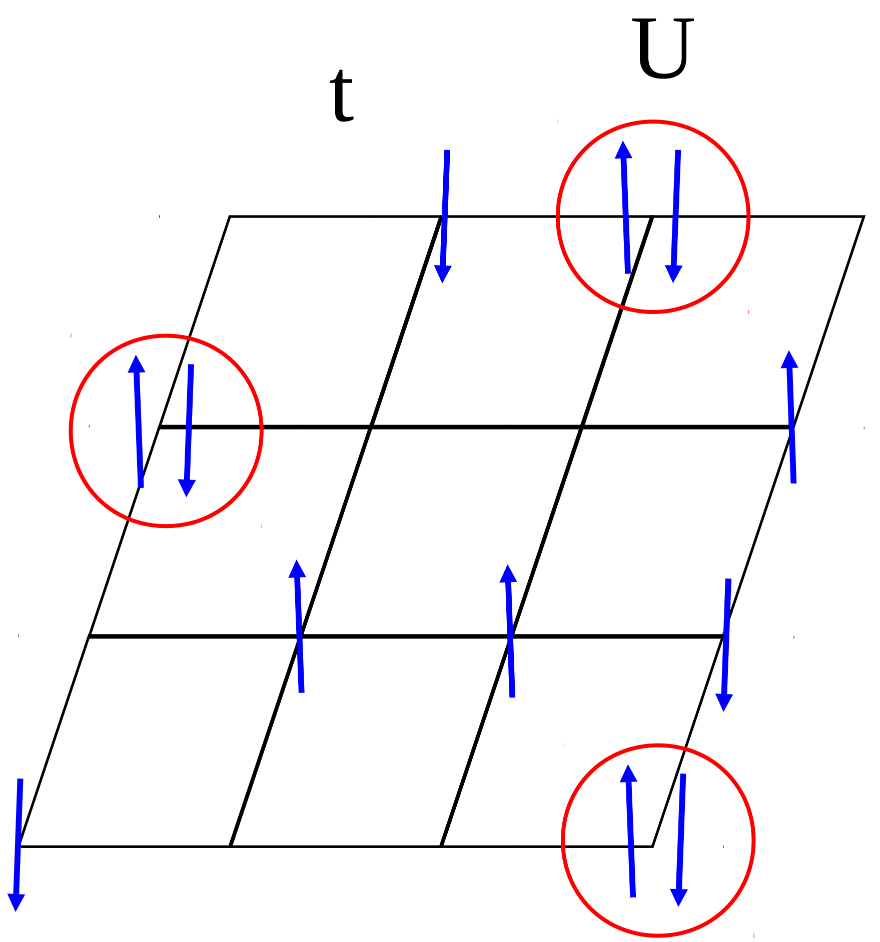
Transition metal oxides- band structure

LDA bands for $LaCoO_3$



- hopping from TM ions mostly through oxygen
- *p*-e_g hybridization => broad e_g band
  CF splitting
- relative position of *d* and *p* bands not necessarily correct

Electron correlations and Hubbard model



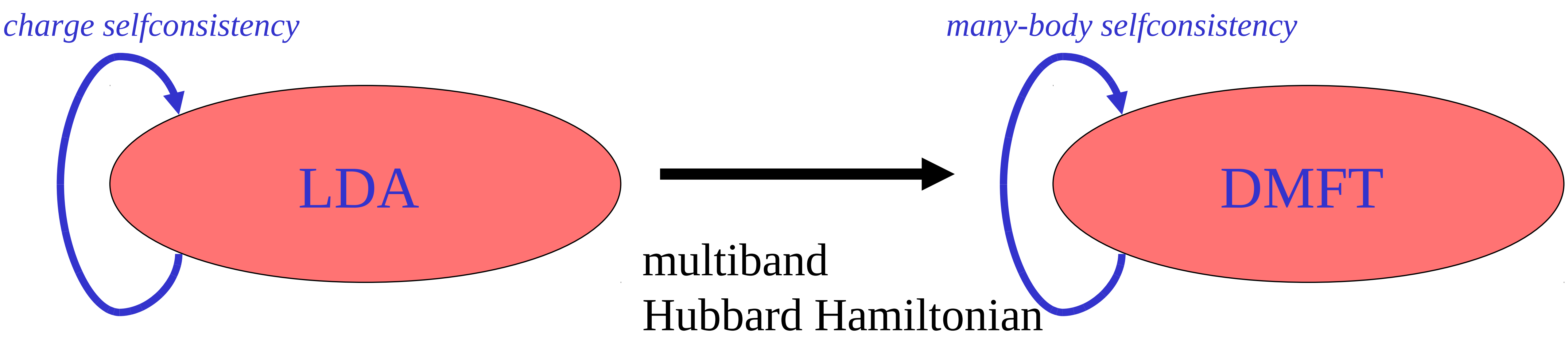
• competition between kinetic and interaction energy: itinerancy vs localization

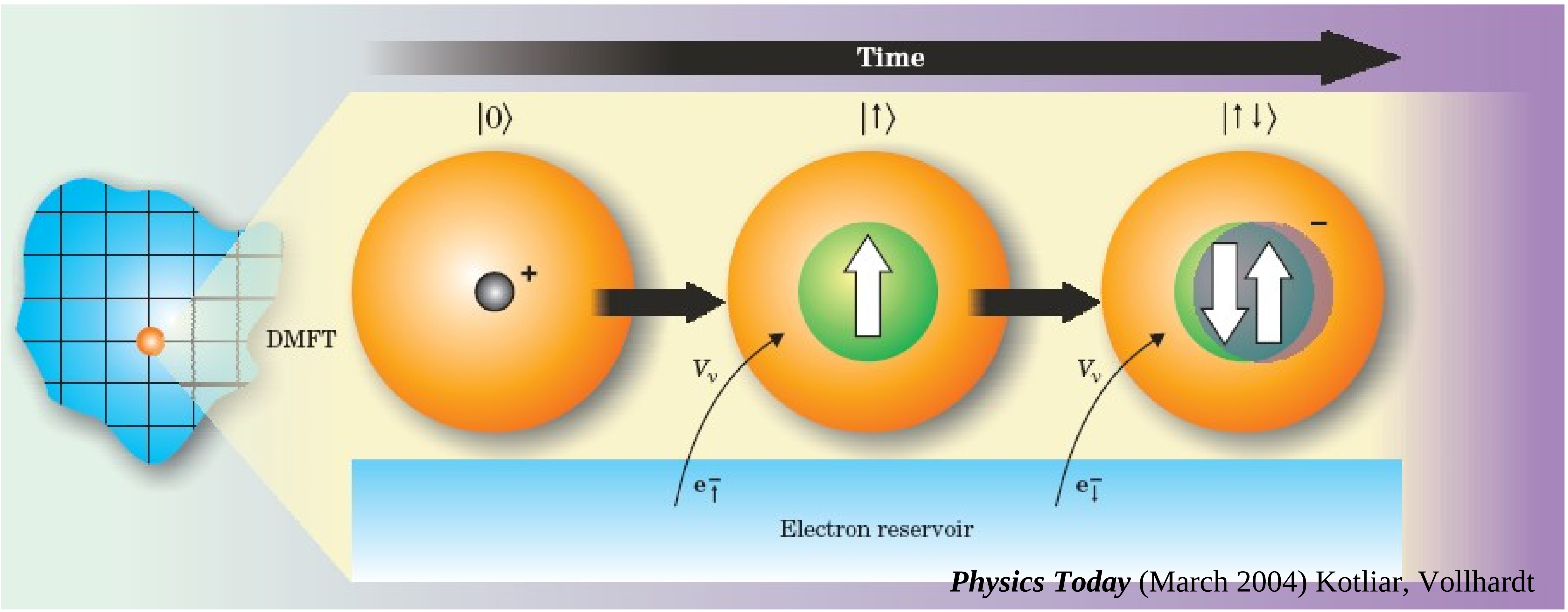
• localization -> large (quasi)degeneracy-> temperature (entropy) becomes important parameter

• emergence - new (non-fermionic) degrees of freedom appear, e.g. local spin, orbital-pseudospin -> possibility of new ordered states

• fluctuations of the emergent degrees of freedom - both quantum mechanmical and statistical

Dynamical Mean-Field Theory (LDA+DMFT)



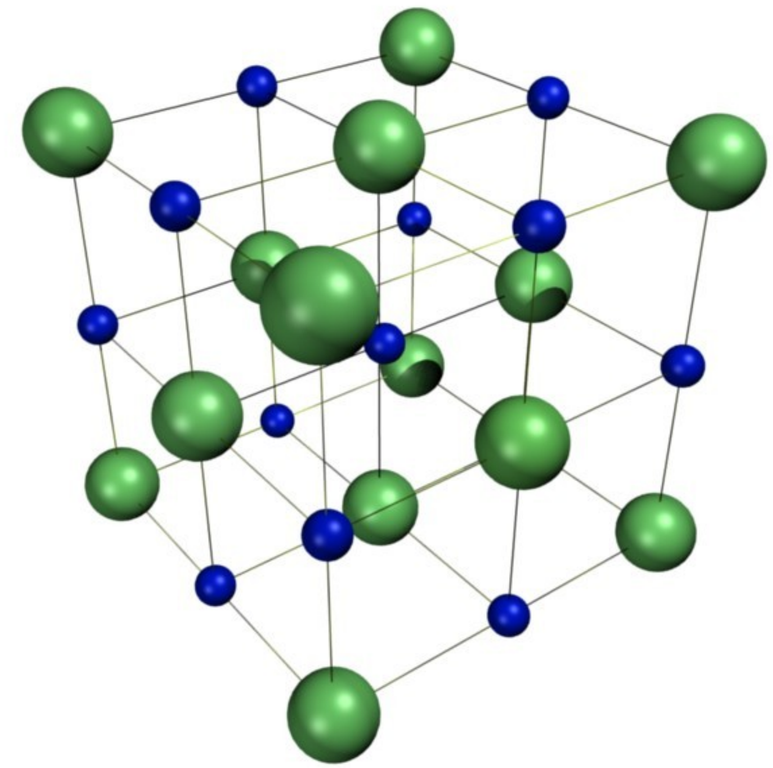


Physics Today (March 2004) Kotliar, Vollhardt

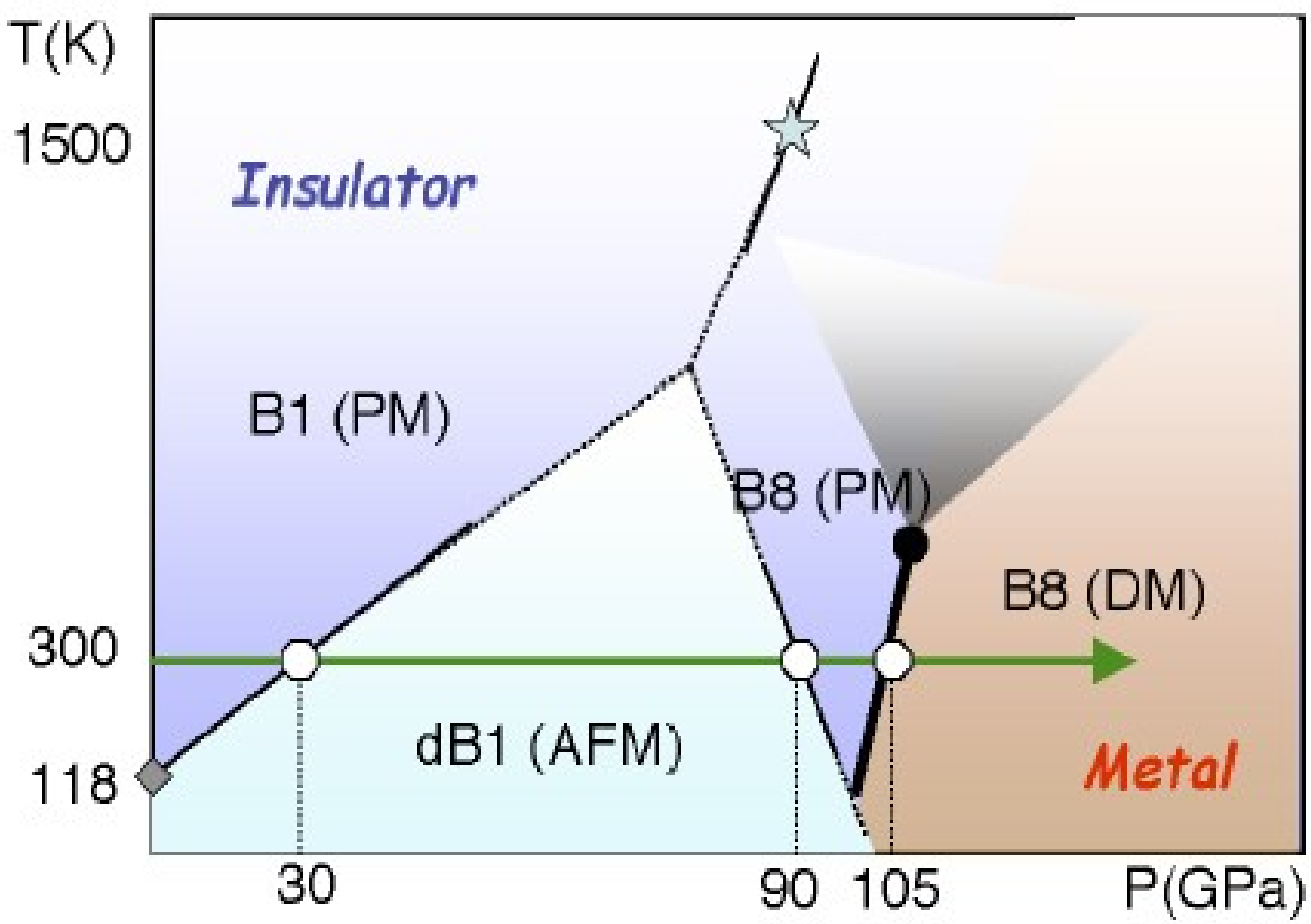
A. Georges et al. Rev. Mod. Phys. ***68****, 13 (1996*)

MnO experimental summary

$Mn^{2+} O^{2-}$ => d^5 local configuration



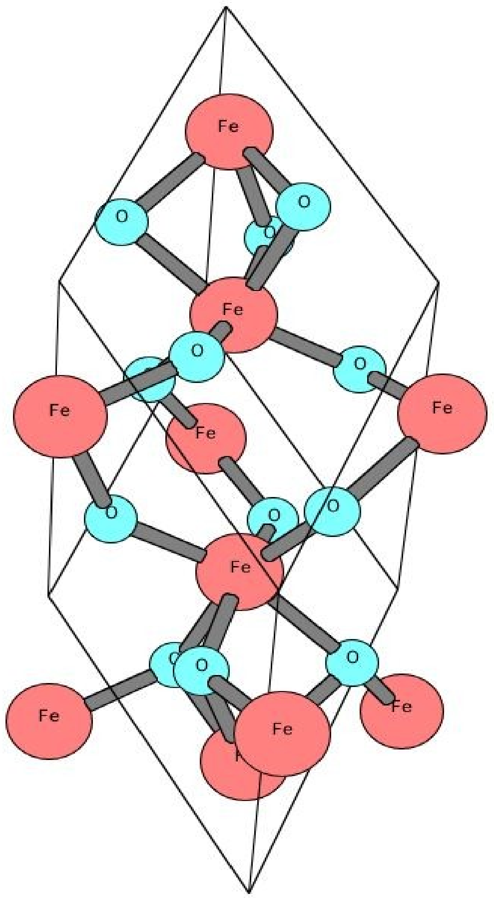
Conceptual phase diagram of MnO



- moment collapse
- insulator -> metal transition
- volume collapse
- structural transition

