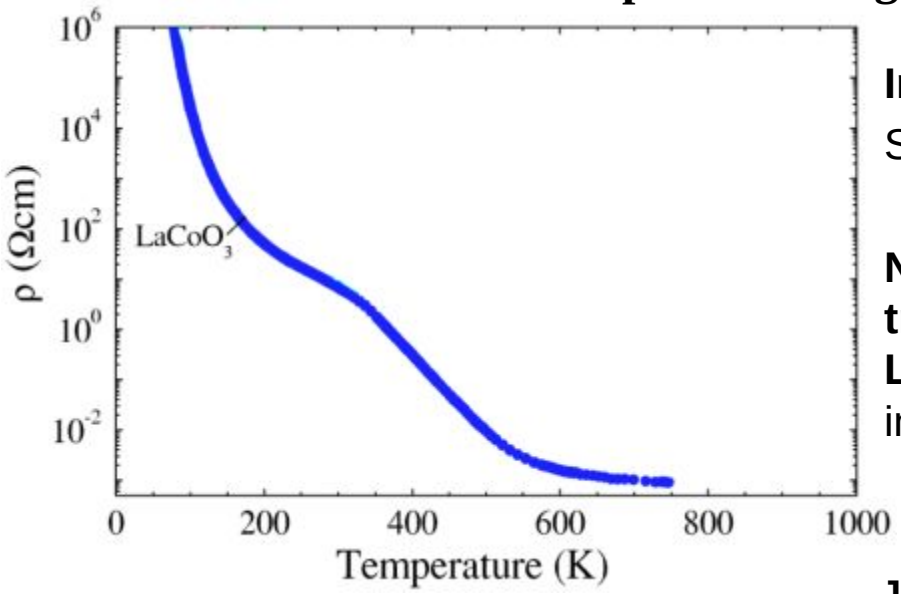
Temperature dependent electronic structure of Mott insulators with singlet spin state

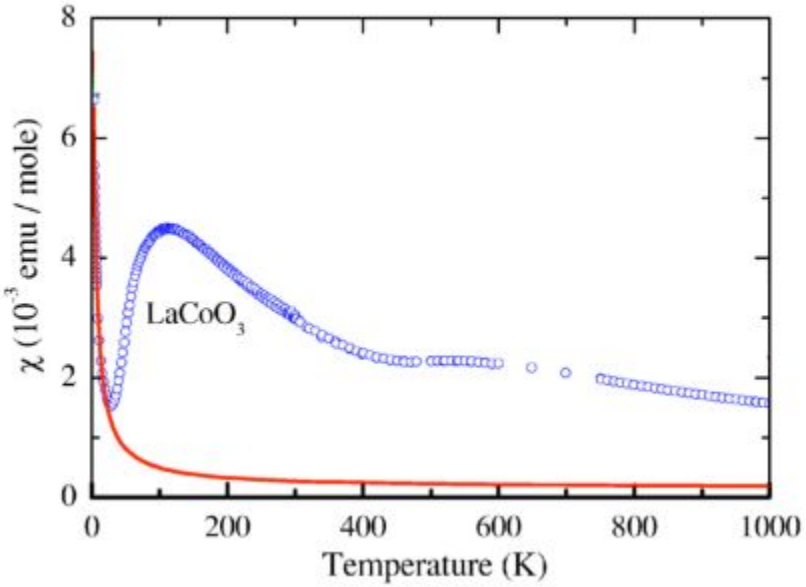
Sergey Ovchinnikov

L.V.Kirensky Institute of Physics Siberian Branch of RAS Krasnoyarsk

Transport and magnetic properties of $LaCoO_3$



J. Baier et al., Phys. Rev. B 71, 014443 (2005)



Spin state transition from non magneticat T ≈ 0 K с переход в парамагнитное.

Insulator at T < 100 K the energy **gap Eg ≈ 0,2 eV.**
S. Yamaguchi et al., Phys. Rev. B 53, R2926 (1996)

Narrow-gap semiconductor with gap Eg smothly **transforms into metal with heating at T ~ Eg, in $LaCoO_3$ Eg = 2300K**, experiment reveals smoth insulator metal transition at **$T_{ПМД}$ = 550 – 600K**

-**J.B. Goodenough 1958г. T=0 LS (S=0), T≠0 HS (S=2)**

- S_{eff}≈1 from Curie law, HS vs IS?

-**small gap** between LS and HS states results in one **maximum at T~150K**, the second peak is unclear Δ_S

Two-stage spin state transition LS-IS at T≈100K and

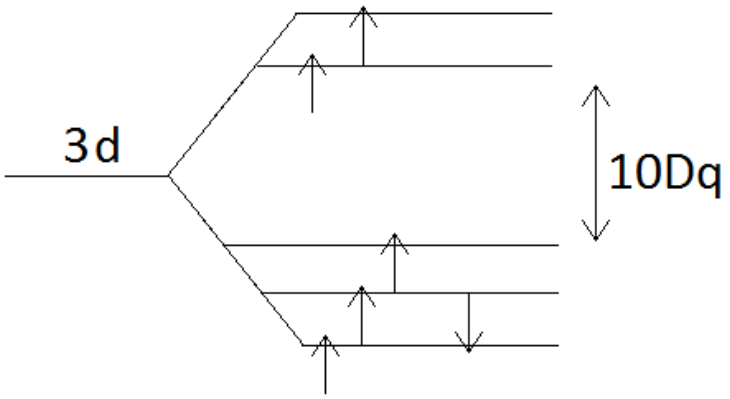
IS-HS at T=500-600K (K. Asai et al., J.Phys.Soc.J. 67, 290 (1998) results in **two-peak susceptibility** but

contradicts EPR (S. Noguchi et al., Phys. Rev. B 66, 094404 (2002)),

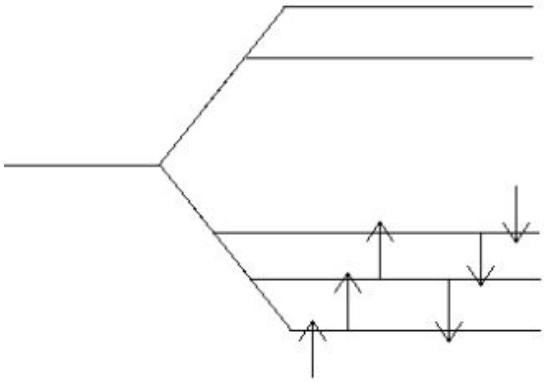
XMCD(M.Haverkort et al., Phys. Rev. Lett. 97, 176405 (2006))

INS (A. Podlesnyak et al., Phys. Rev. Lett. 97, 247208 (2006))

Energy of d6 ion in a cubic crystal field



d^6, S=2 (HS)



d^6, S=0 (LS)

$$E_S = E_{LS} - E_{HS}$$ Spin gap $$E_S = 2(4J - 10Dq)$$

Crystal field increases under pressure

$$10Dq(P) = 10Dq(0) + \alpha_\Delta \cdot P$$

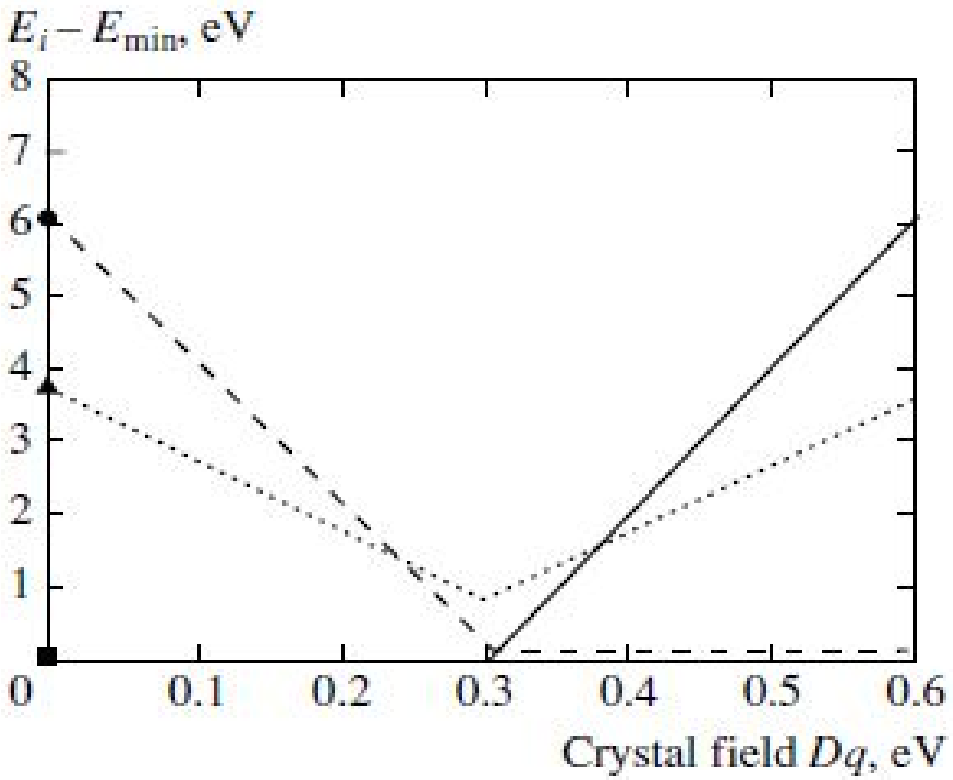


Fig. 1. Tanabe–Sugano diagram for the cobalt ion in a cubic crystal field. The solid line marked by a square stands for the HS state; the dotted line with a triangle, for the IS state; and dashed line with a circle, for the LS state. The calculations were carried out at $U_d = 4$ eV and $V_d = 2.48$ eV.