C. S. Yoo et al., Phys. Rev. Lett. ***94****, 115502 (2005)*

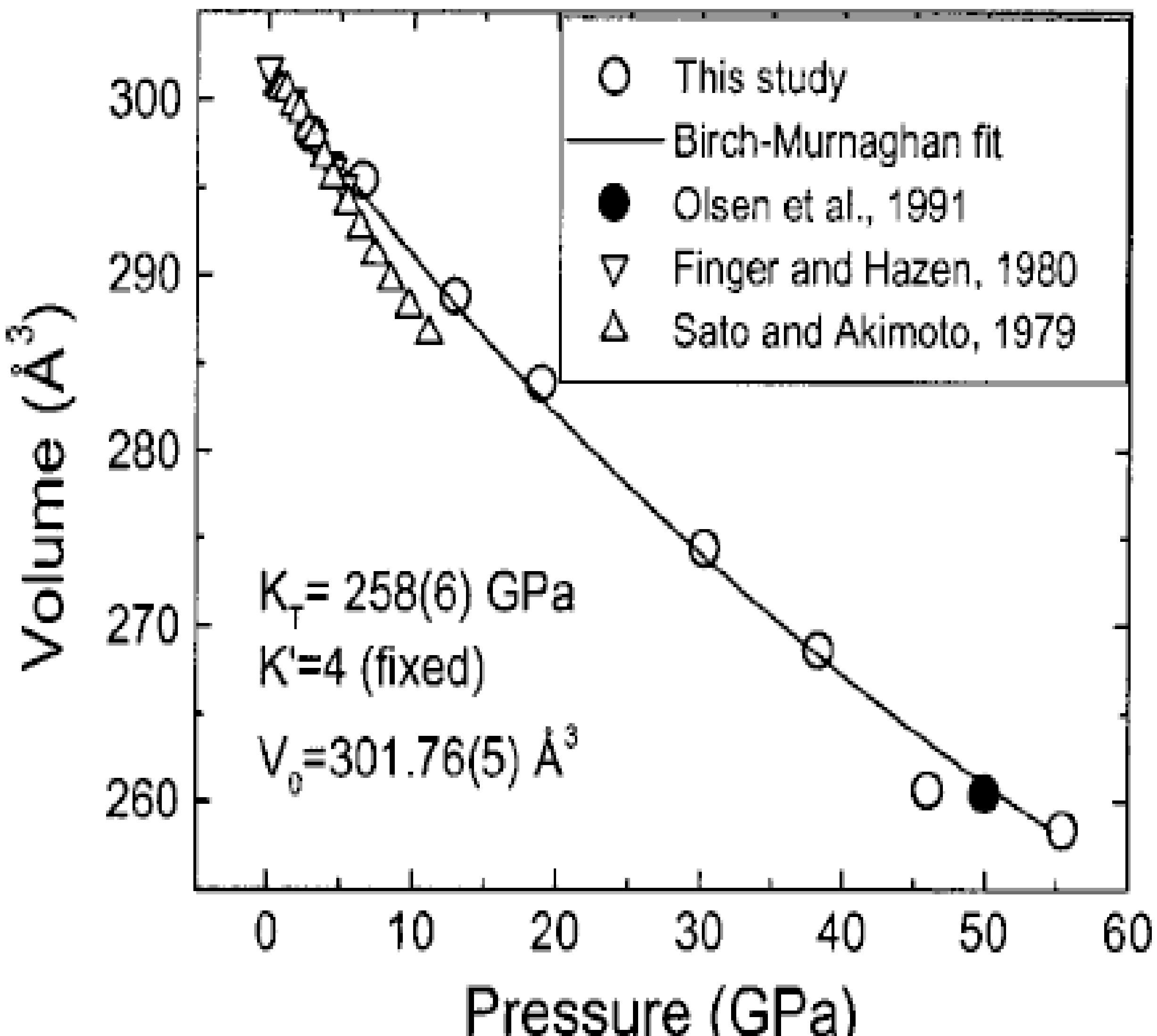
Fe_2O_3 experimental summary



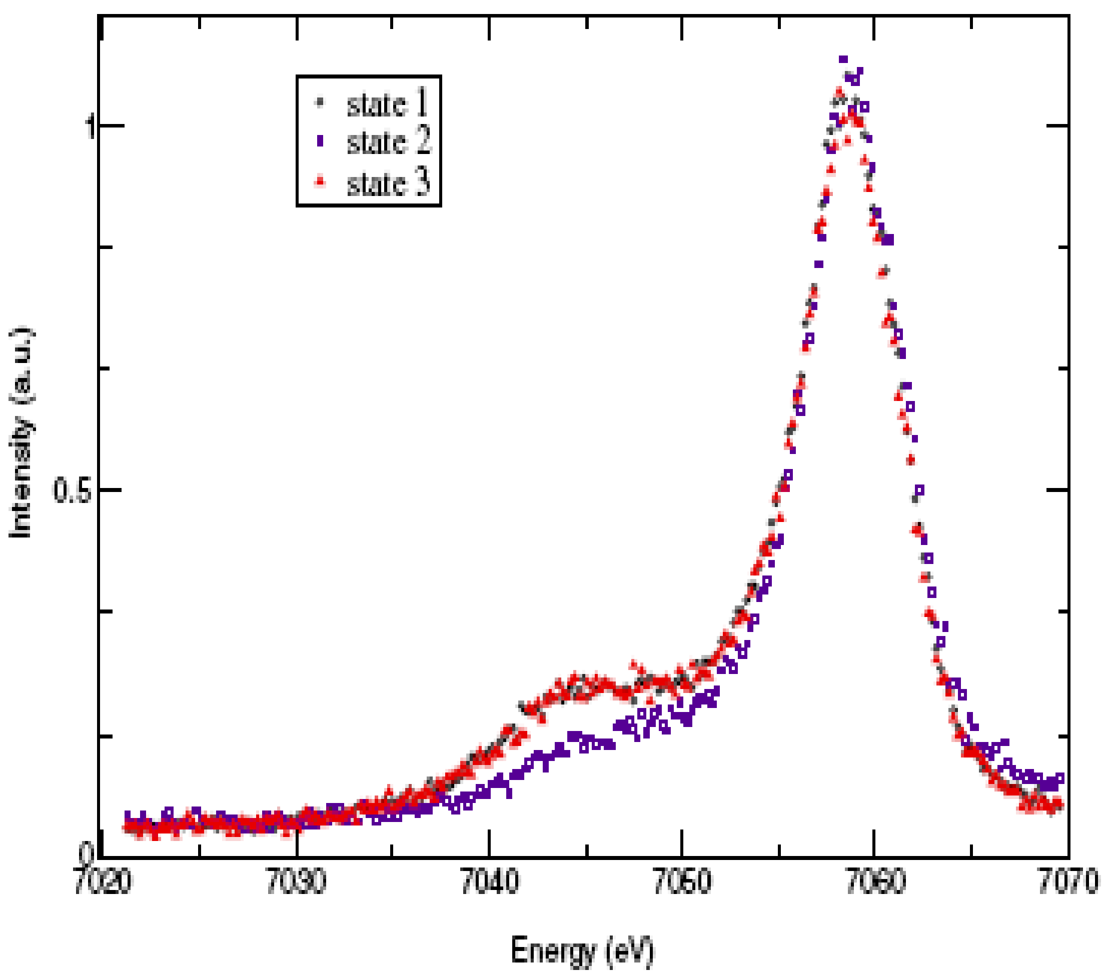
$Fe_2^{3+}O_3^{2-}$ => d^5 local configuration

Fe in octahedral coordination

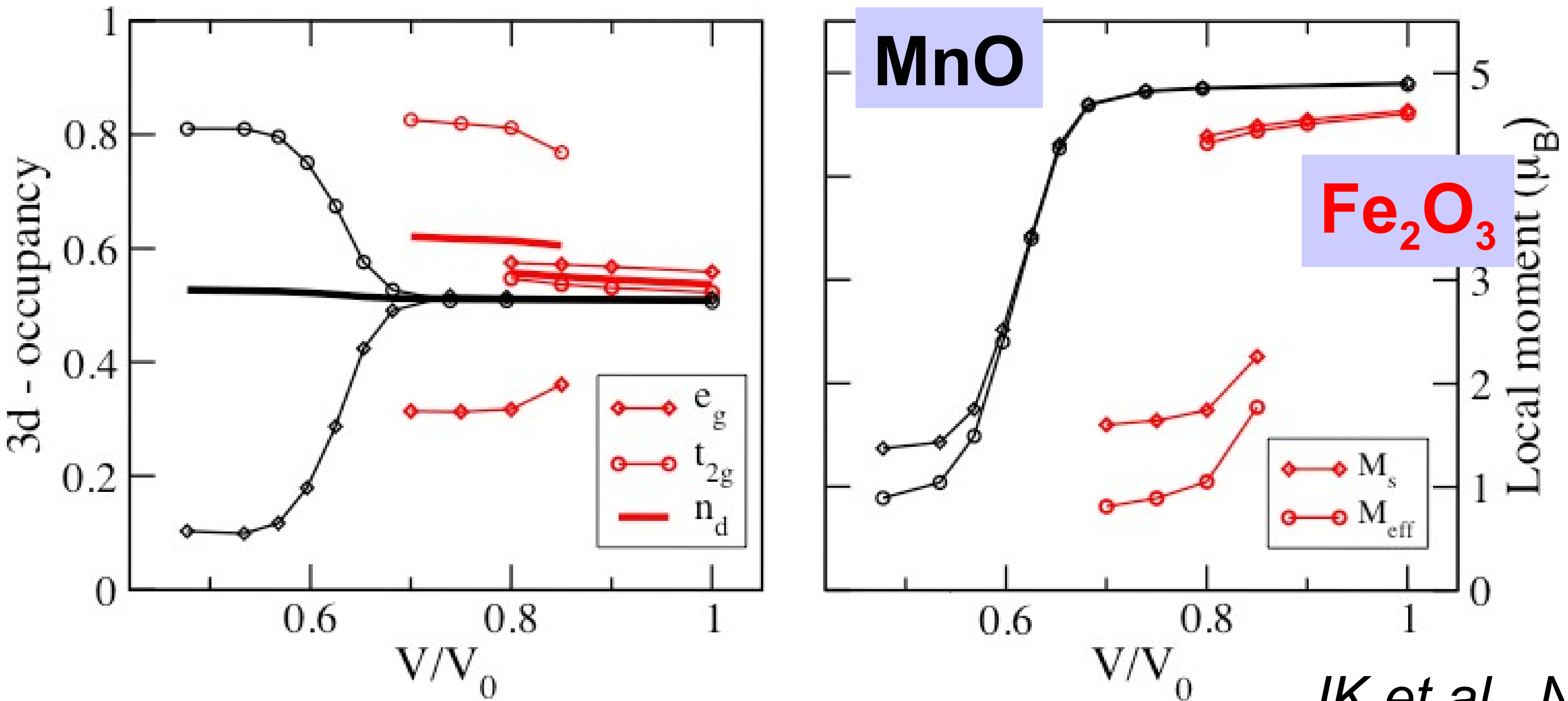
Rosenberg et al., Phys. Rev. B ***65****, 064112 (2002)*



Badro et al., Phys. Rev. Lett. ***89****, 205504 (2002)*

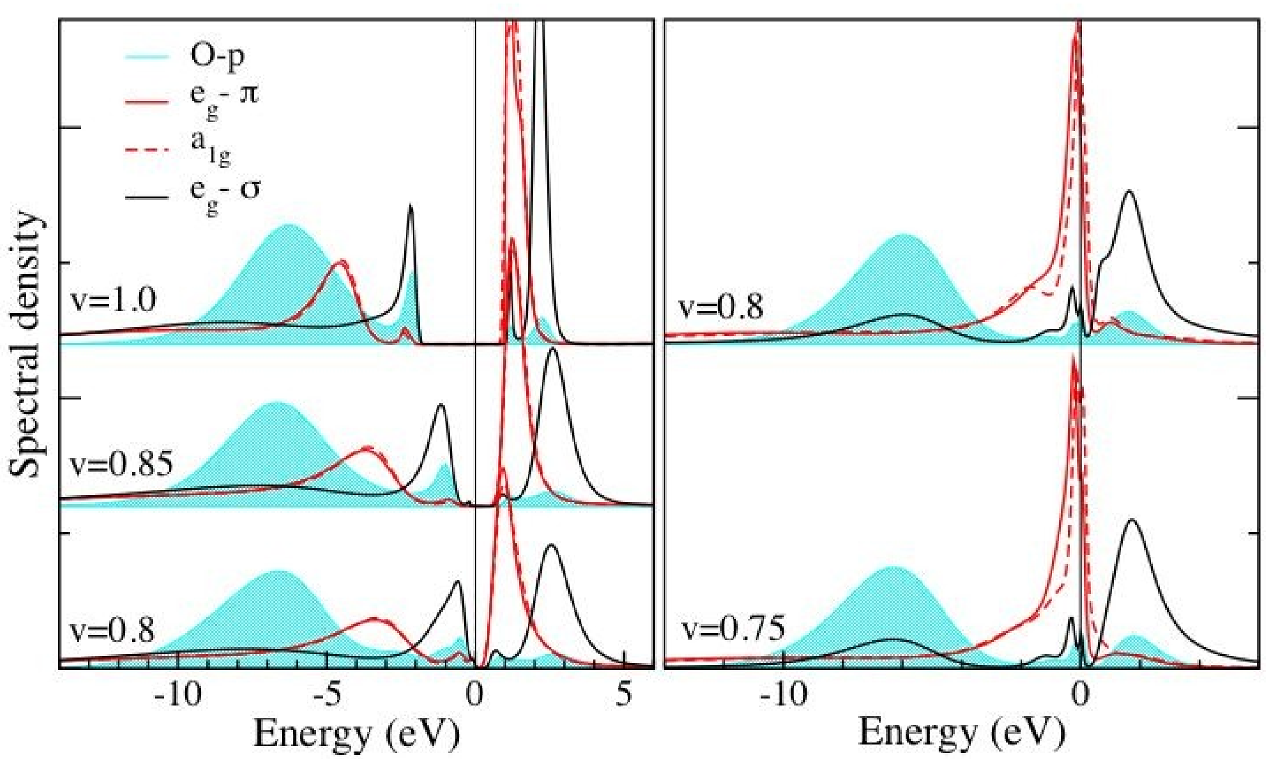


Pressure driven spin state transition

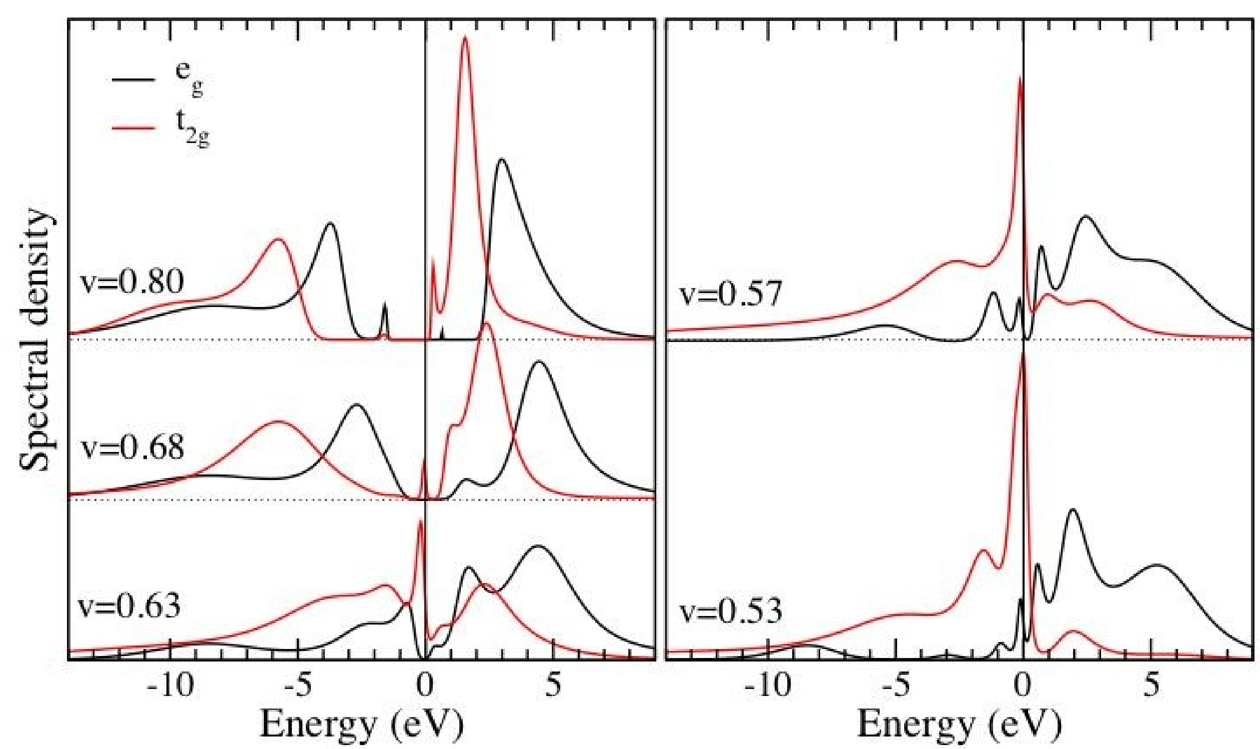


JK et al., Nature Materials ***7****, 198 (2008)*
JK et al., Phys. Rev. Lett. ***102****, 146402 (2009)*

Fe$_2$O$_3$

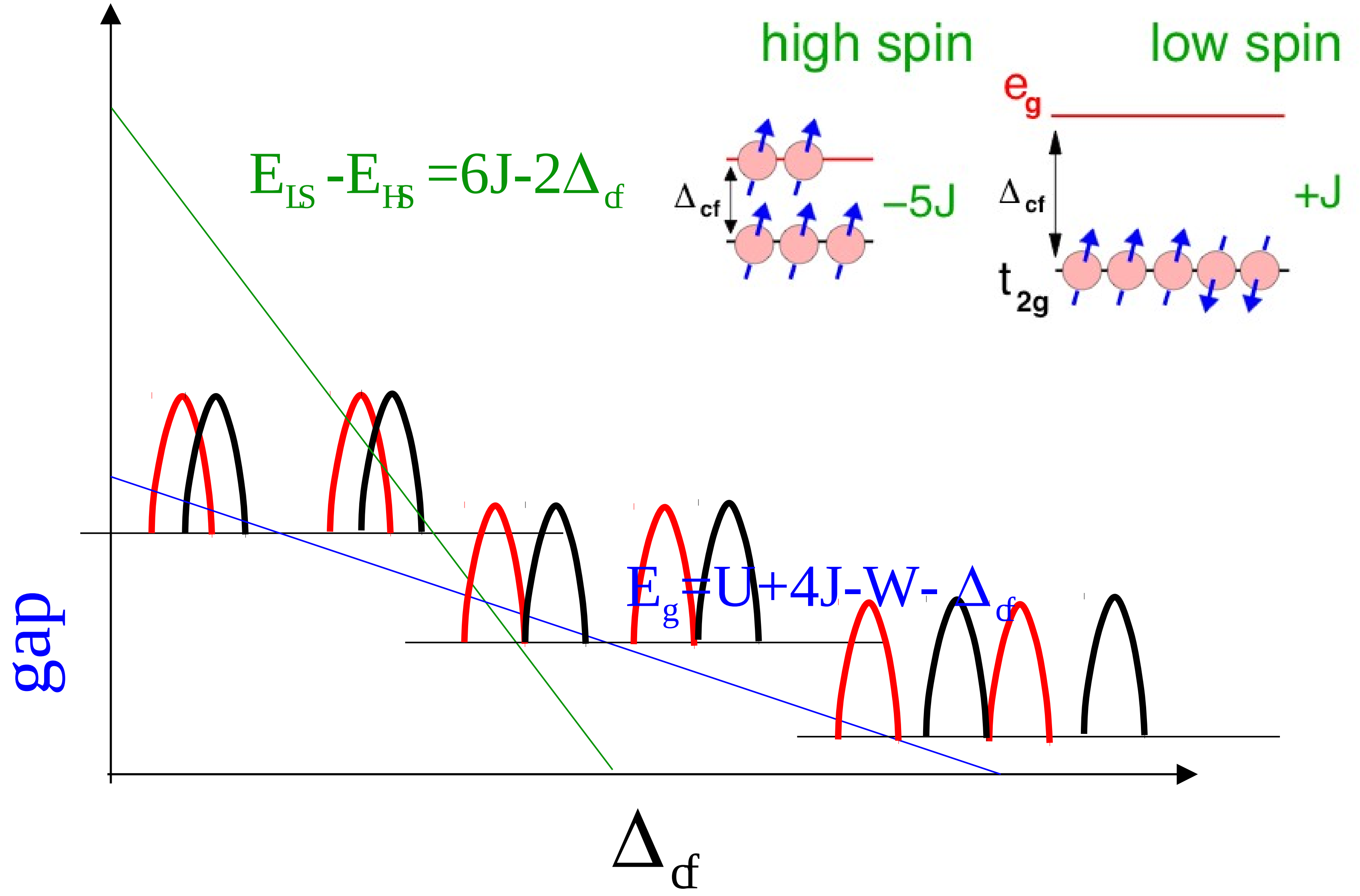


MnO



Pressure induced metallization

Gap closing vs local spin state transition



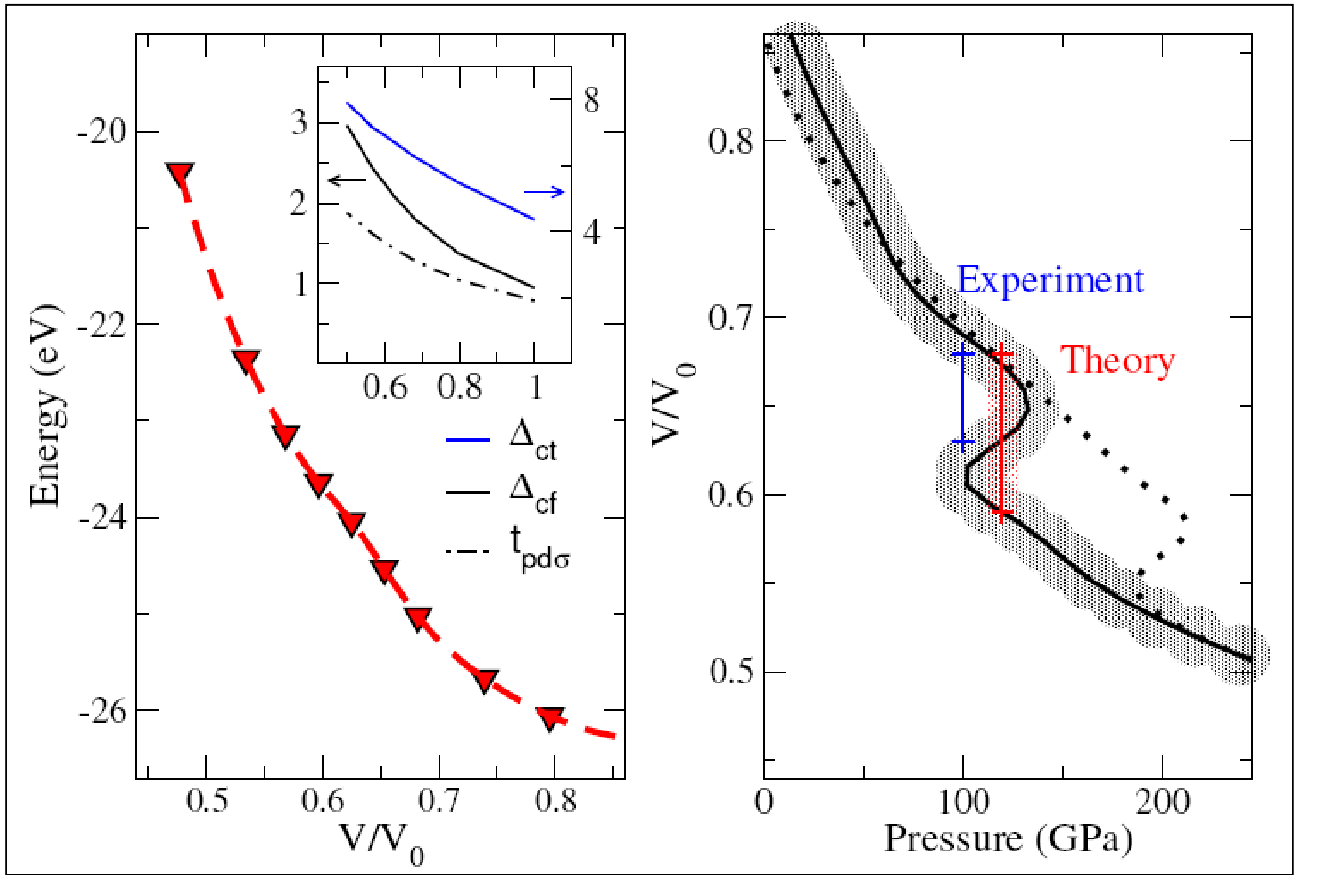
Pressure induced transitions - summary

two scenarios:

- **local state transition** - atomic physics dominates
  metallicity is slave to atomic constraints
- **gap closing** - hopping plays active role in the transition

Energy scale:
~ 1 eV/atom

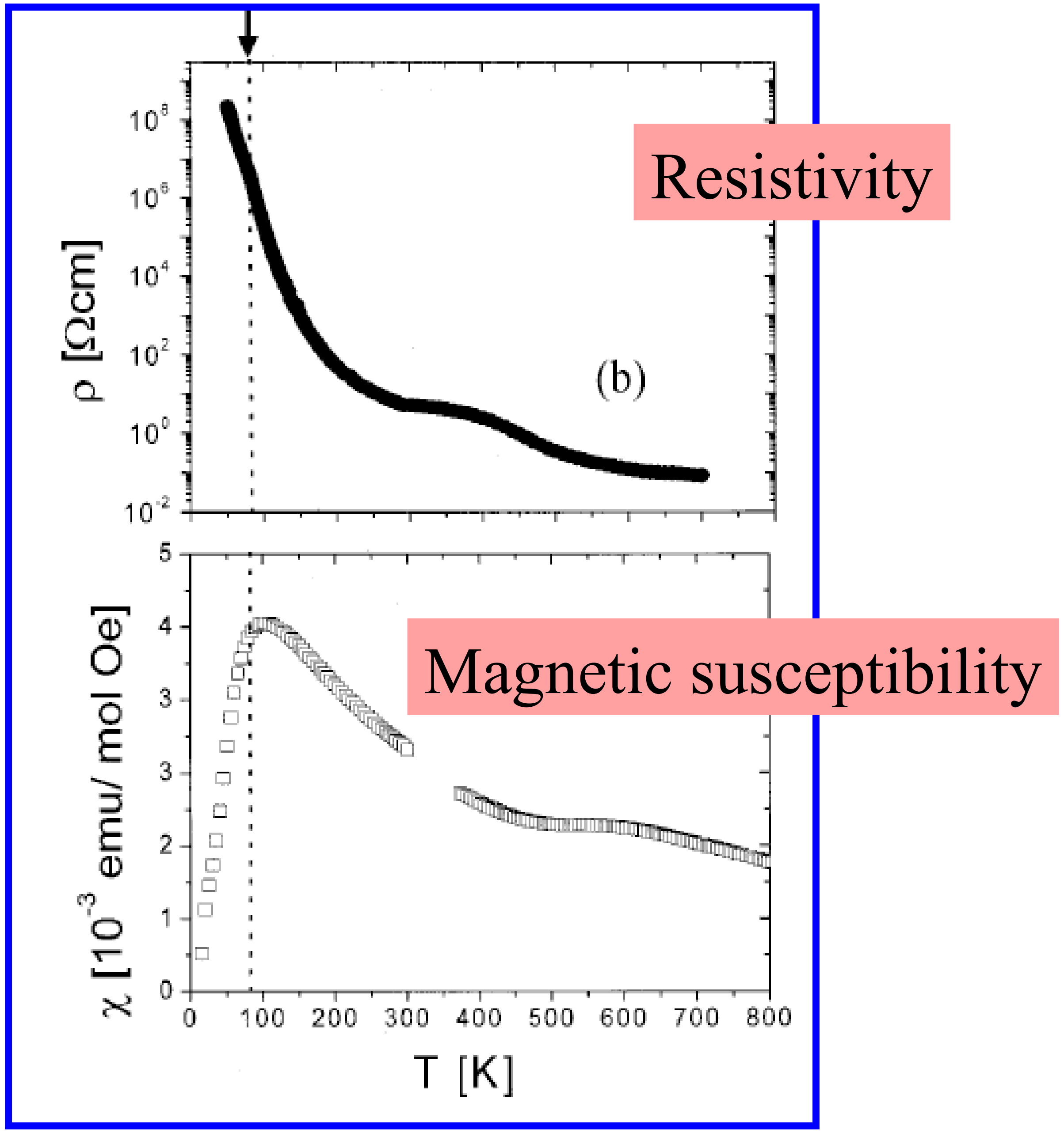
Pressure scale:
10-100 GPa
(~ 1 GPa width)



What happens right at the transition?

What happens right at the transition?

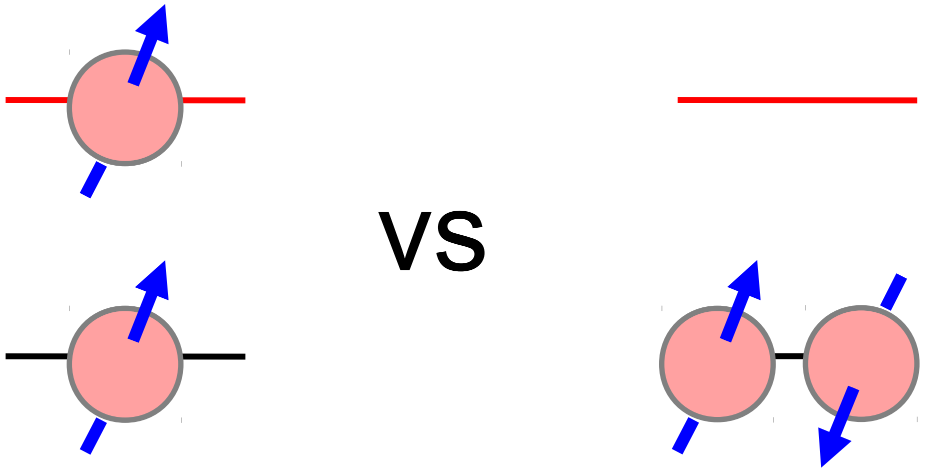
$LaCoO_3$ - nature did the fine tuning job for us !