Absence of S=1 ground state in Tanabe-Sugano diagram for d6 configuration

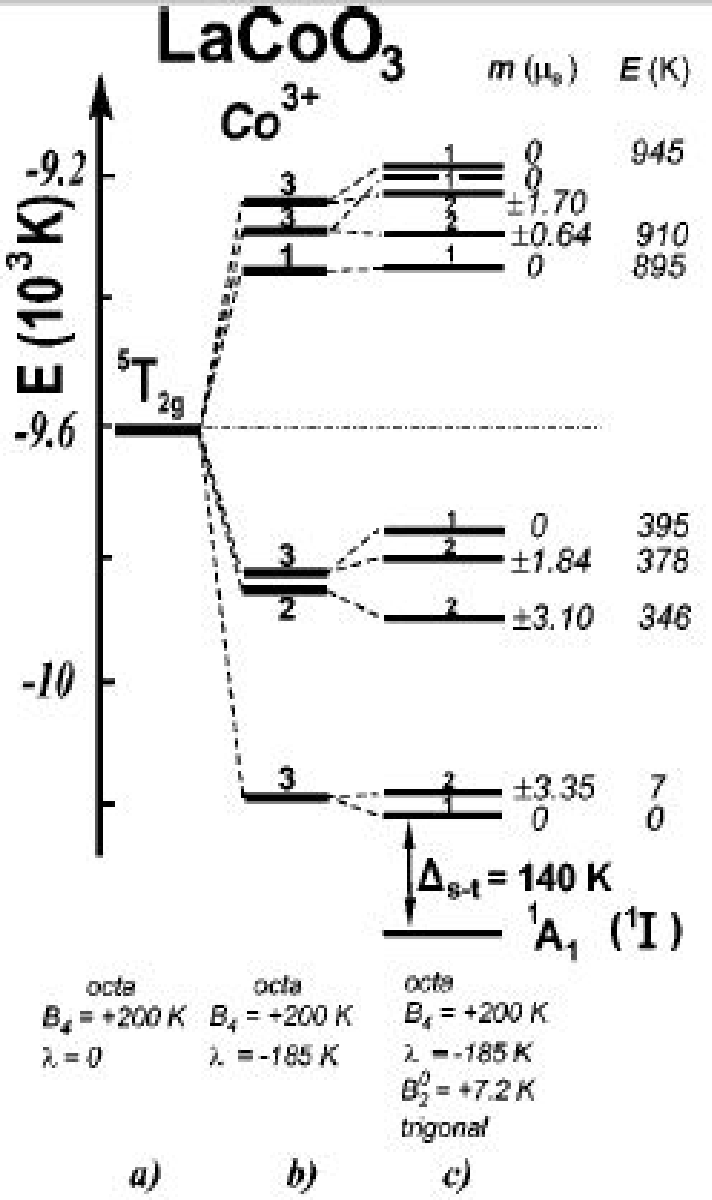


FIG. 6. Calculated low-energy electronic structure of the Co^{3+} ion in $LaCoO_3$ originating from the $^5T_{2g}$ cubic subterm with the $^1A_1$ singlet ground subterm put 140 K below the lowest $^5T_{2g}$ state.

Full atomic multiplet calculations reproduce well the ESR experiment

Z. Ropka and R.J. Radwanski, Phys. Rev. B 67, 172401 (2003)

HS d6: S=2, L=1

J=1, J=2, J=3

Review of the Generalized Tight-Binding (GTB) method

[*S.G. Ovchinnikov and I.S. Sandalov, Physica C 161, 607 (1989)*]

$$H = \sum_{f,\lambda,\sigma} (\varepsilon_\lambda - \mu) n_{f\lambda\sigma} + \sum_{f \neq g} \sum_{\lambda,\lambda',\sigma} T_{fg}^{\lambda\lambda'} c_{f\lambda\sigma}^{+} c_{f\lambda'\sigma} + \frac{1}{2} \sum_{f,g,\lambda,\lambda'} \sum_{\sigma_1,\sigma_2,\sigma_3,\sigma_4} V_{fg}^{\lambda\lambda'} c_{f\lambda\sigma_1}^{+} c_{f\lambda\sigma_3} c_{g\lambda'\sigma_2}^{+} c_{g\lambda'\sigma_4}$$

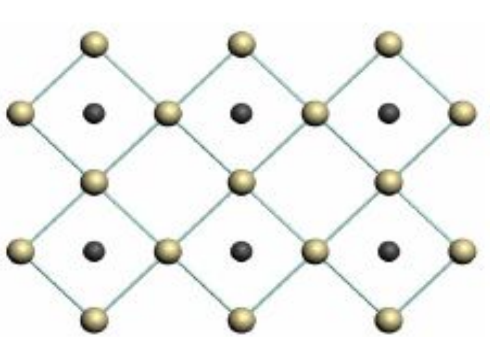
$$H = H_0 + H_1.$$

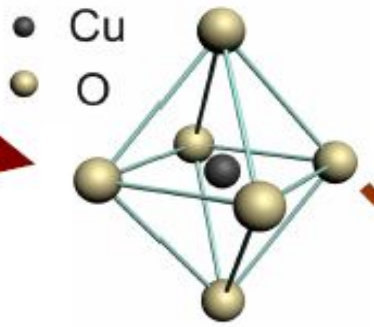
$$H_0 = \sum_i H_c(i), \qquad H_1 = \sum_{i,j} H_{cc}(i,j).$$

Cluster perturbation theory: Synthesis of local quasiparticles exact treatment and Hubbard perturbation from the atomic limit

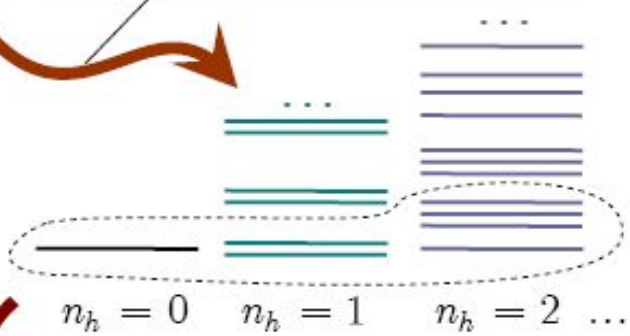
Generalized tight binding method as a perturbative realization of Lehmann view

The GTB method consists of 3 steps:





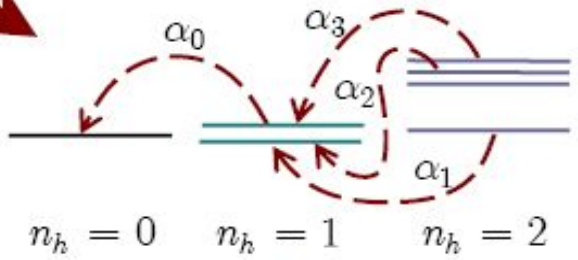
I. Exact diagonalization of $H_c(i) \rightarrow |p\rangle = |m, n_h\rangle,\ \varepsilon_p$

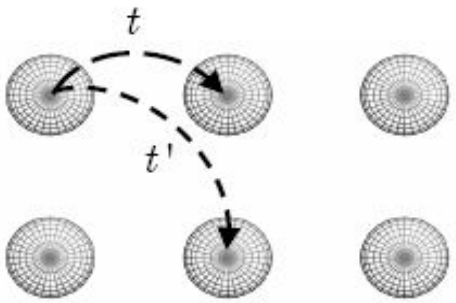


II. The intracell X-operators are constructed:

$$X_f^n \leftrightarrow X_f^{p,q} \equiv |p\rangle\langle q| = |m, n_h\rangle\langle m', n_h'|$$

$$a_{f\lambda\sigma} = \sum_n \gamma_{\lambda\sigma}(n) X_f^n$$





III. Hamiltonian in the X-representation:

$$H = \sum_{f,p} (\varepsilon_p - N\mu) X_f^{pp} + \sum_{f \neq g} \sum_{n,n'} t_{fg}^{nn'} X_f^{n\dagger} X_g^{n'}$$

Dyson equation in the X-method

Val'kov, Ovchinnikov 2001

$$a_{k\lambda} = \sum_m \gamma_\lambda(m) X_k^m \qquad X_k^m \equiv X_k^{p,q}$$

Single-electron GF: $$G_{\lambda\lambda'}(k,\omega_n) = \sum_{m,m'} \gamma_\lambda(m)\,\gamma_{\lambda'}(m')\,D^{mm'}(k,\omega_n)$$

$$D^{mm'}(k,\omega_n) = \left\langle\left\langle X_k^m \middle| X_k^{m'}\right\rangle\right\rangle_{\omega_n}$$

Dyson equation:

$$\hat{D}(k,\omega_n) = \left[\hat{G}_0^{-1}(\omega_n) - \hat{P}(k,\omega_n)\,t_k + \hat{\Sigma}(k,\omega_n)\right]^{-1}\hat{P}(k,\omega_n)$$

local propagator

hopping

self-energy

strength operator

Strength operator $\hat{P}(k,\omega_n)$ results from X-operators algebra
(similar to spin algebra → Baryakhtar, Yablonsky, Krivoruchko, 1983)
Renormalization of the spectral weight (oscillator strength) due to $\hat{P}(k,\omega_n)$

"Hubbard I" approximation:

$$\hat{\Sigma} = 0, \quad P^{mm'} \to F(m)\,\delta_{mm'}, \quad G_0^{mm'}(\omega_n) = \delta_{mm'} / \left\{i\omega_n - \left(\varepsilon_p - \varepsilon_q\right)\right\},$$

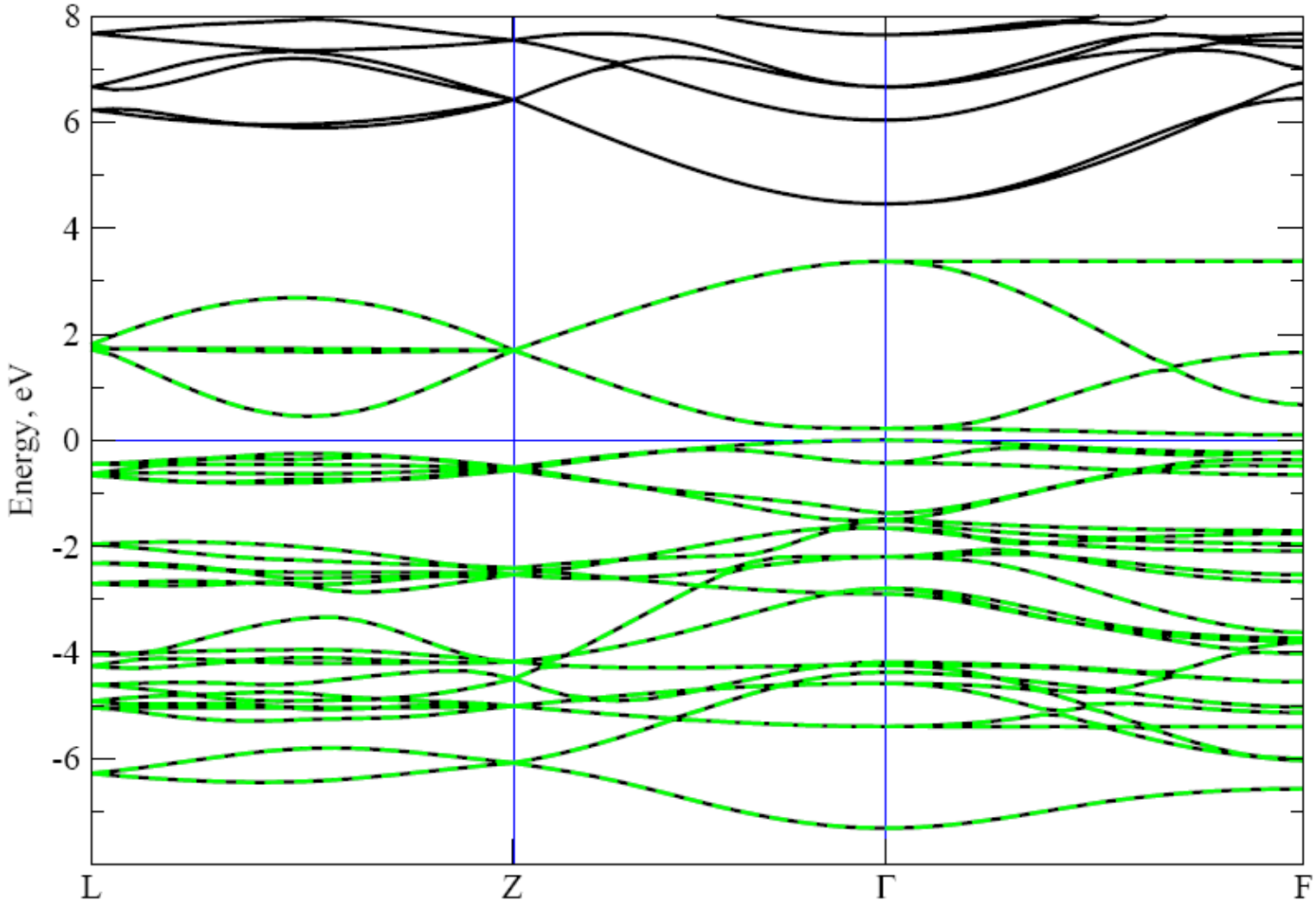
$$F(m) = \langle X^{pp}\rangle + \langle X^{qq}\rangle, \quad m = m(p,q)$$

Hybrid LDA+GTB scheme without fitting parameters

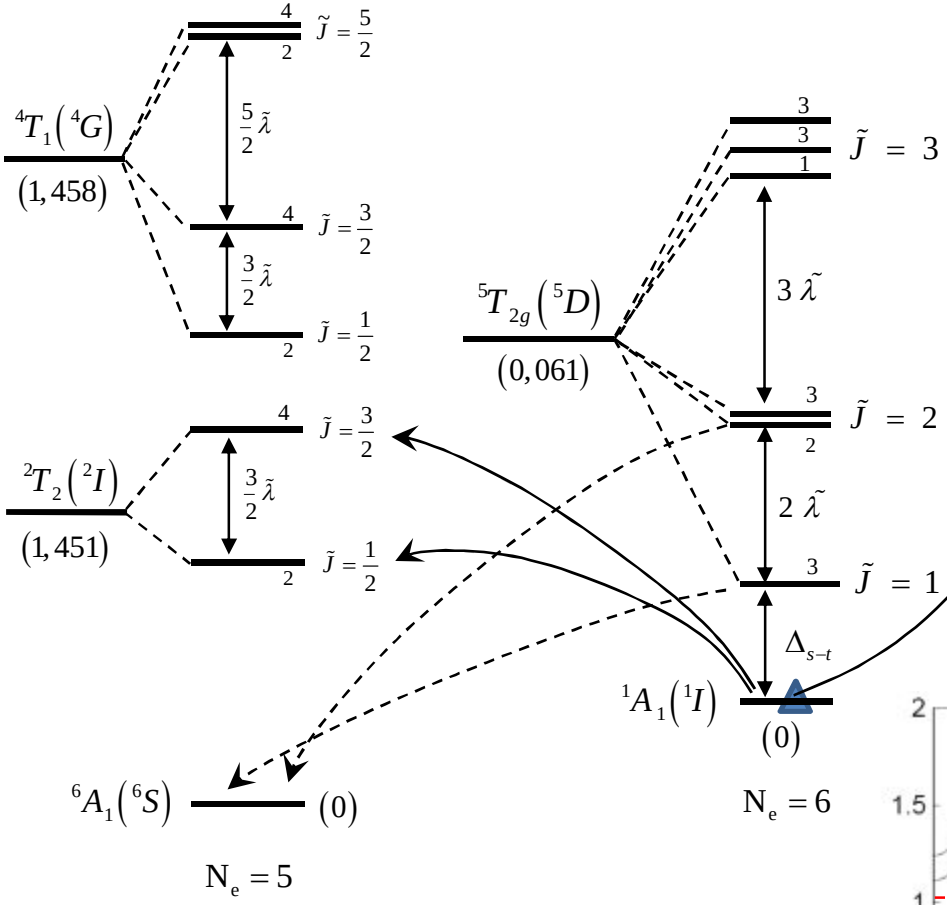
(in collaboration with prof.V.I.Anisimov group, Ekaterinburg, (Korshunov, Ovchinnikov, etal, Phys.Rev.B 2005))

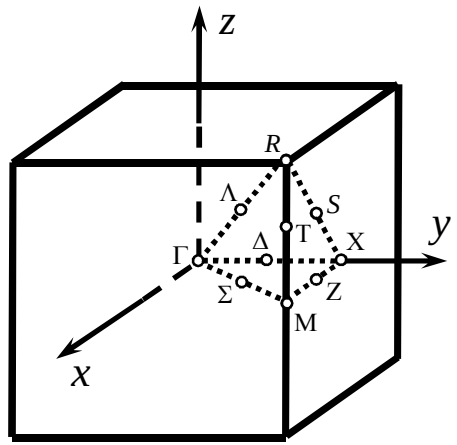
- Projection of LDA band structure and construction the Wannier functions for p-d –model
- *Ab initio* calculation of p-d –model parameters
- Quasiparticle band structure GTB calculations in the strongly correlated regime with *ab initio parameters*

LDA (black) and projected to d(Co)p(O) basis
LaCoO3 band structure (all 5 d and 3 p orbitals)
Orlov, Nekrasov, Pchelkina etal., JETP 2011