- d^6 state for Co^{3+} valence
- S=0 LS vs S=2 or 1 ? HS
- $E_{LS} < E_{HS}$, $E_{HS} - E_{LS} \sim kT$

Two-band Hubbard model

$$H = \sum_{i,\sigma}((\Delta - \mu)n^a_{i,\sigma} - \mu n^b_{i,\sigma}) + \sum_{\langle ij\rangle,\sigma}(t_{aa}a^\dagger_{i,\sigma}a_{j,\sigma} + t_{bb}b^\dagger_{i,\sigma}b_{i,\sigma})$$
$$+ U\sum_i(n^a_{i,\uparrow}n^a_{i,\downarrow} + n^b_{i,\uparrow}n^b_{i,\downarrow}) + (U-2J)\sum_{i,\sigma}n^a_{i,\sigma}n^b_{i,-\sigma}$$
$$+ (U-3J)\sum_{i,\sigma}n^a_{i,\sigma}n^b_{i,\sigma}$$

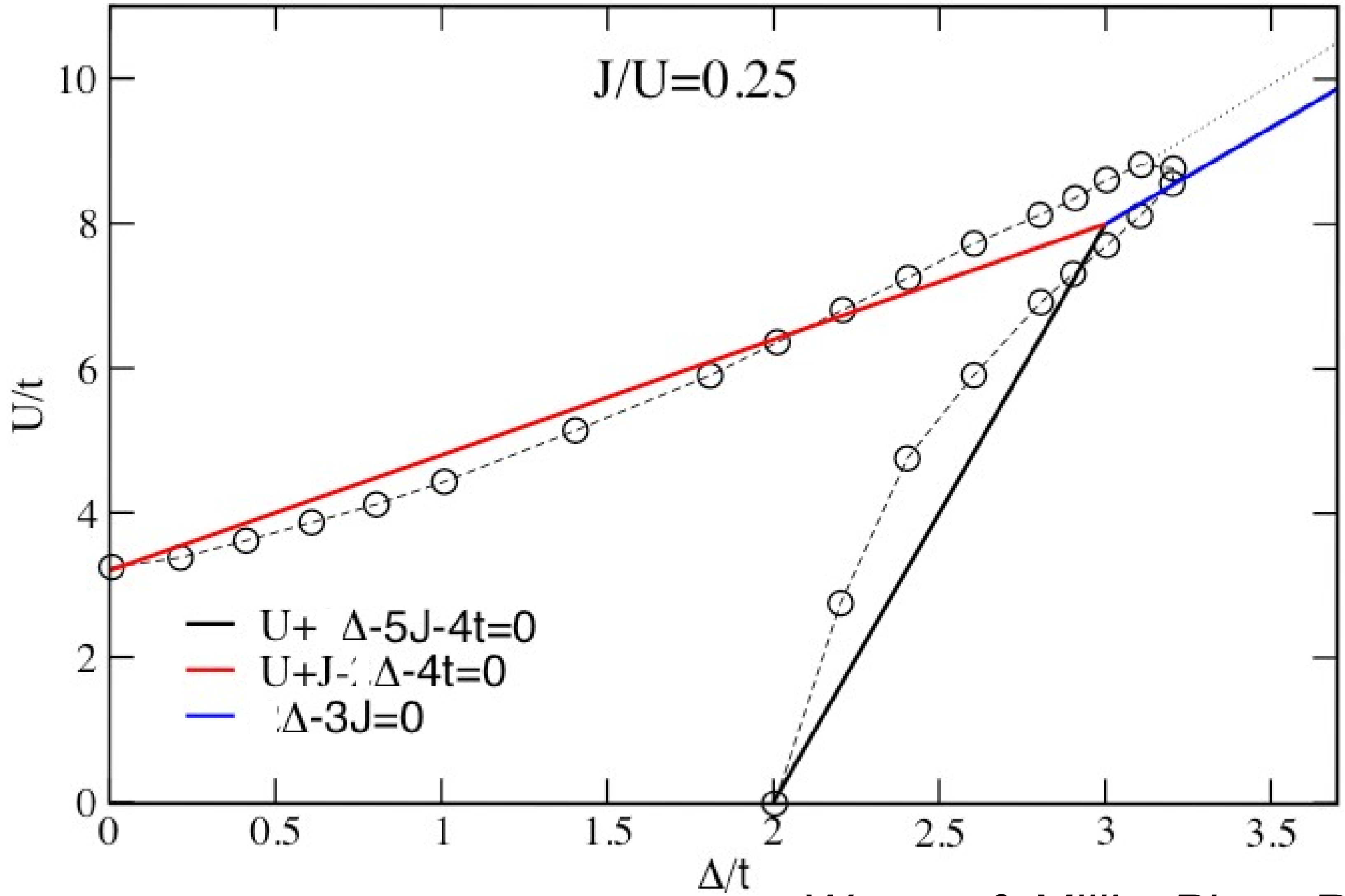


U-Δ phase diagram

Δ - crystal field

J/U - fixed

2D - bipartite lattice (square lattice)



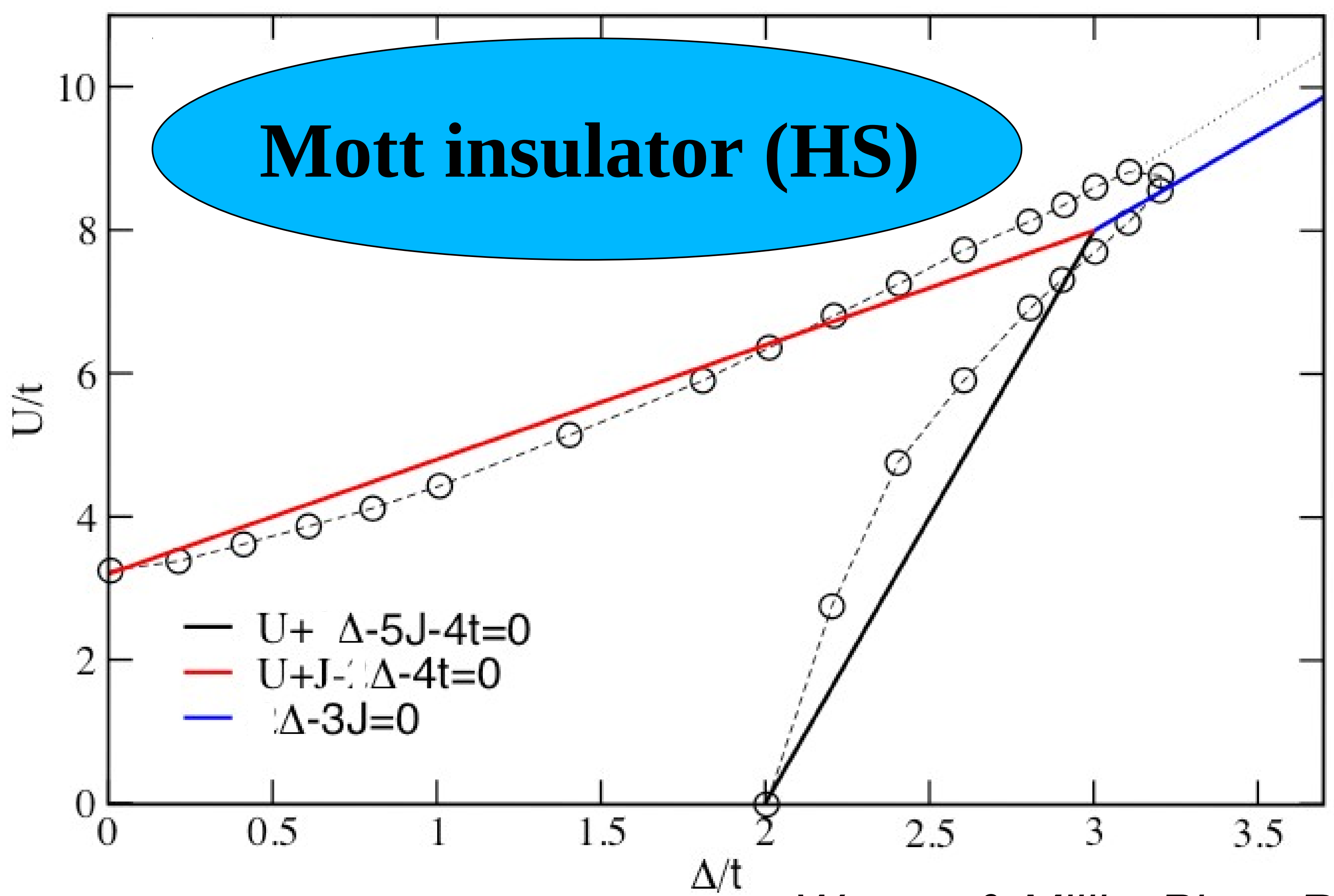
Werner & Millis, Phys. Rev. Lett. ***99,*** *126405 (2007)*
JK et al. Eur. Phys. J. Special Topics ***180****, 5 (2009)*

U-Δ phase diagram

Δ - crystal field

J/U - fixed

2D - bipartite lattice (square lattice)



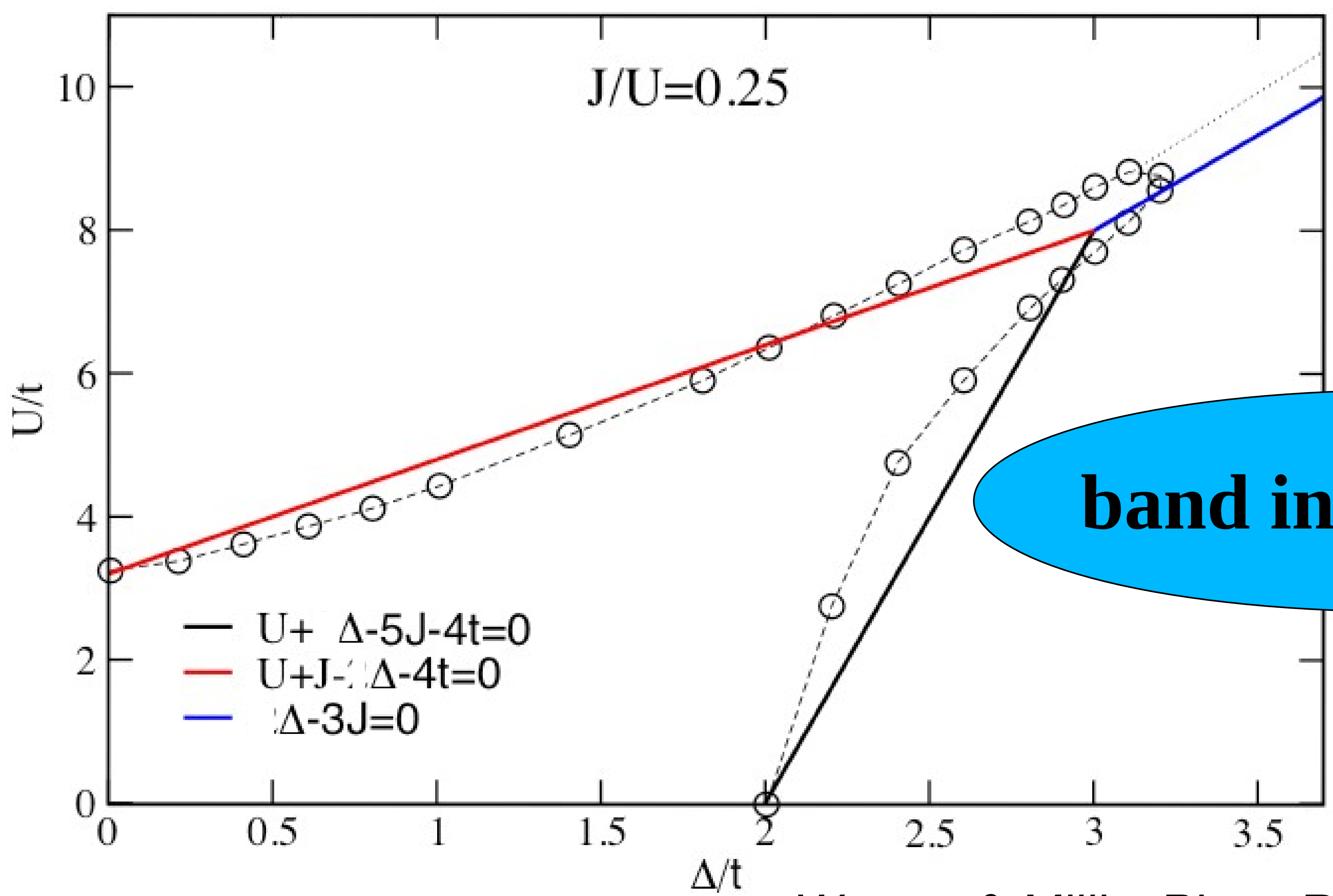
Werner & Millis, Phys. Rev. Lett. ***99,*** *126405 (2007)*
JK et al. Eur. Phys. J. Special Topics ***180****, 5 (2009)*

U-Δ phase diagram

Δ - crystal field

J/U - fixed

2D - bipartite lattice (square lattice)



band insulator (LS)

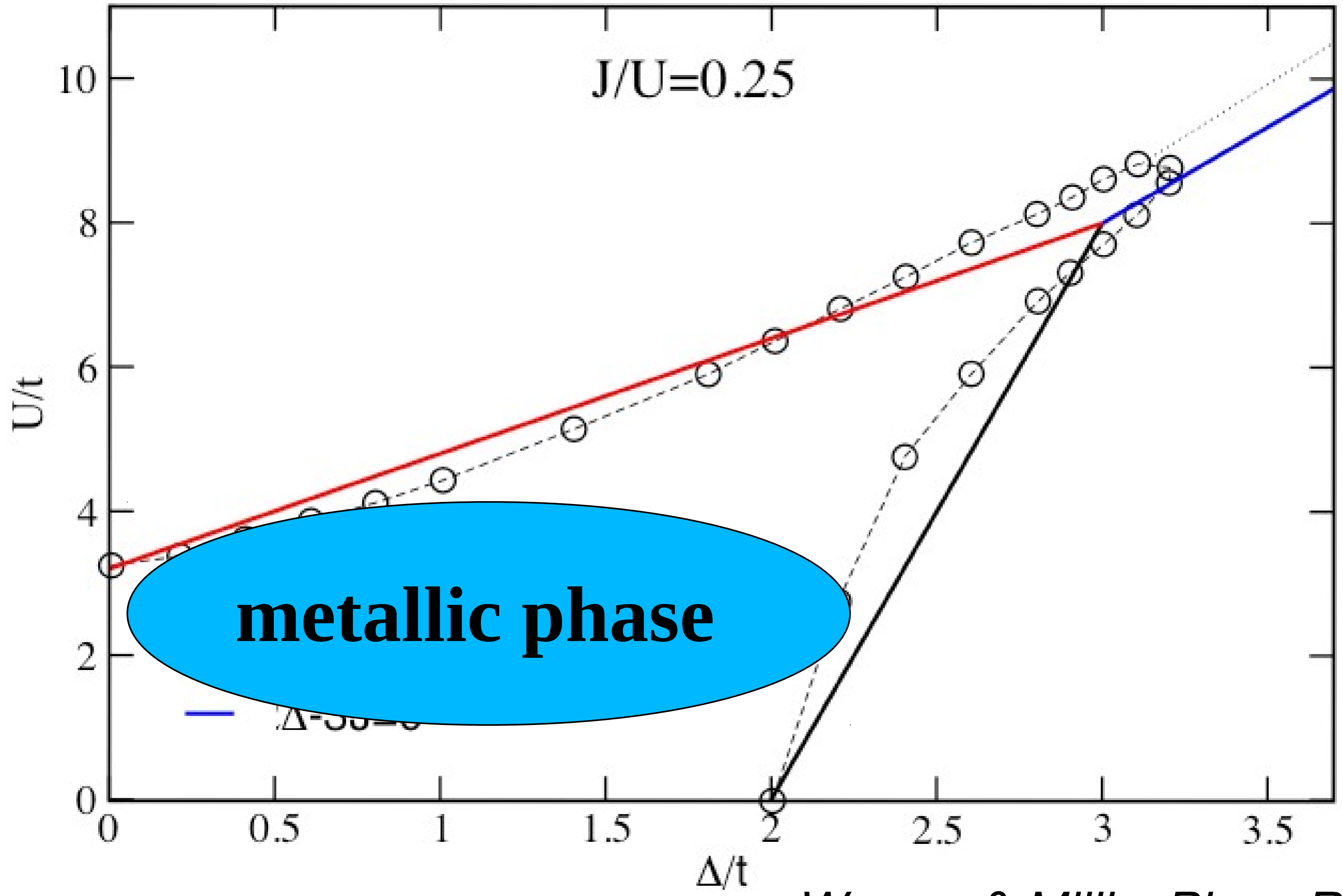
Werner & Millis, Phys. Rev. Lett. ***99,*** *126405 (2007)*
JK et al. Eur. Phys. J. Special Topics ***180****, 5 (2009)*

U-Δ phase diagram

Δ - crystal field

J/U - fixed

2D - bipartite lattice (square lattice)

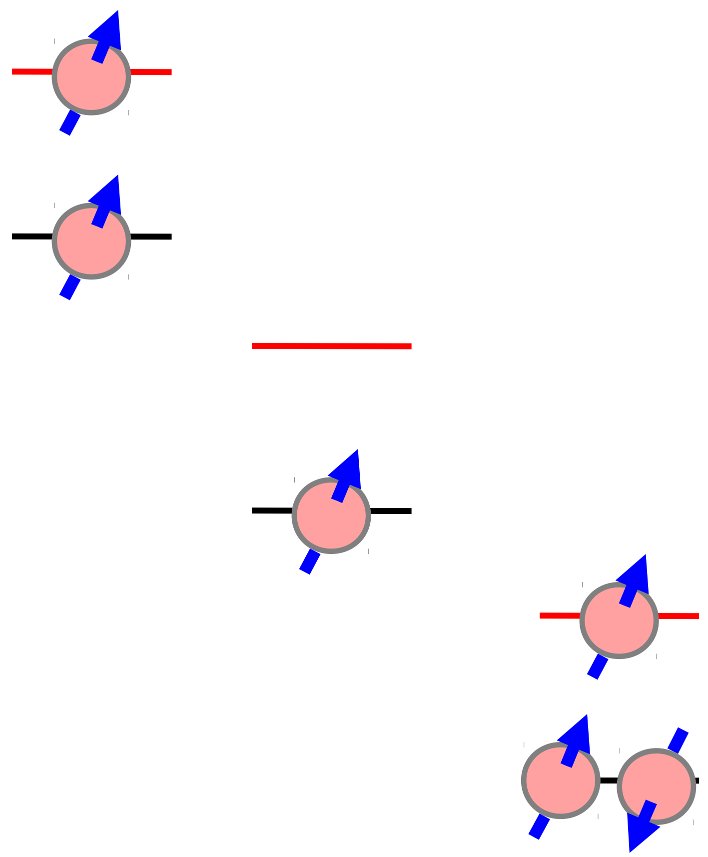


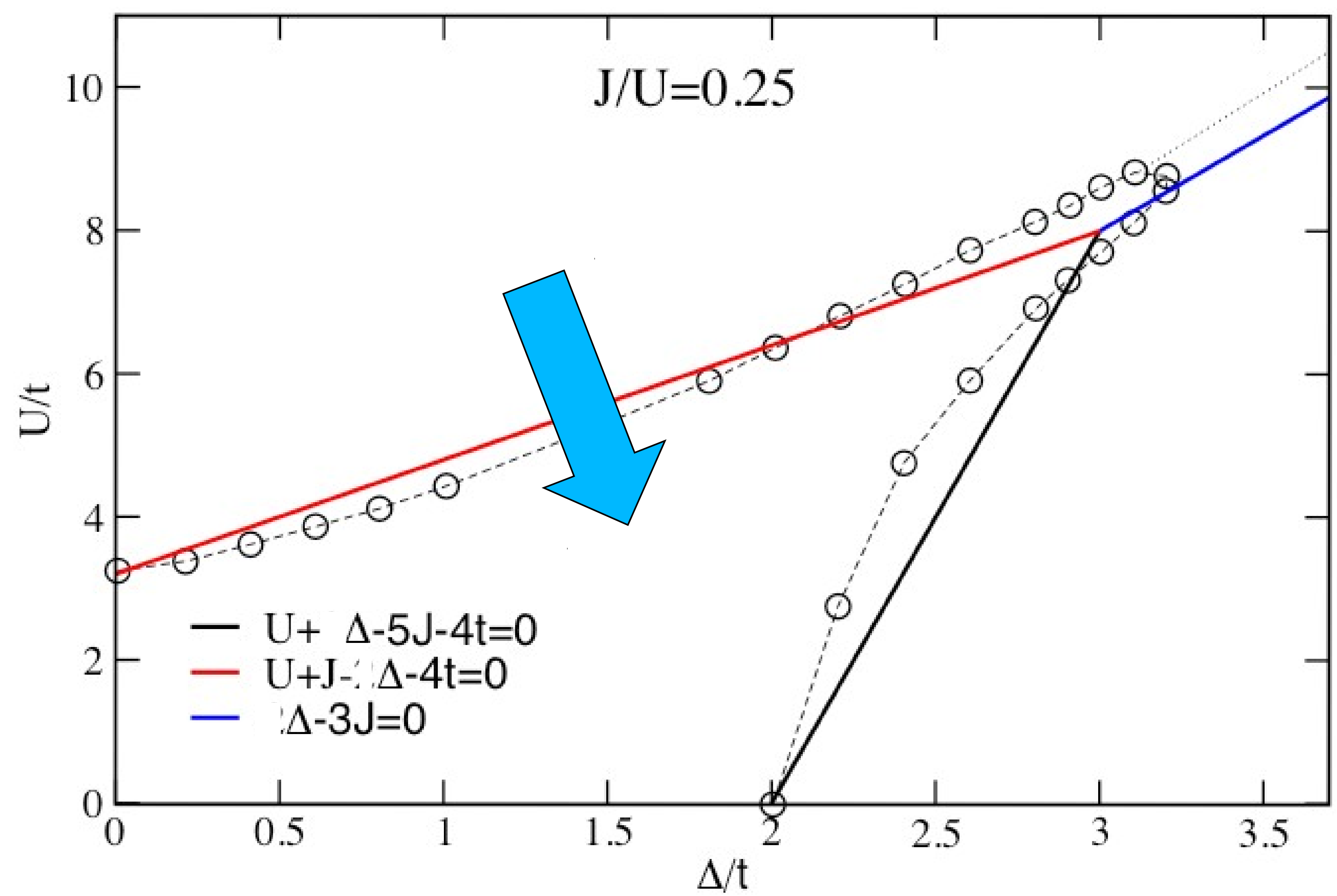
Werner & Millis, Phys. Rev. Lett. ***99,*** *126405 (2007)*
JK et al. Eur. Phys. J. Special Topics ***180****, 5 (2009)*

Gap closing

'Mott gap = 0'

E_g=2E(N)-E(N-1)-E(N+1)

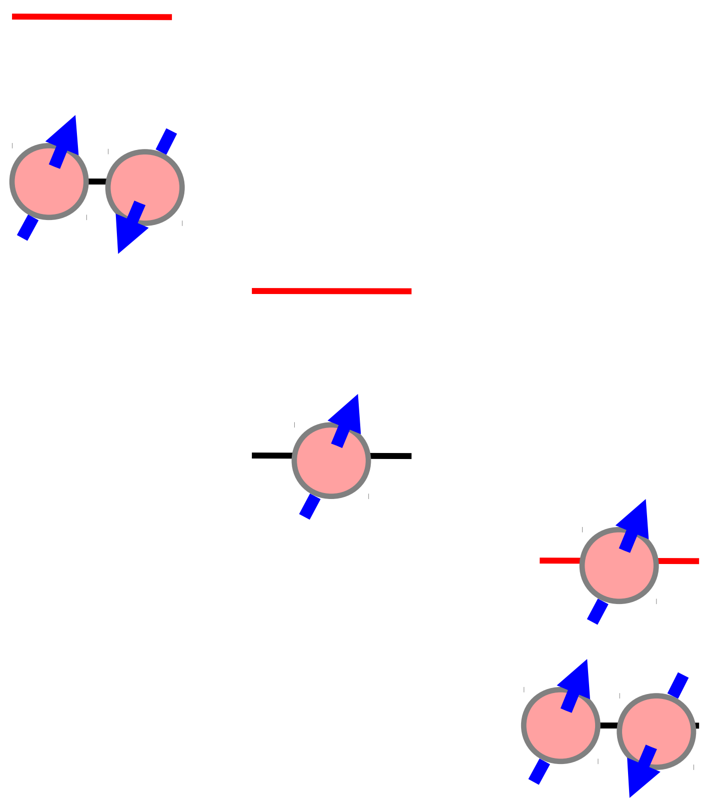


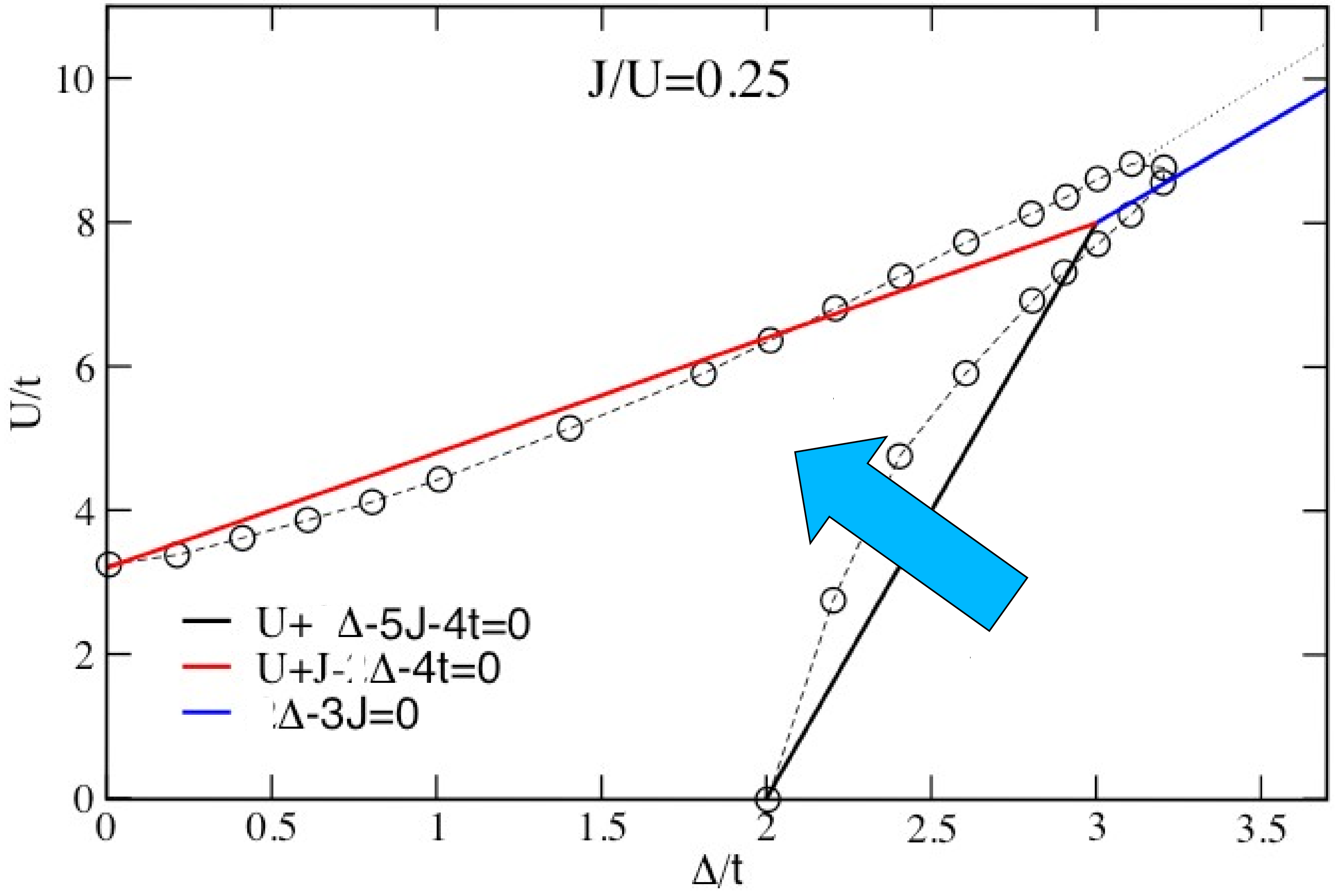


Band gap

'Band gap = 0'

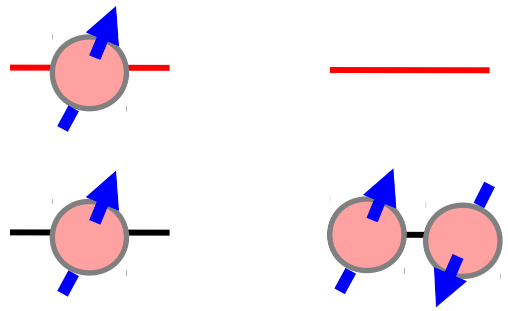
$E_g = 2E(N) - E(N-1) - E(N+1)$

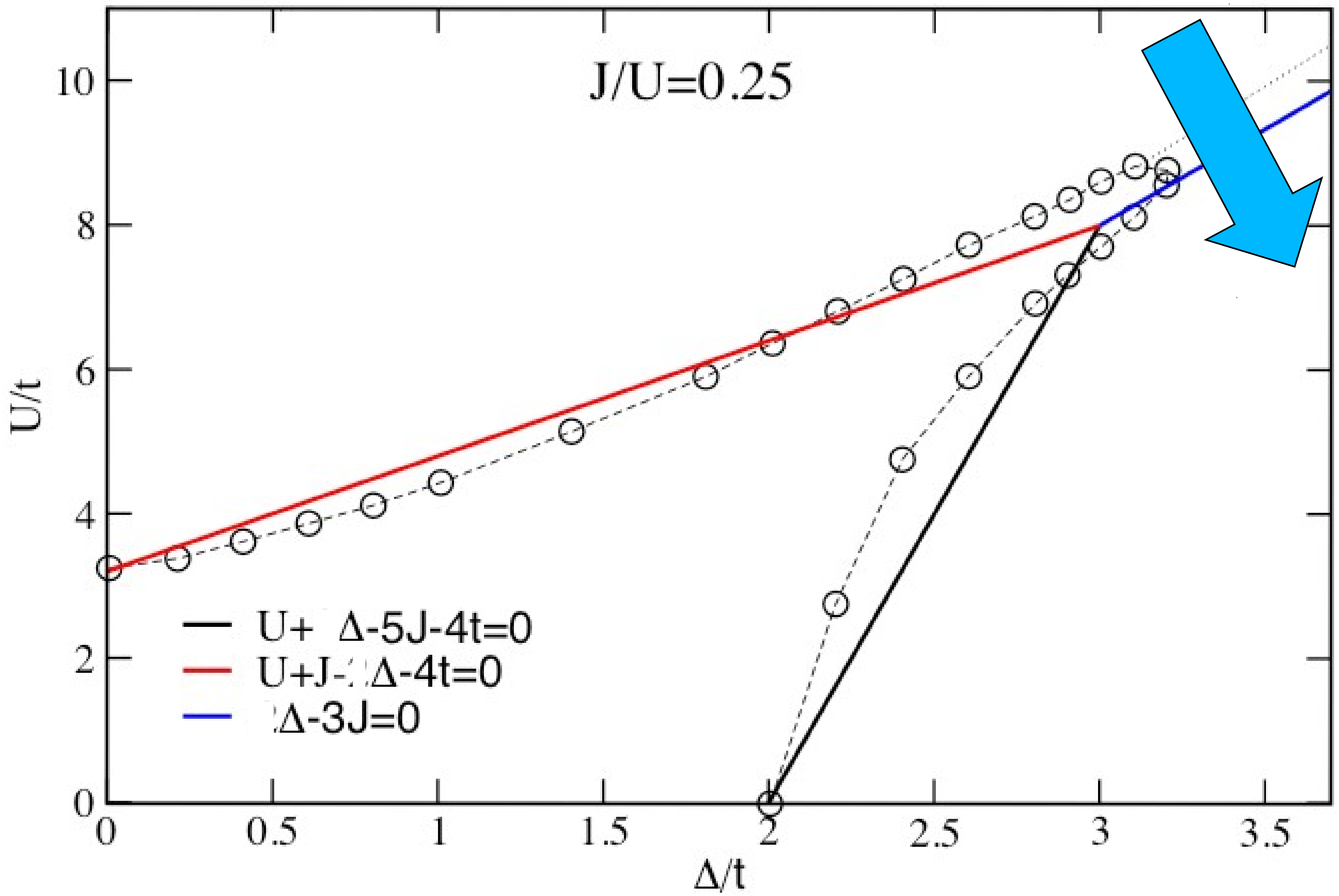




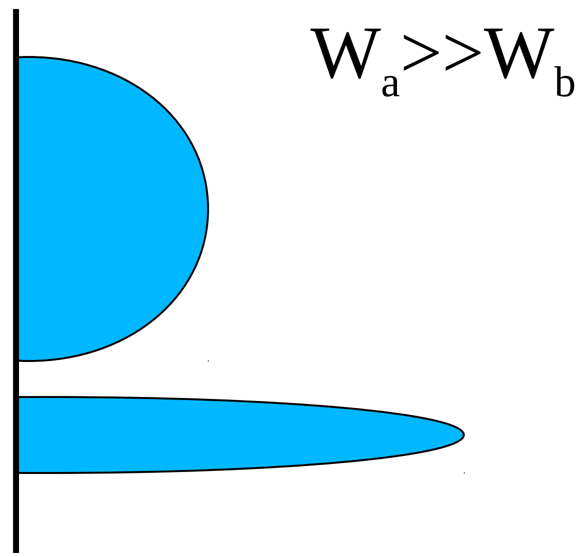
Local state transition

‘E(HS)-E(LS) = 0’