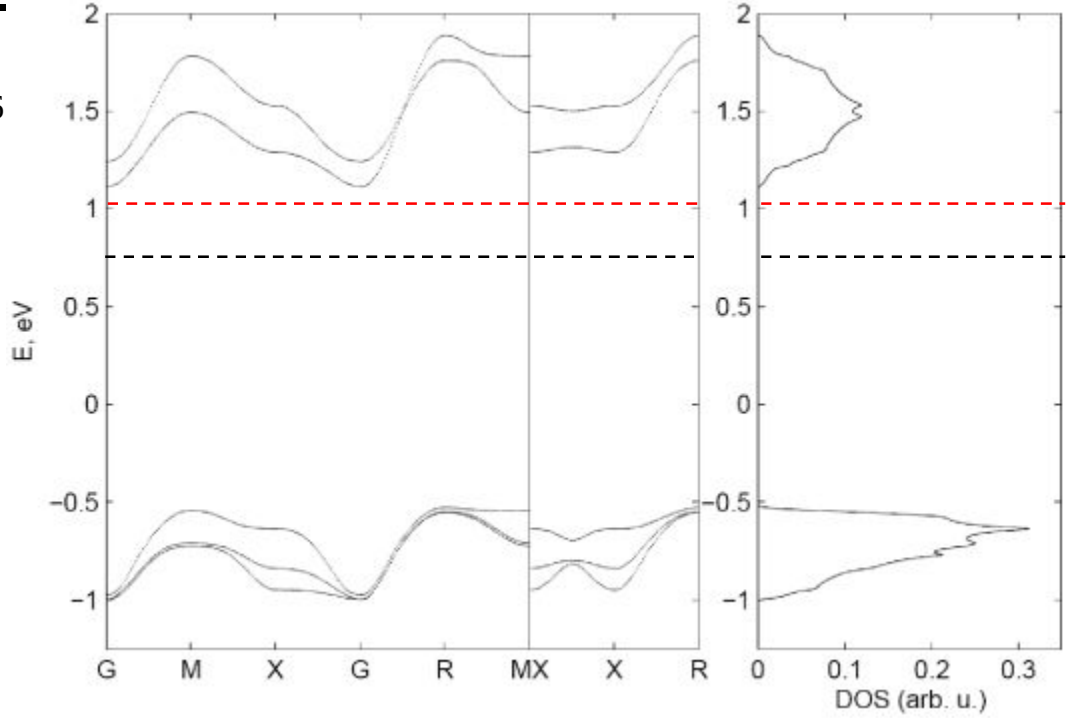


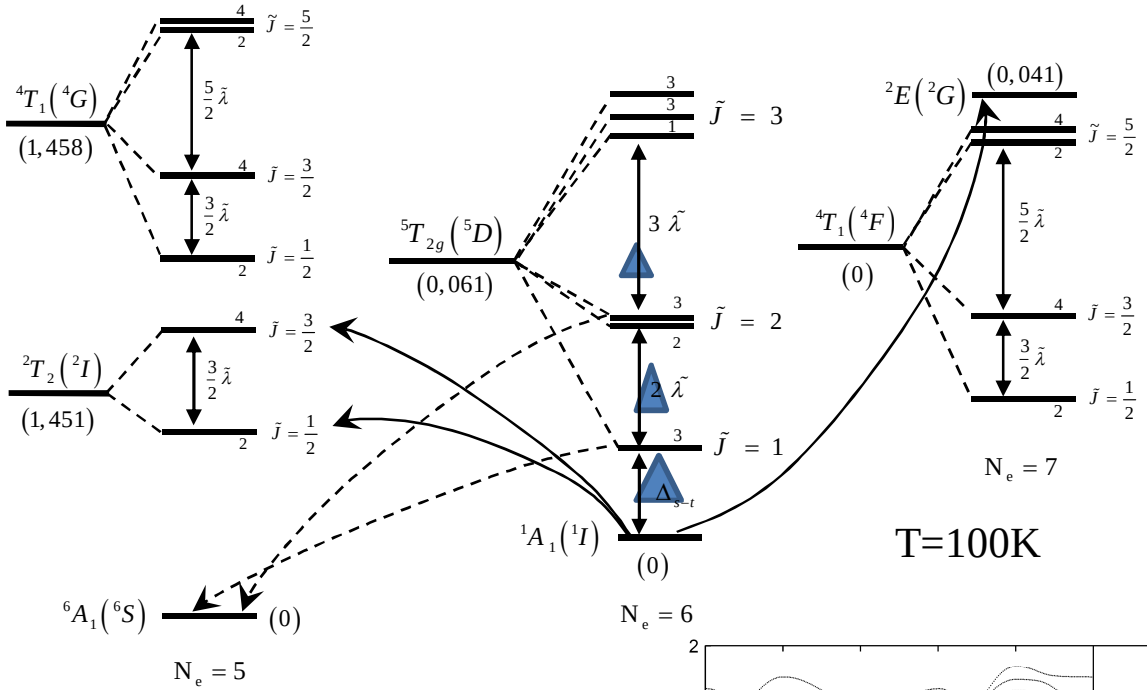
LaCoO3





Low energy terms for Co+3 and electron addition and removal configurations





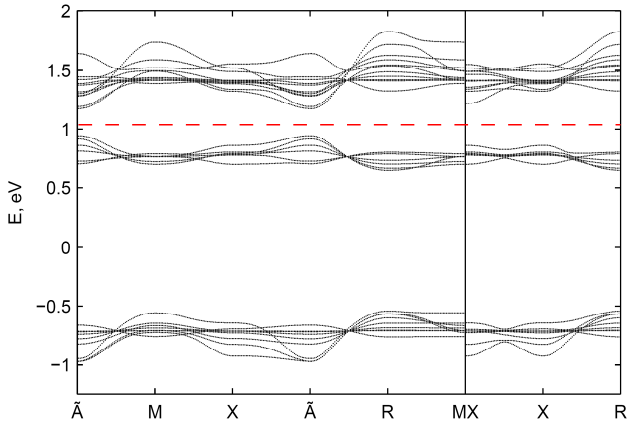
Ovchinnikov. Orlov
Nekrasov, Pchelkina
JETP 2011

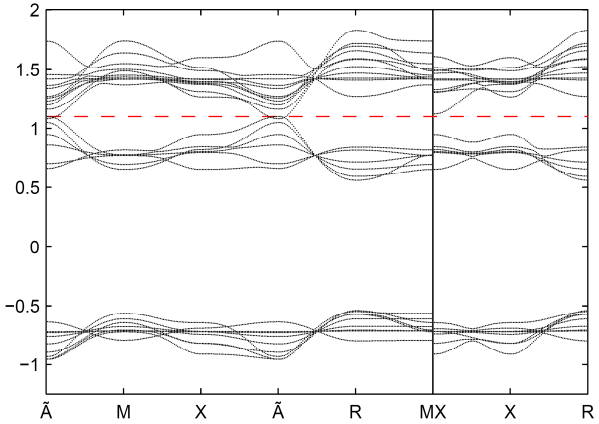
In-gap states result in gap decreasing and metallization at