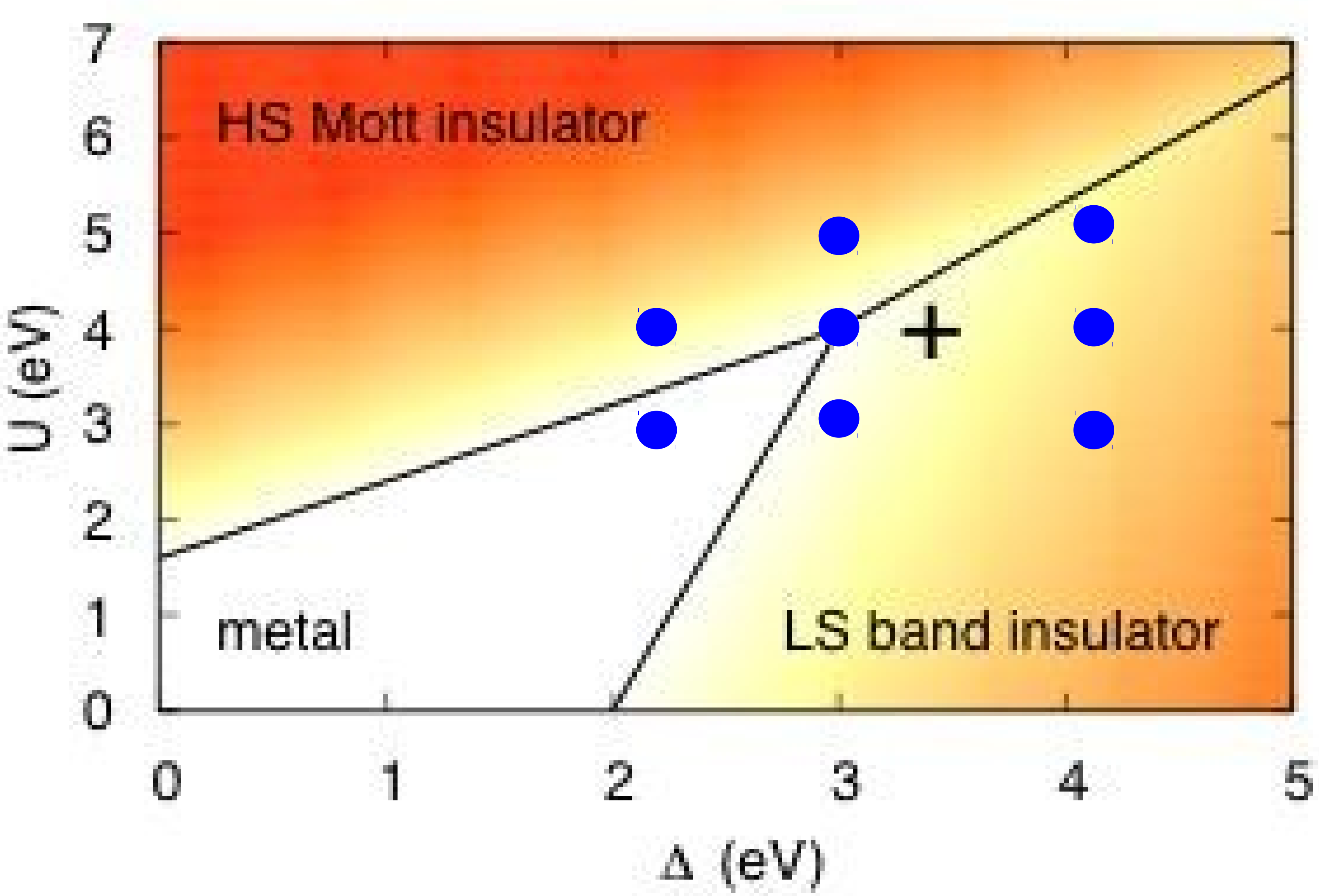




The model - stoichiometric filling=2e



Two sublattice order allowed



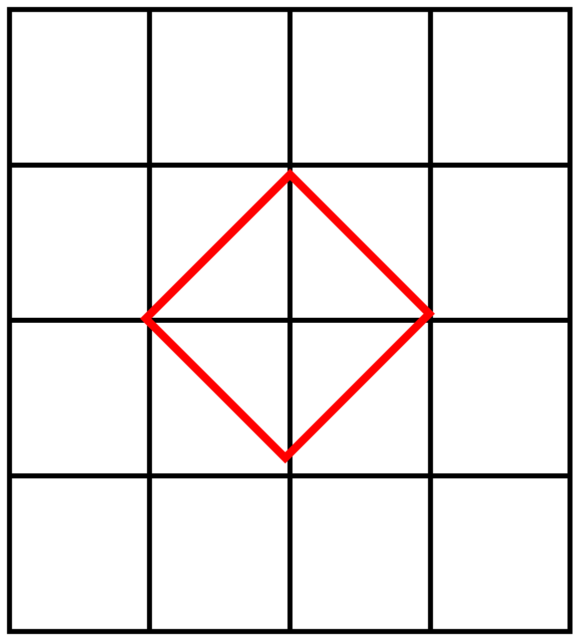
Computational parameters:

W_a=3.6

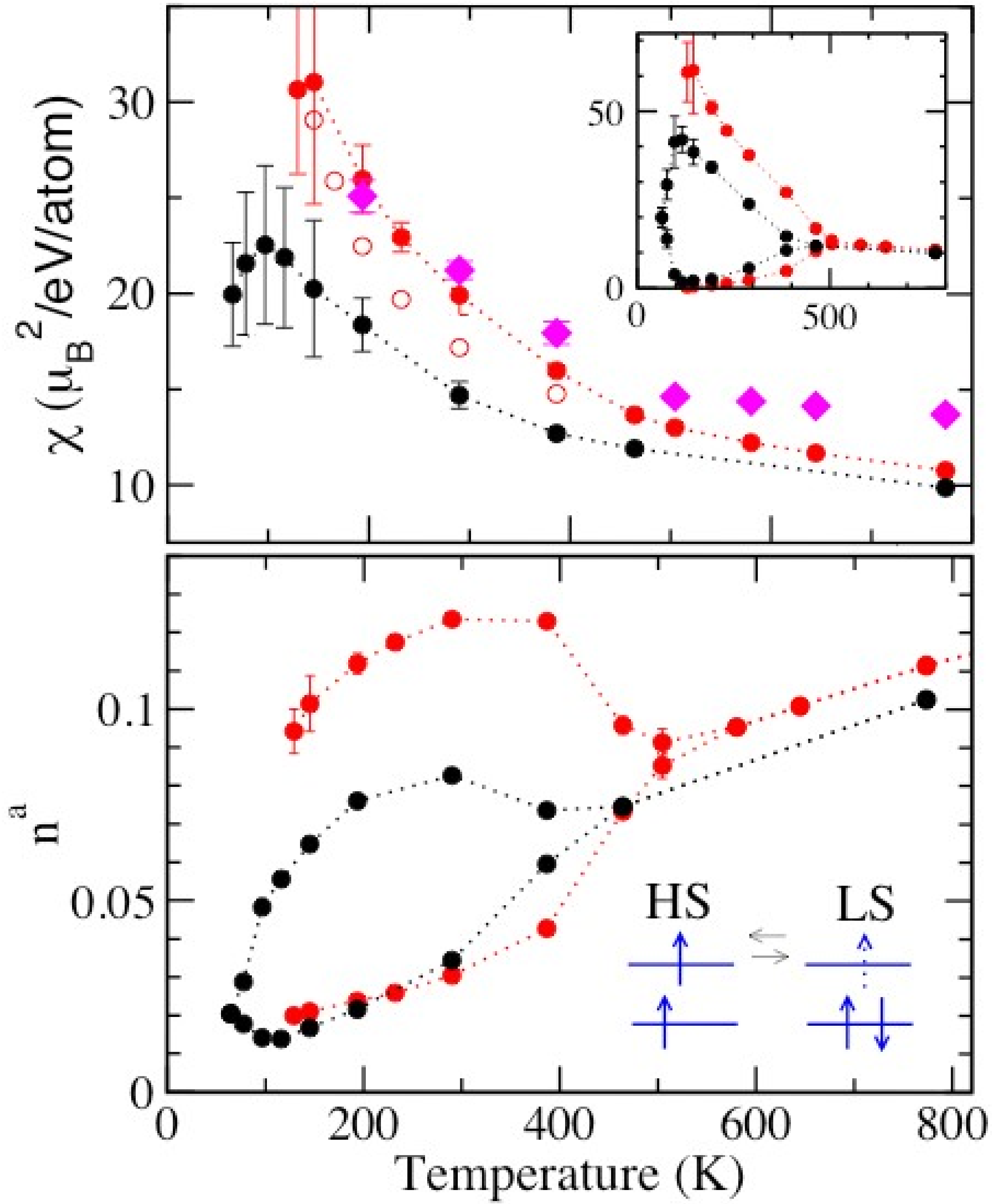
W_b=0.4

U=4, J=1

Unit cell:



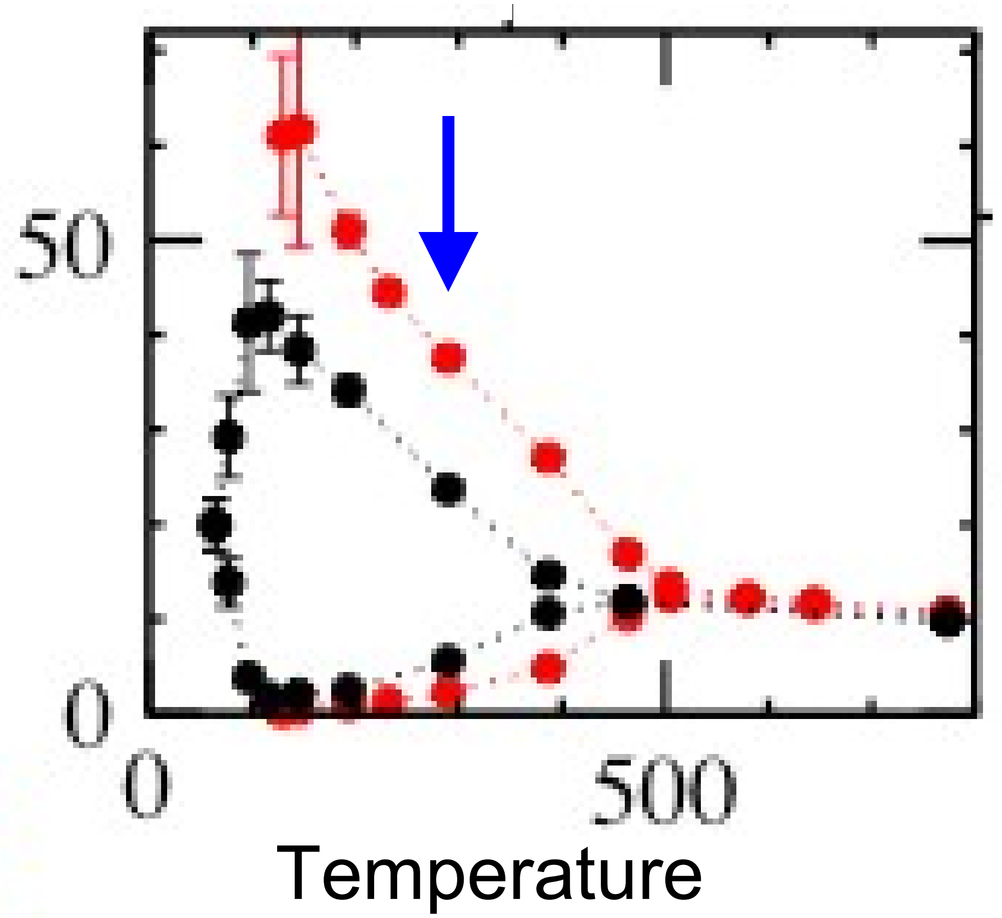
Spin susceptibility and disproportionation



Δ-3J=0.42
local susceptibility
Δ-3J=0.40
local susceptibility
local susceptibility (homog. ph.)
uniform susceptibility

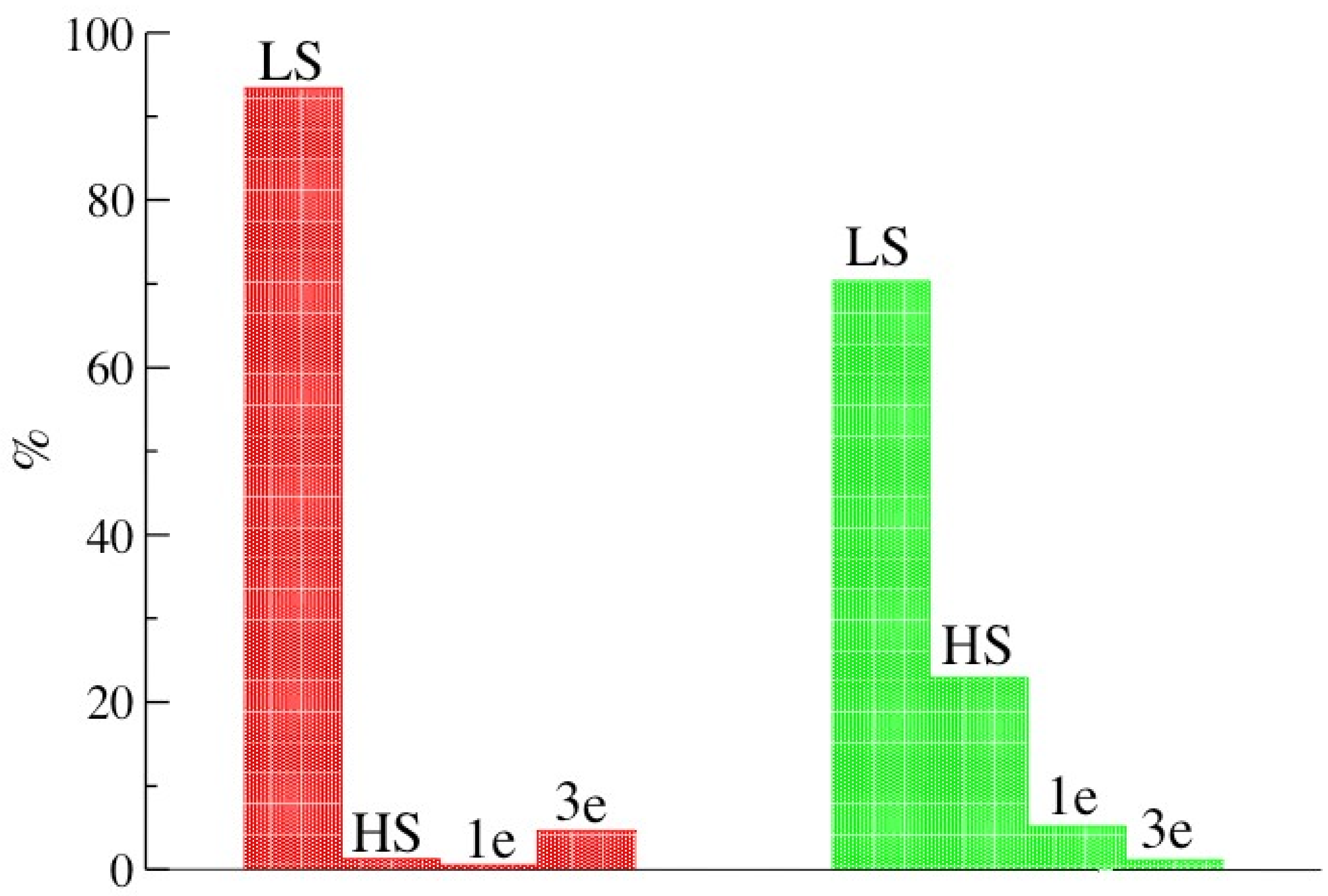
Site occupancy n^a (upper band)
Δ-3J=0.42
Δ-3J=0.40