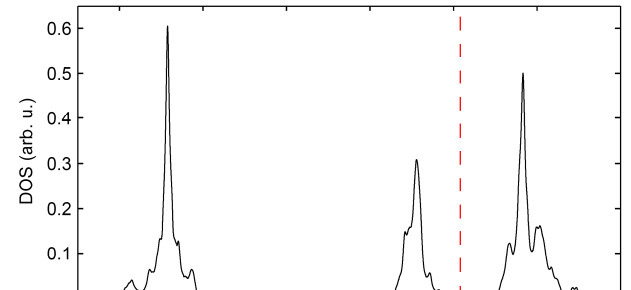
T(MIT)=585K

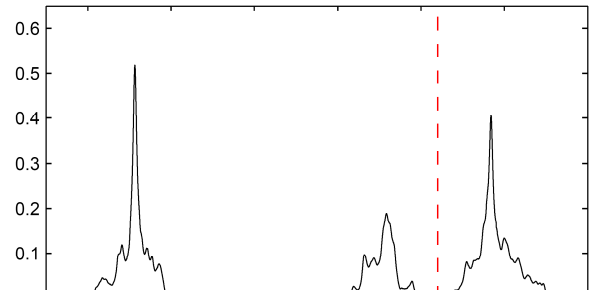
T=100K

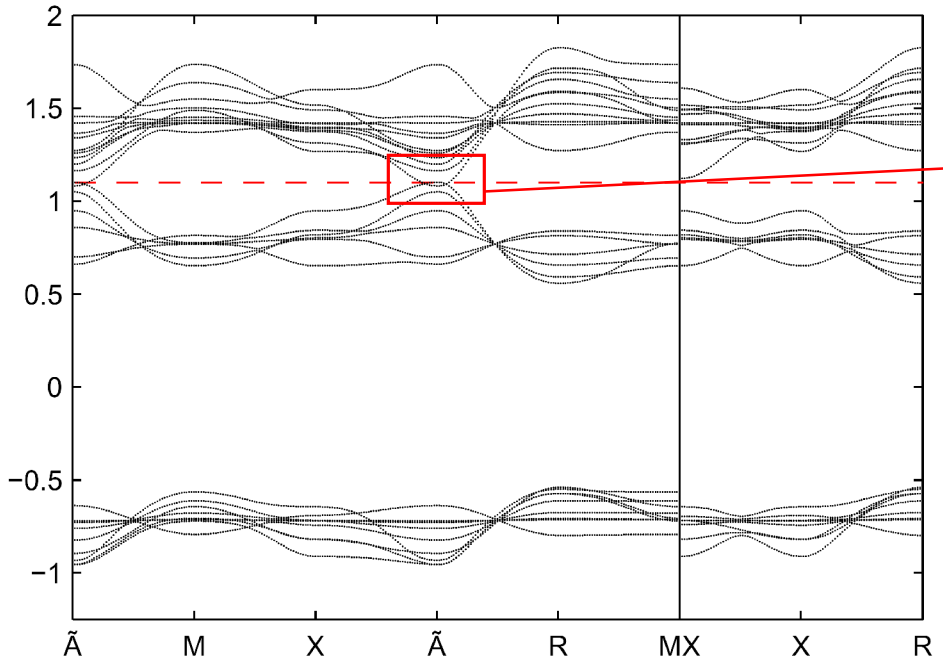
T=585K

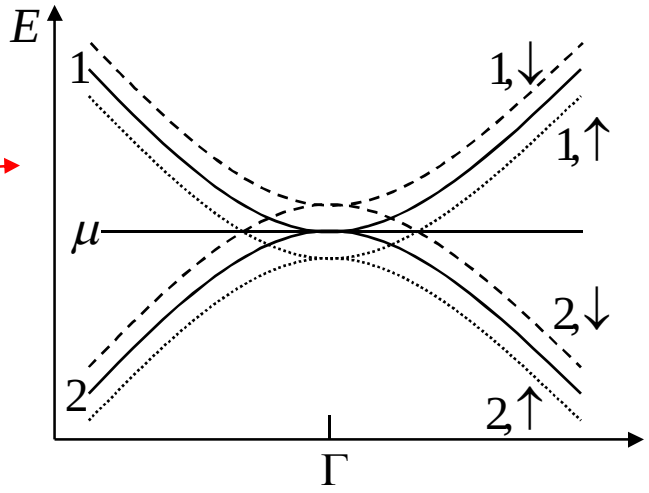






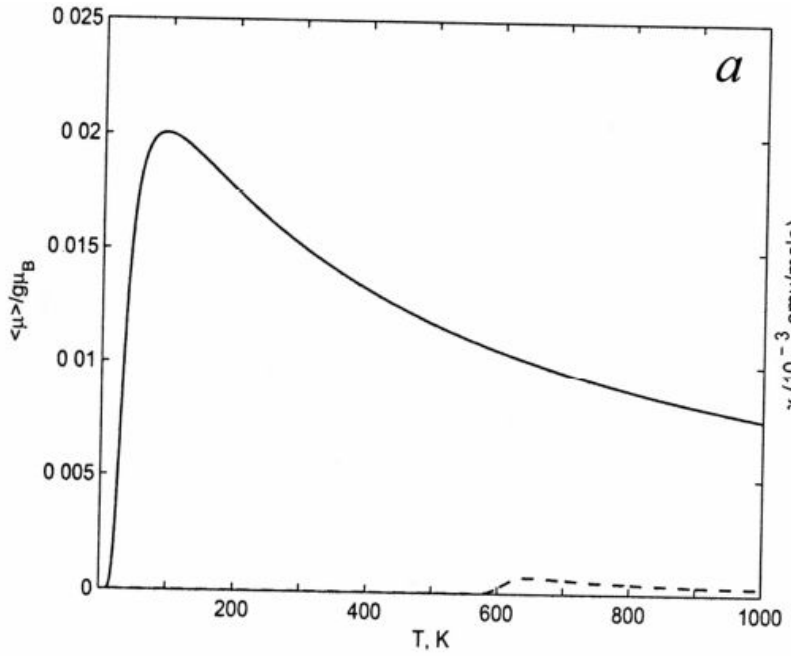


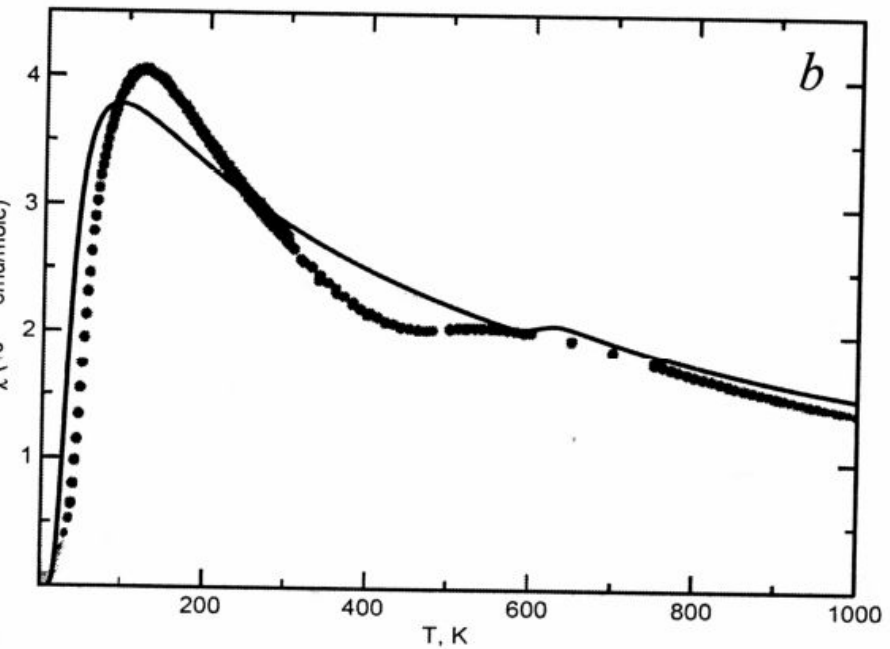


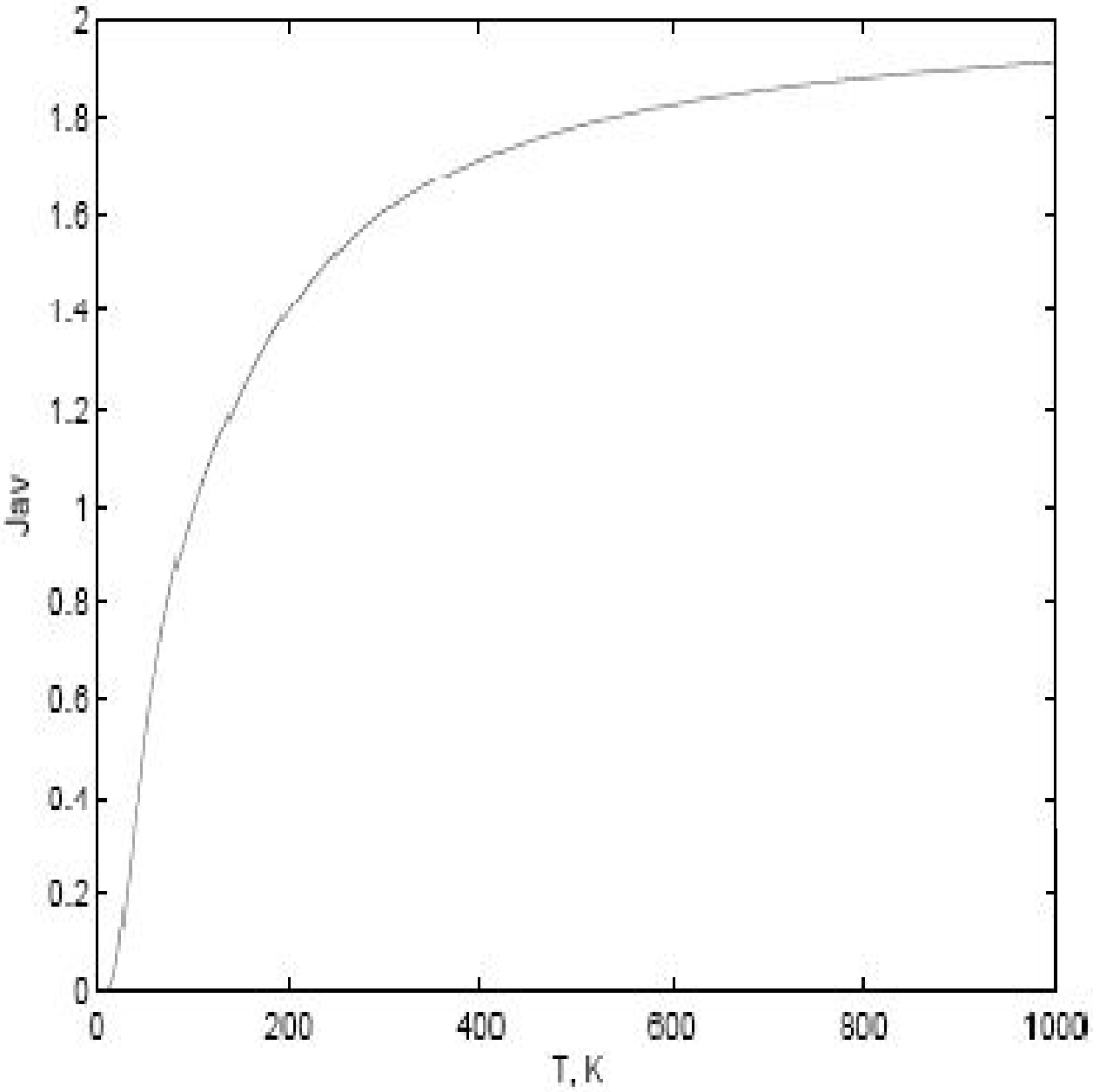


$$\varepsilon_k = \frac{\hbar^2}{2m^*}\left(k_x^2 + k_y^2 + k_z^2\right) = \frac{\hbar^2}{2m^*}k^2 \qquad m^* = 4.8\ m_e$$

$$\langle S_z \rangle = \frac{1}{2}\left\{n_{1\uparrow} - n_{1\downarrow} + n_{2\uparrow} - n_{2\downarrow}\right\}$$