JK & Krapek, Phys. Rev. Lett. ***106****, 256401 (2011)*

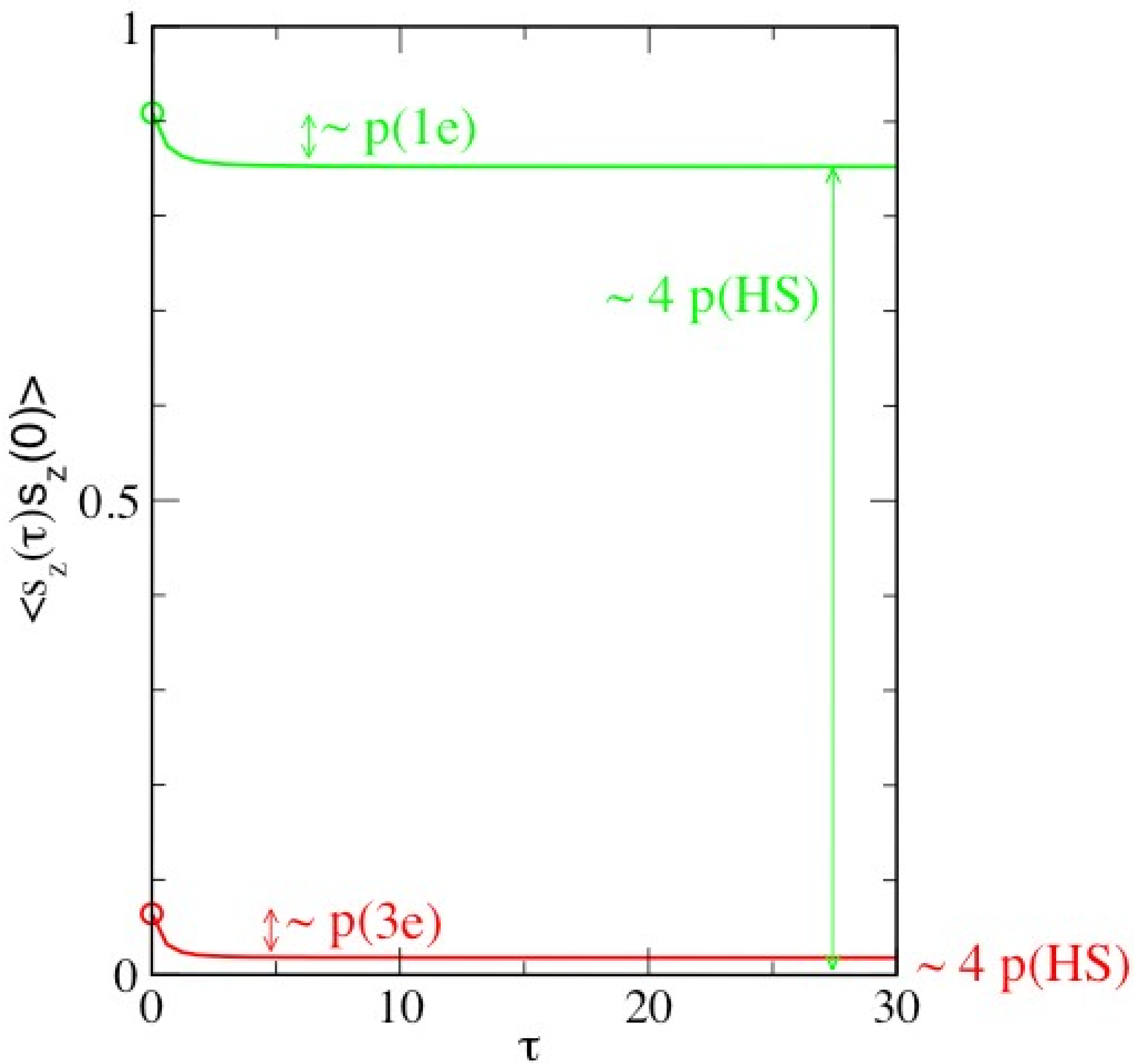


short excursions
vs
statistical mixture

Local state statistics

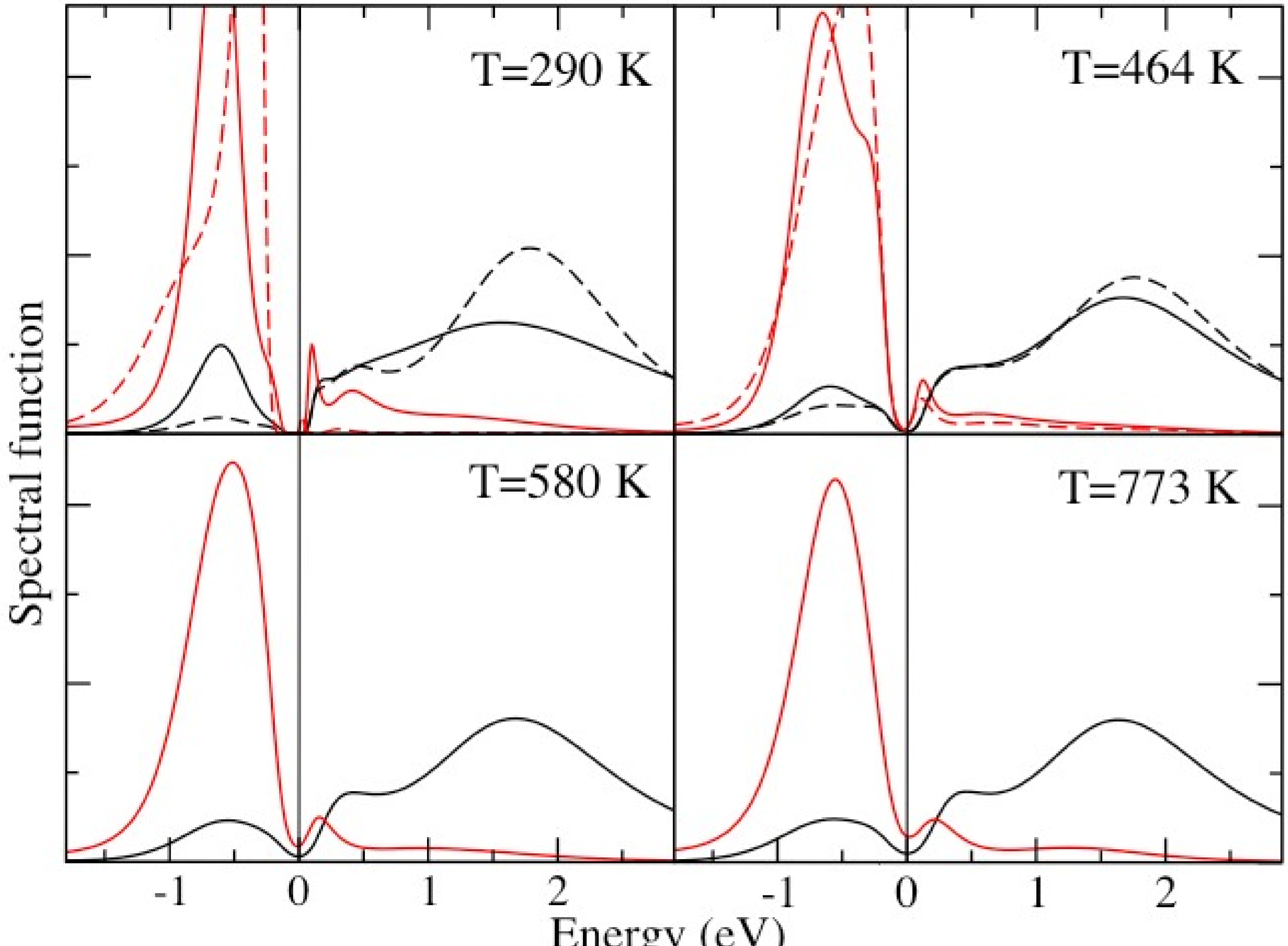


Spin-spin correlations



One-particle spectra

$A_{aa}(\omega)$ (black line)
$A_{bb}(\omega)$ (red line)



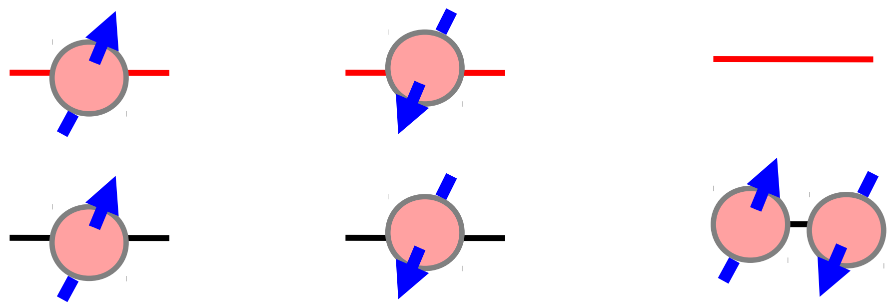
disproportionated

homogeneous

Low-energy model

Integrate out the charge fluctuations:

• keep 3 local states



• treat hopping as perturbation

Hamiltonian

$$\tilde{H} = \xi_0 \sum_{i,\sigma} n^{\mathrm{HS}}_{i,\sigma} + \sum_{\langle ij\rangle,\sigma} \left(\xi_1 n^{\mathrm{LS}}_i n^{\mathrm{HS}}_{j,\sigma} + \xi_2 n^{\mathrm{HS}}_{i,\sigma} n^{\mathrm{HS}}_{j,-\sigma}\right)$$

$$\xi_0 = \Delta - 3J,\ \xi_1 = -\frac{t_{aa}^2}{U-2J},\ \xi_2 = -\frac{2t_{aa}^2}{U+J}$$

Mean-field free energy

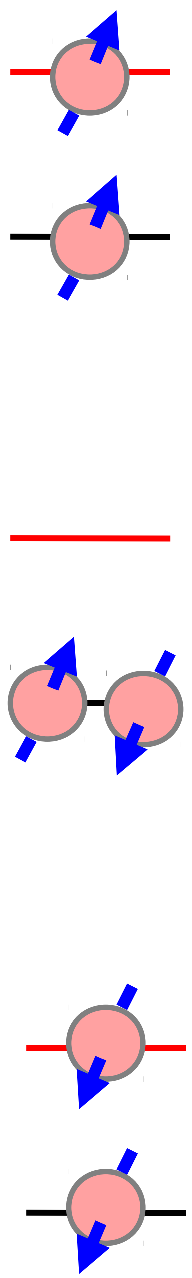
$$F(T) = \frac{\xi_0}{2}(x_A + x_B) + 2\xi_1\left(x_A + x_B - 2x_A x_B\right) - \xi_2 x_A x_B$$
$$+ \frac{T}{2}(1 - x_A)\ln(1 - x_A) + \frac{T}{2}(1 - x_B)\ln(1 - x_B)$$
$$+ \frac{T}{2}x_A \ln(\frac{x_A}{2}) + \frac{T}{2}x_B \ln(\frac{x_B}{2}),$$

Blume-Emery-Griffiths model

$$\tilde{H} = D \sum_i s_i^2 + K \sum_{\langle ij \rangle} s_i^2 s_j^2 + I \sum_{\langle ij \rangle} s_i s_j$$

Blume et al., Phys. Rev. A ***4****, 1071 (1971)*

$$s_i = \begin{cases} 1 \\ 0 \\ -1 \end{cases}$$

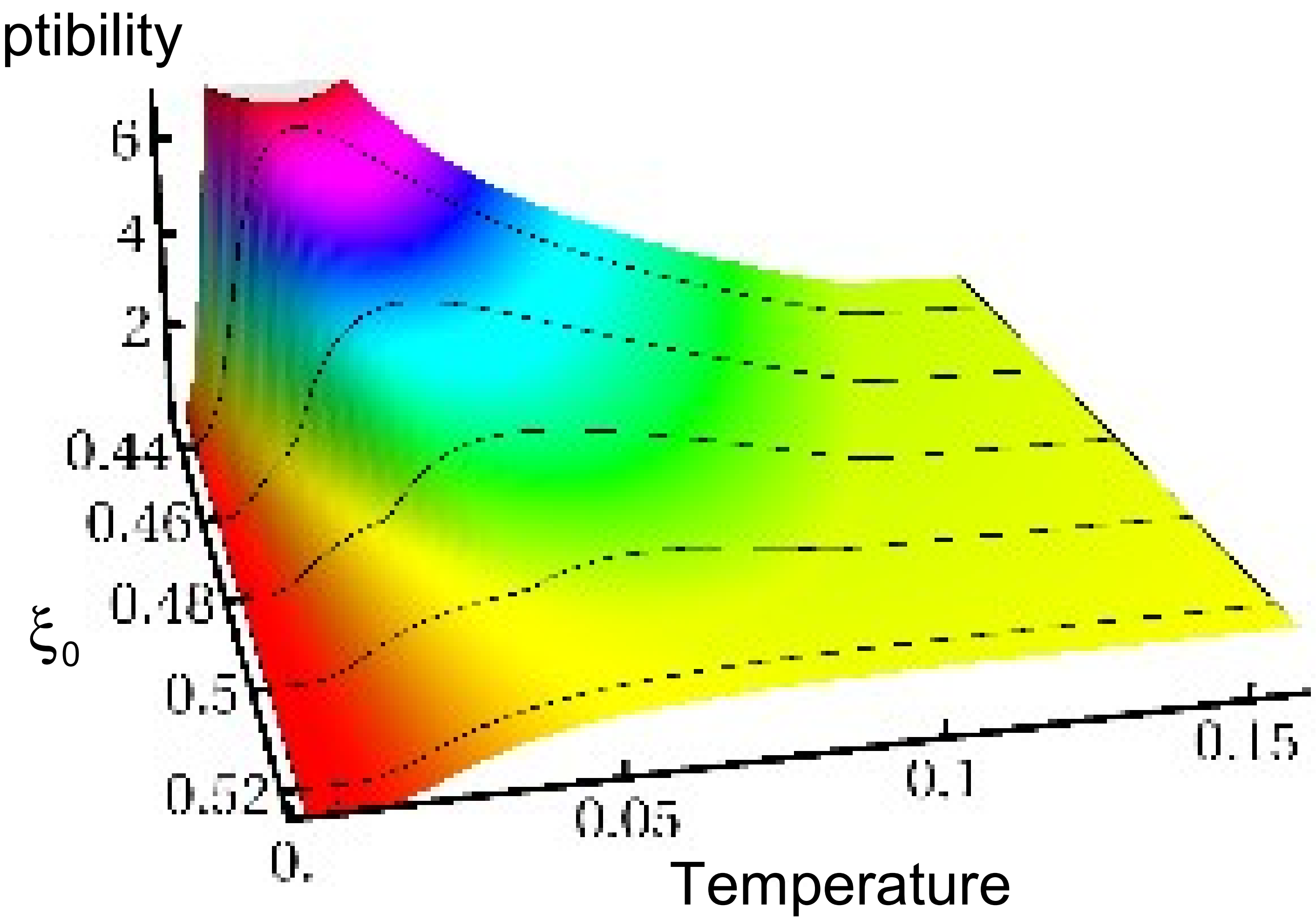


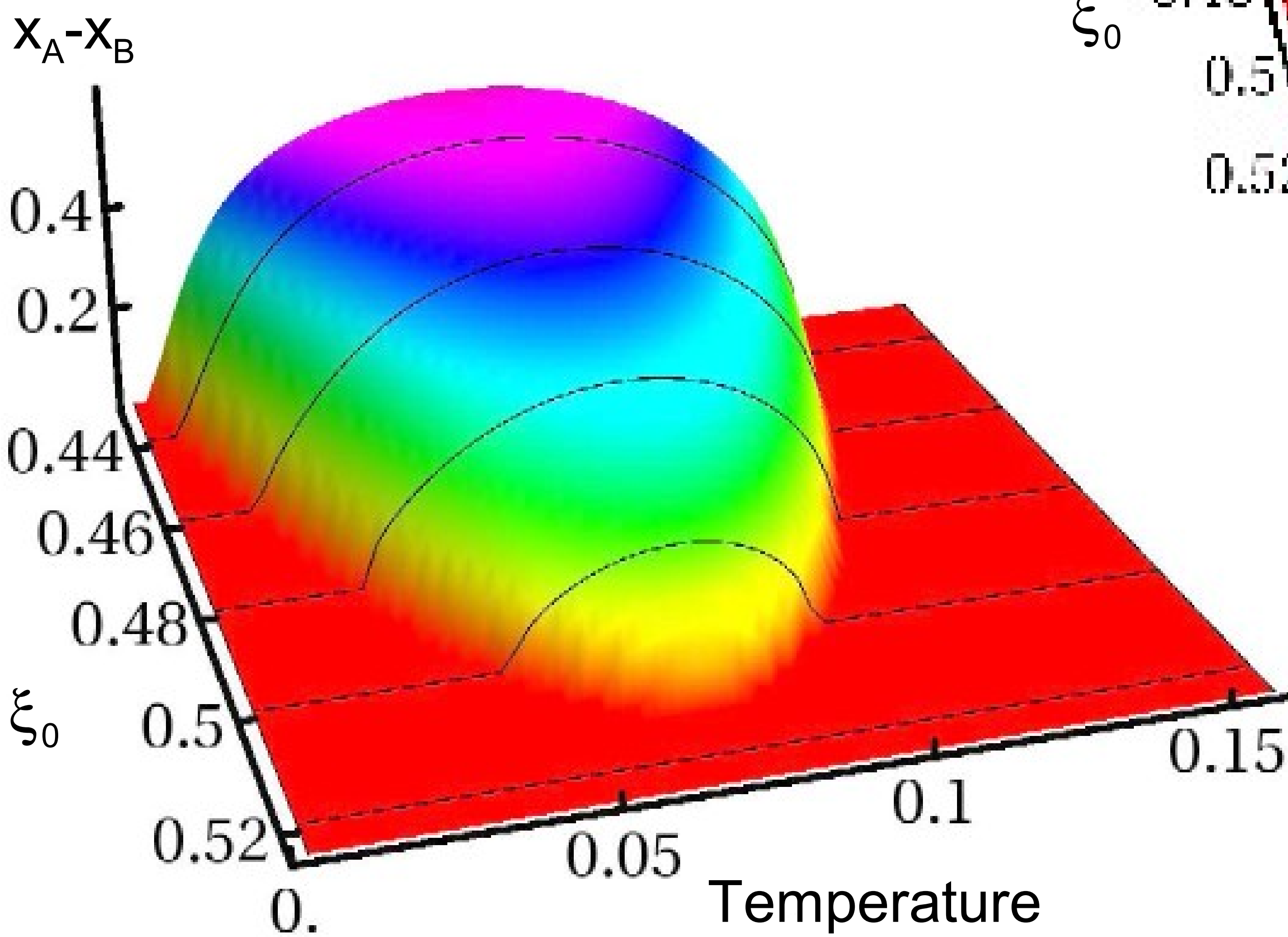
$$D = \Delta - 3J - \frac{Zt^2}{U - 2J}$$

$$K = t^2 \left(\frac{1}{U - 2J} - \frac{1}{U + J} \right)$$

$$I = \frac{t^2}{U + J}$$

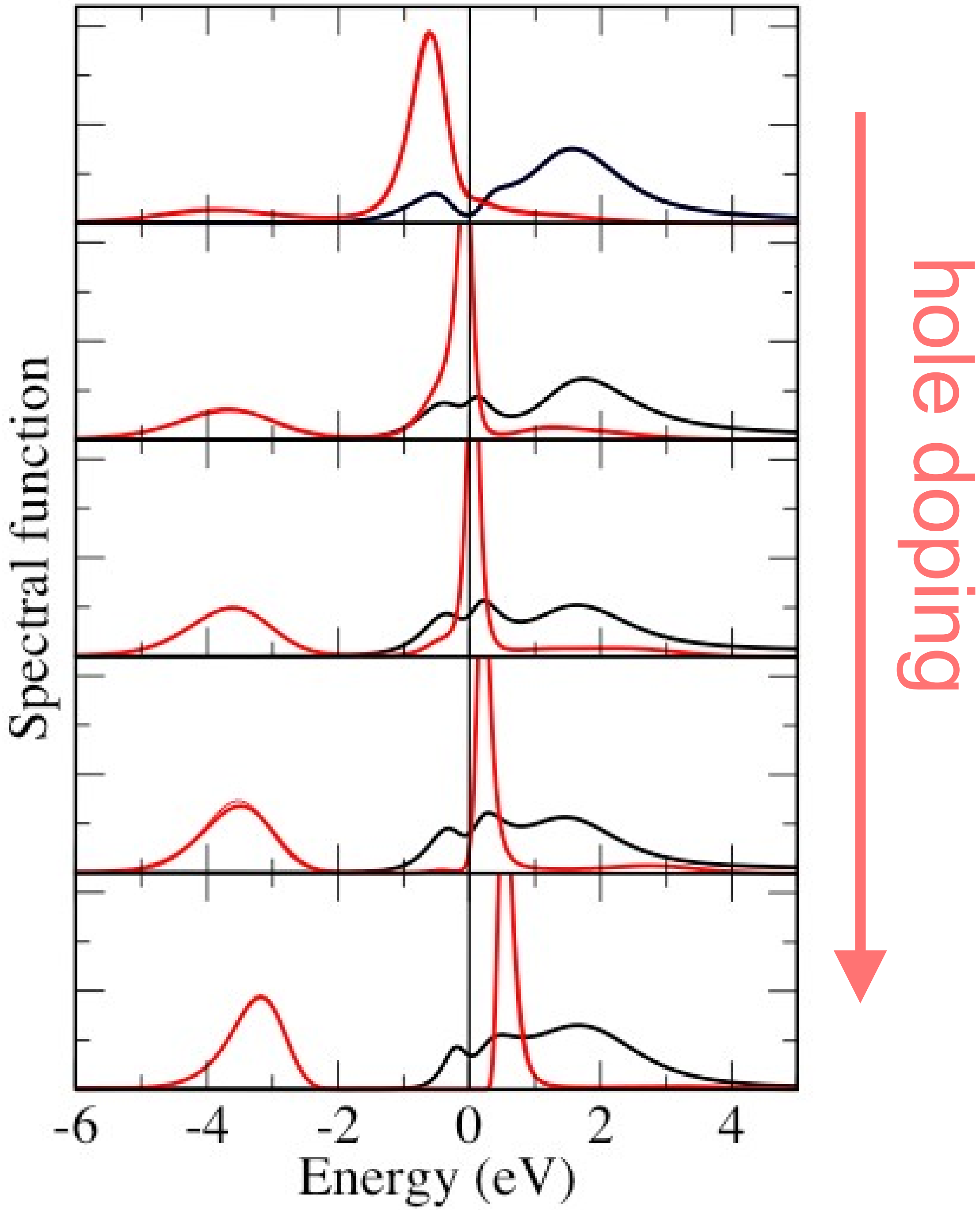
Low-energy model



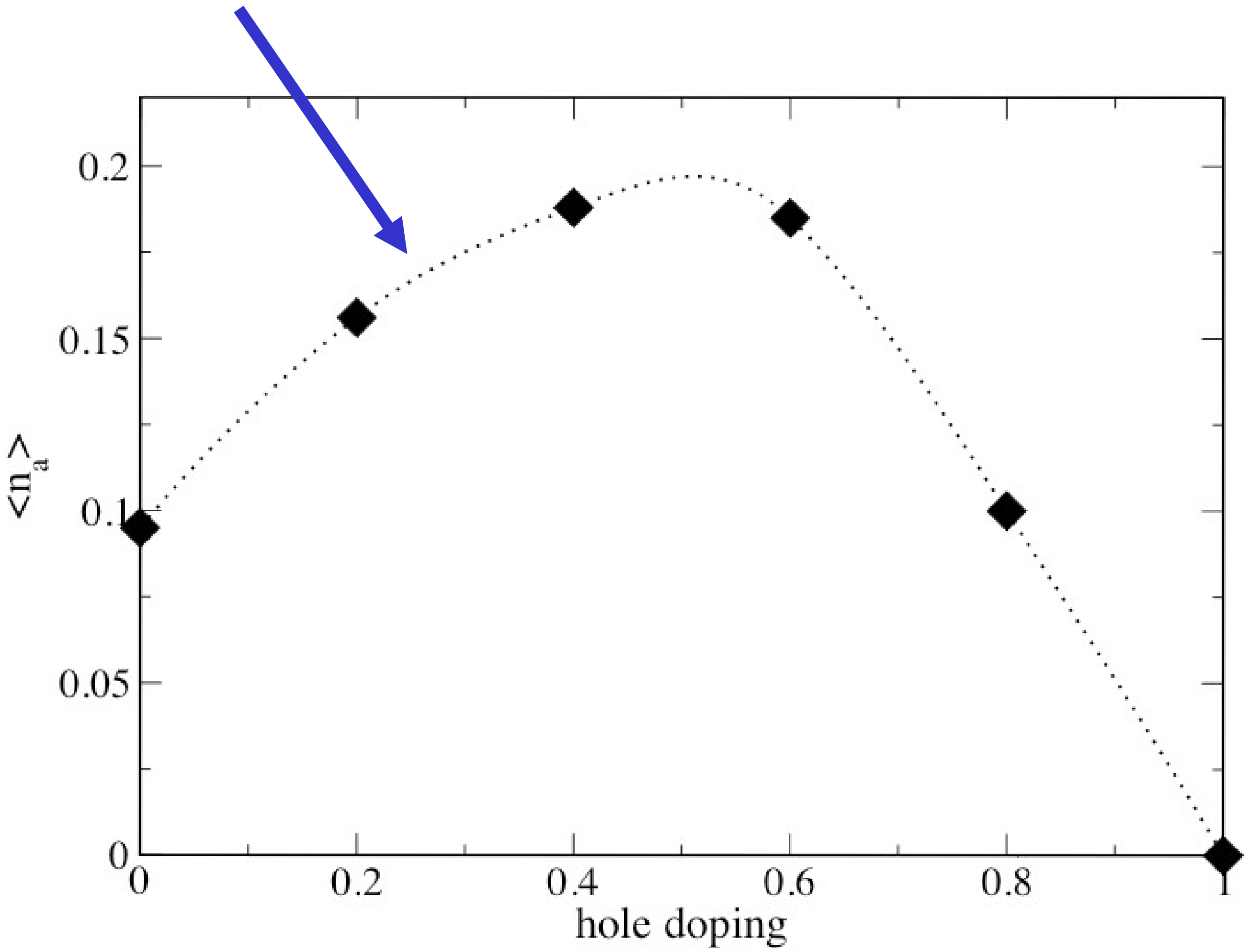


Hole doping

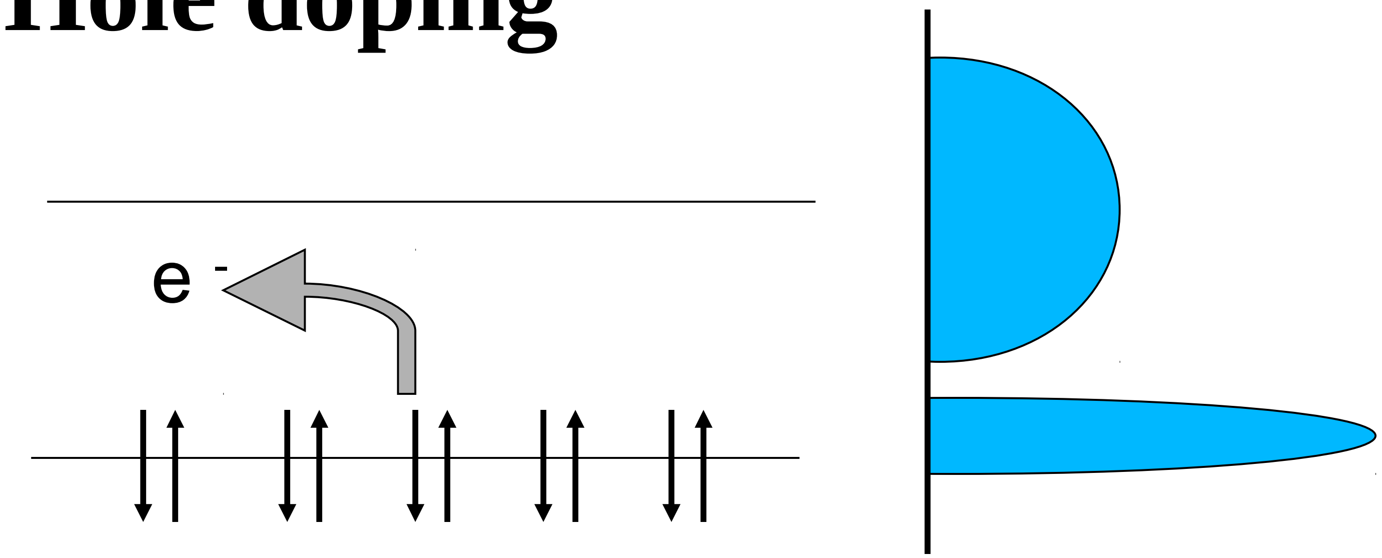
How do we from localized moments to double exchange picture?

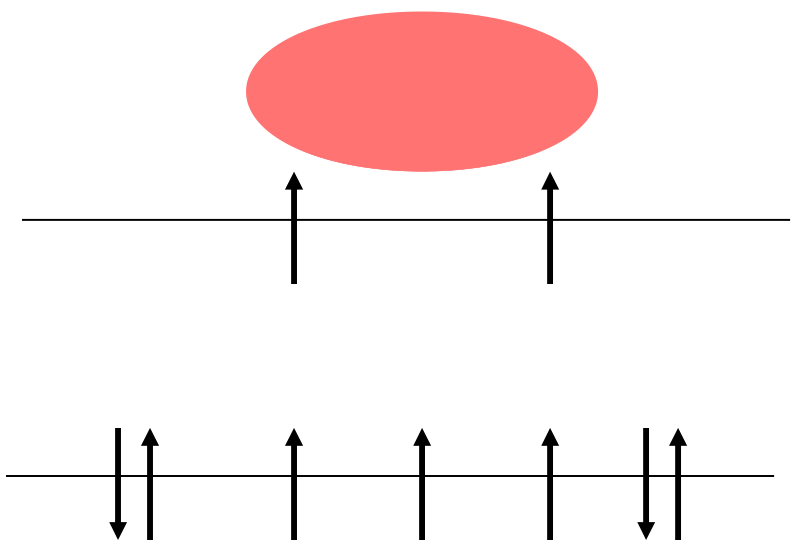


Upper band occupancy increases !

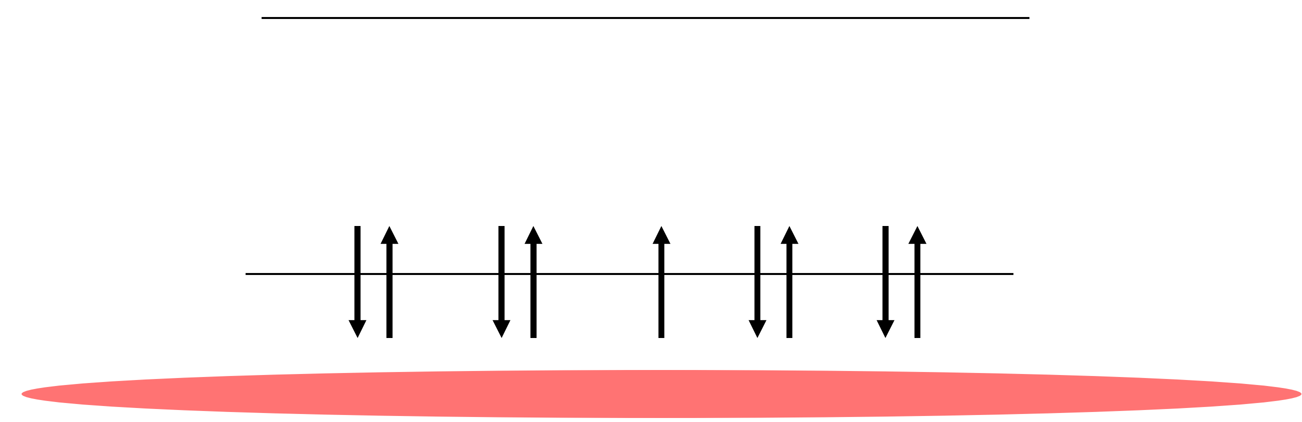


Hole doping





OR



$$\sim -\sqrt{2}t_a + 2\xi_0$$

$$\sim -2t_b$$

localized magnetic polaron

itinerant hole in lower band

Conclusions

- (Quasi)degeneracy of ionic multiplets leads to rich phase diagrams in strongly correlated systems.
- Effective HS-LS attraction at the HS/LS transitions leads to a ordered state with reduced translational symmetry.
- 2-band Hubbard model with crystal field provides fermionic realization of BEG model and introduces new parameter - doping
- Under certain circumstances ($W_a >> W_b$) doping leads to formation of inhomogeneities - magnetic polarons