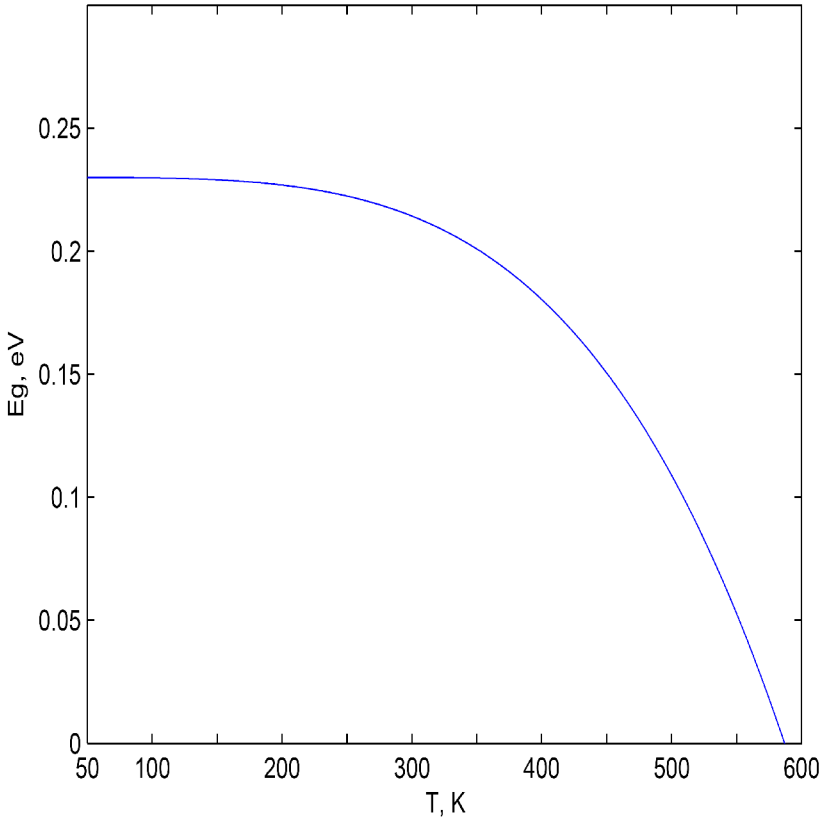


Temperature dependent magnetic moment of Co+3 in $LaCoO_3$

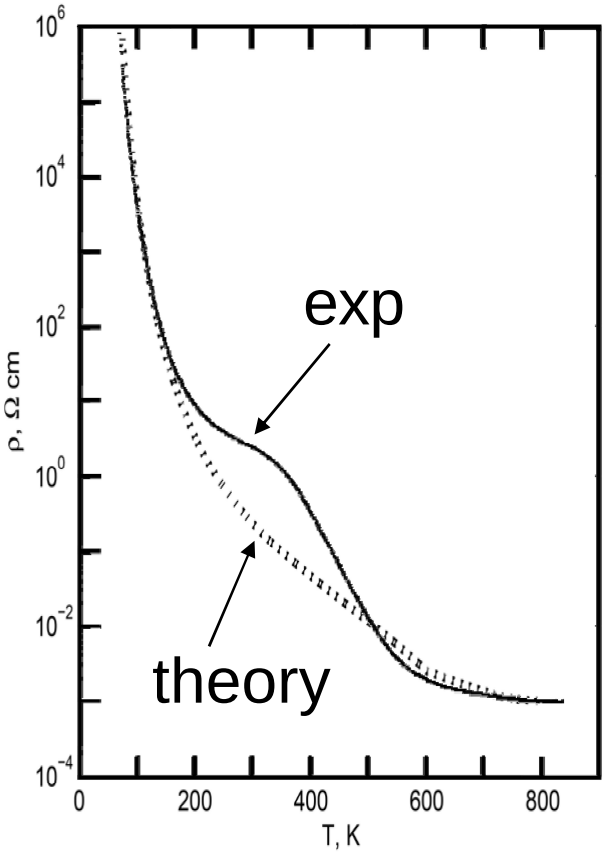
Close to 1

at 100-300K

Mean square root value $\hat{J}_{\text{av}} = \sqrt{\langle \hat{J}^2 \rangle}$

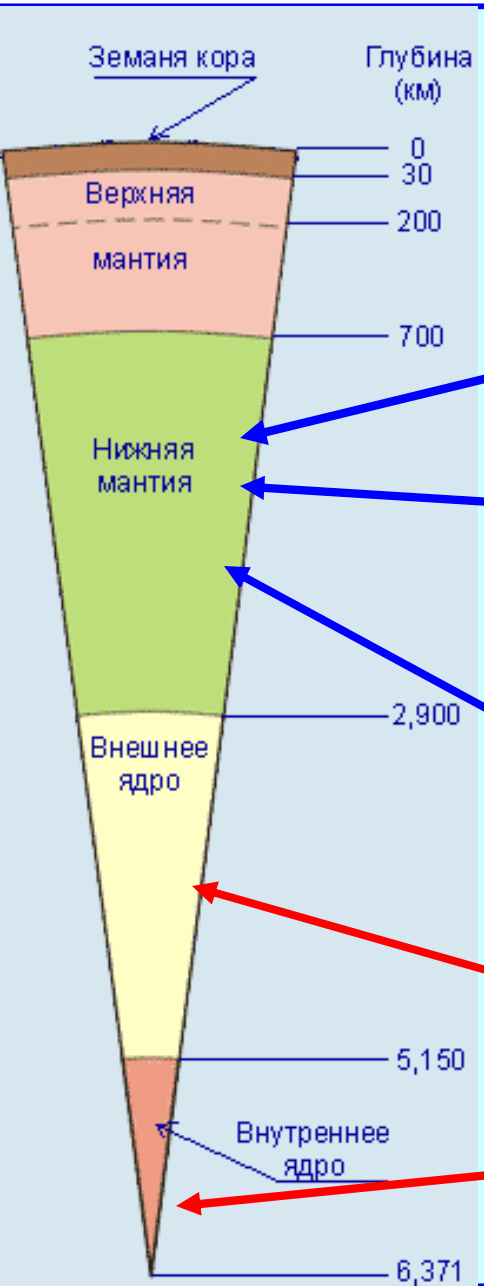


The activation energy vs T in LaCoO3



The resistivity from temperature dependent concentration

Electronic and magnetic properties of magneziowustite Mg1-xFexO at P-40-140GPa and T~2000K



$(Mg,Fe)SiO_3$ (~70 %)

(Mg, Fe)O (~20-30 %)

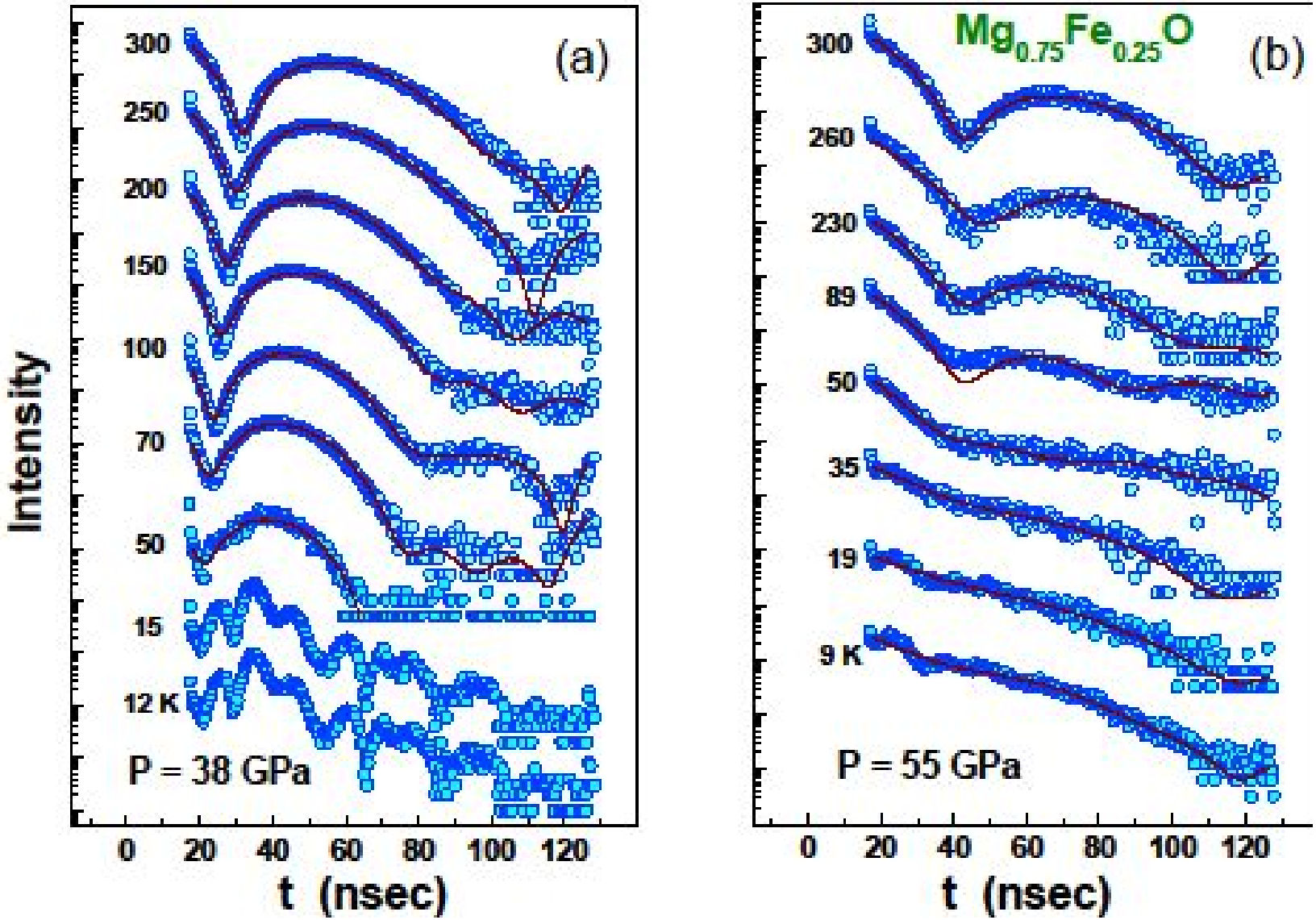
Oxides:
Ca, Na, K, Al, Fe (~10%)

FeO, NiO(~9%)

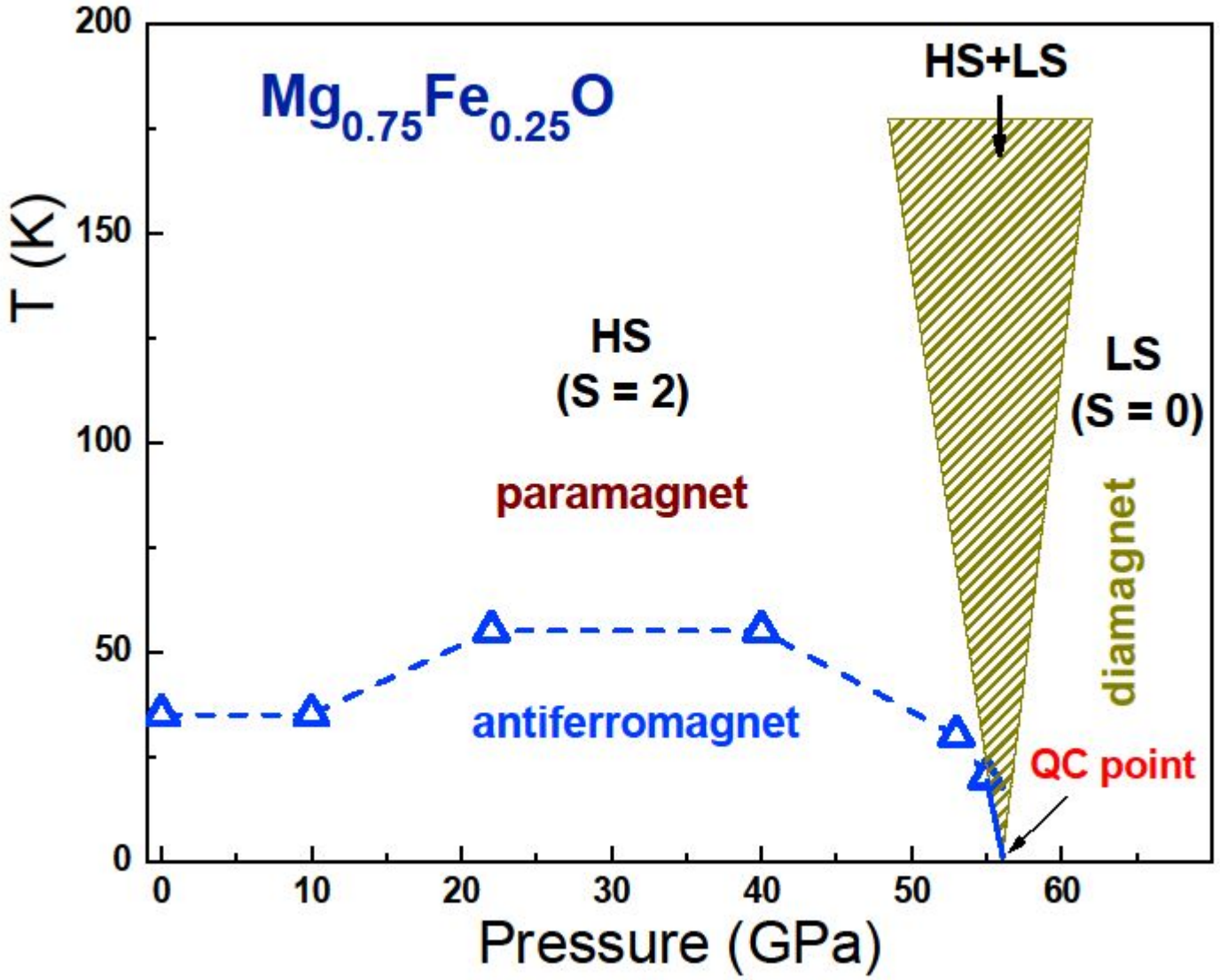
Fe, Ni(~9%)

1. Mg-silikate perovskite is insulator up to pressure 143GPa (K.Ohta etal, 2008).
2. Mg1-xFexO with fcc 3d lattice has percolation threshold 14.2% . Thus conductivity and magnetism at x>0.142 are determined by FeO.
3. 20% of magneziowustite in nonmagnetic nonconducting matrix in the low Earth mantle is above the percolation threshold. Metallic MW will result in conducting mantle.
4. Mott-Hubbard insulator-metal transition under high pressure is expected due to bandwidth increase. LDA+DMFT calculations have revealed metal FeO at P=60GPa (Shorikov, Pchelkina, Anisimov etal. PRB 2010). Not confirmed experimentally.
5. Alternative transition is high spin-low spin crossover due to the crystal field increase under high pressure

Low-temperature synchrotron Mössbauer spectra of $(Mg_{0.75},Fe_{0.25})O$ at 38 GPa (a) and 55 GPa (b). High-frequency quantum beats indicate a magnetic ordering of Fe^{2+} ions in the HS state, whereas the low-frequency quantum beats indicate the paramagnetic state of Fe^{2+} ions in the HS state. Absence of the quantum beats indicates the occurrence of the diamagnetic state of the LS Fe^{2+} ion



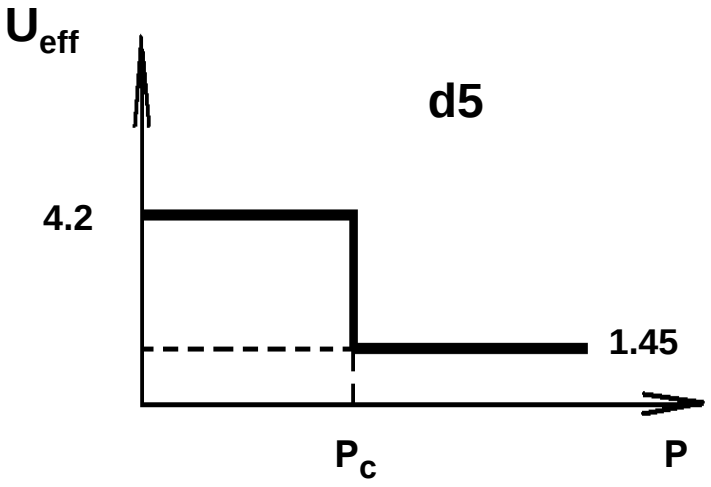
Experimental phase diagram (Lyubutin,Struzhkin etal., arxiv 2011)

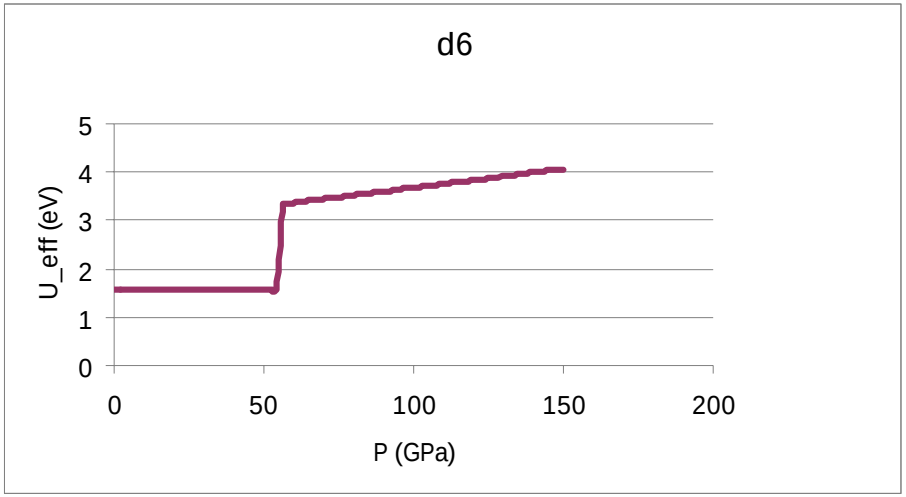


Effect of spin crossover on the effective Hubbard U

(S.G.Ovchinnikov, JETP 2008)

Ueff (dn) = E0(n+1) +E0(n-1) -2E0(n)





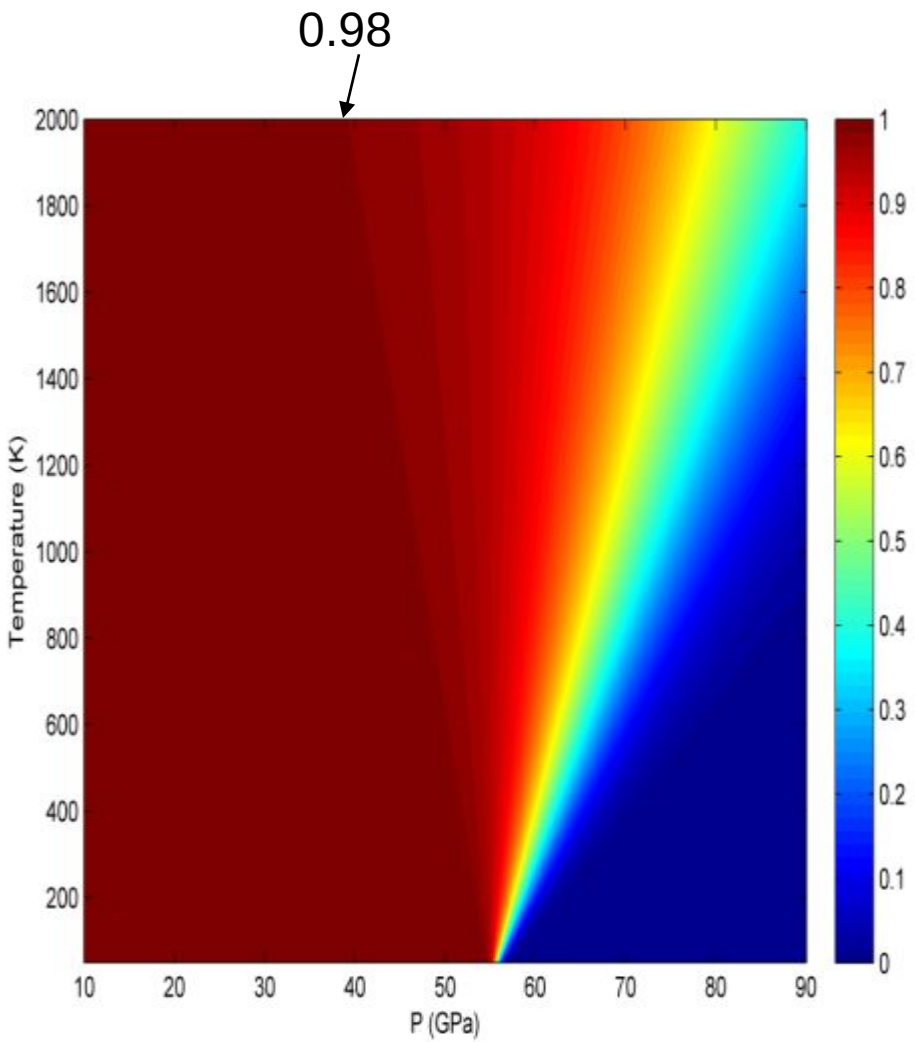
Effect of multiplet degeneracy of HS and LS Fe(+2) on the phase diagram

$$Fe^{2+}(d^6): \quad HS, \quad S=2, \quad L=1 \quad g_{HS}=(2S+1)(2L+1)=15$$
$$LS, \quad S=0, \quad L=0 \quad g_{LS}=1$$

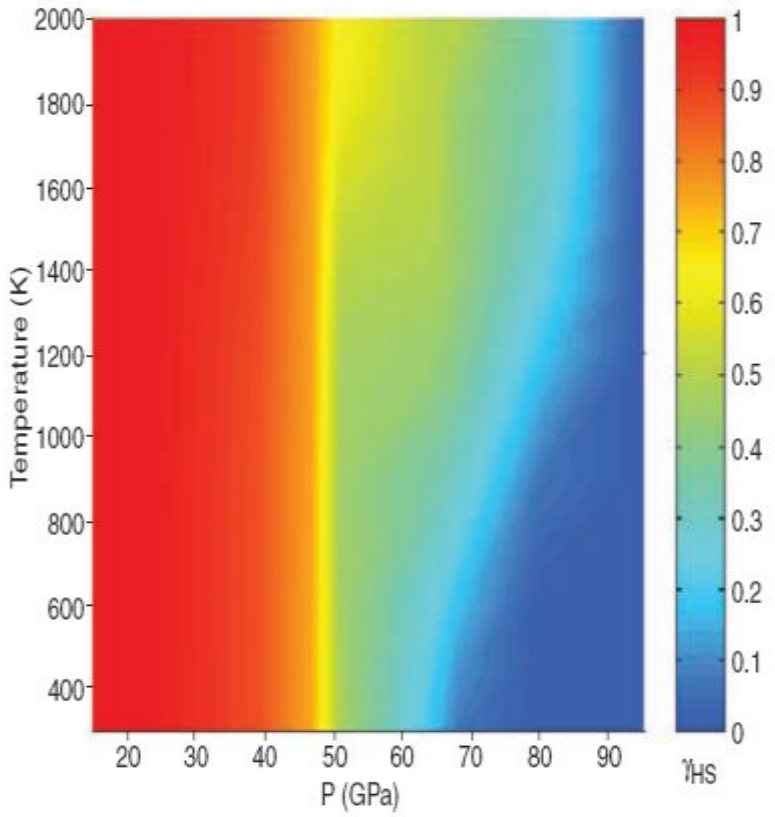
Partitition function $$Z = g_{HS} e^{-E_{HS}/kT} + g_{LS} e^{-E_{LS}/kT}$$

HS fraction $$n_{HS}(P,T) = \frac{1}{1+\frac{g_{LS}}{g_{HS}}\exp\left(\frac{E_{HS}-E_{LS}}{kT}\right)}$$

Сравнение расчета и эксперимента



Calculations (sgo 2011)

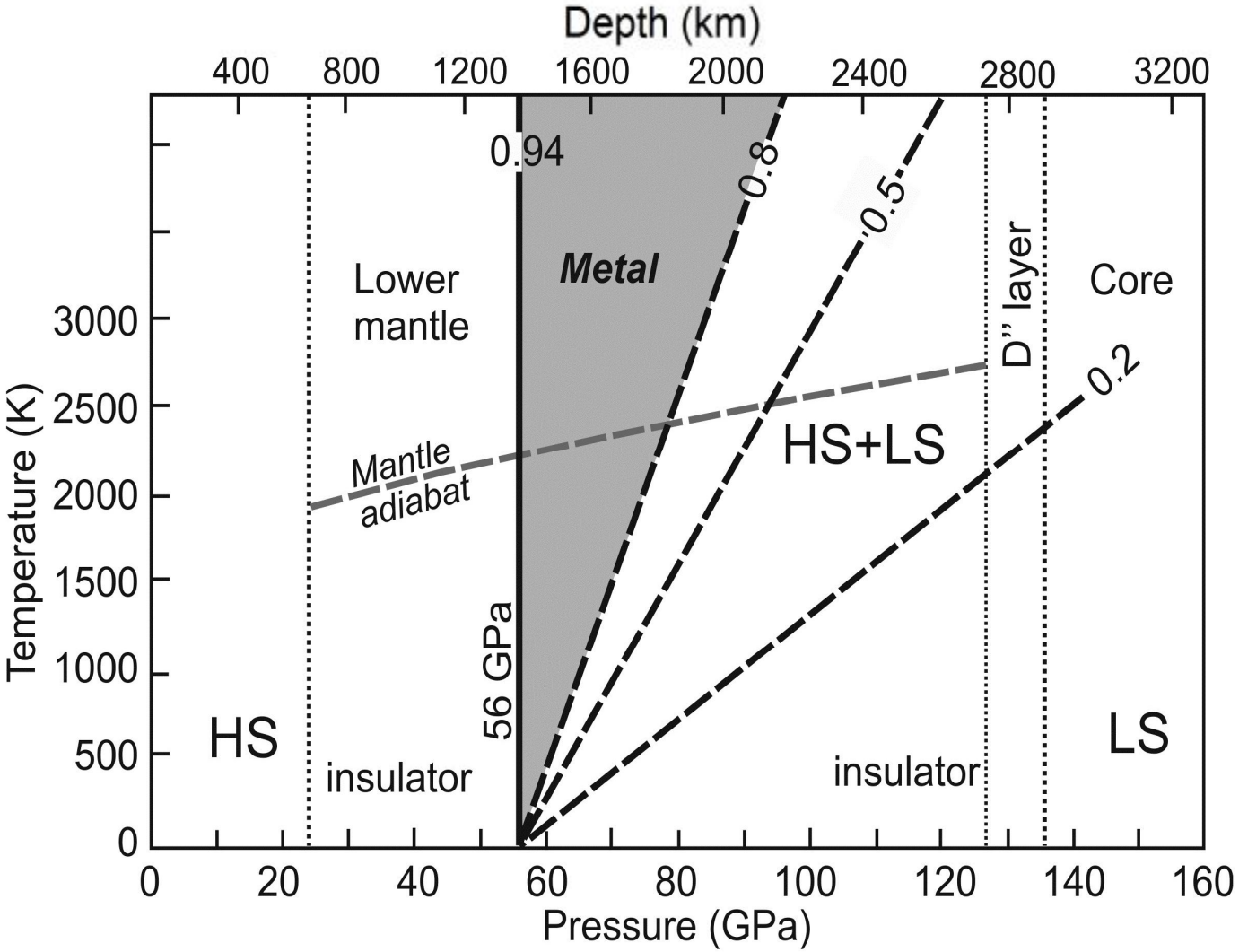


XES with laser heating

(Lin etal, Science 2007)

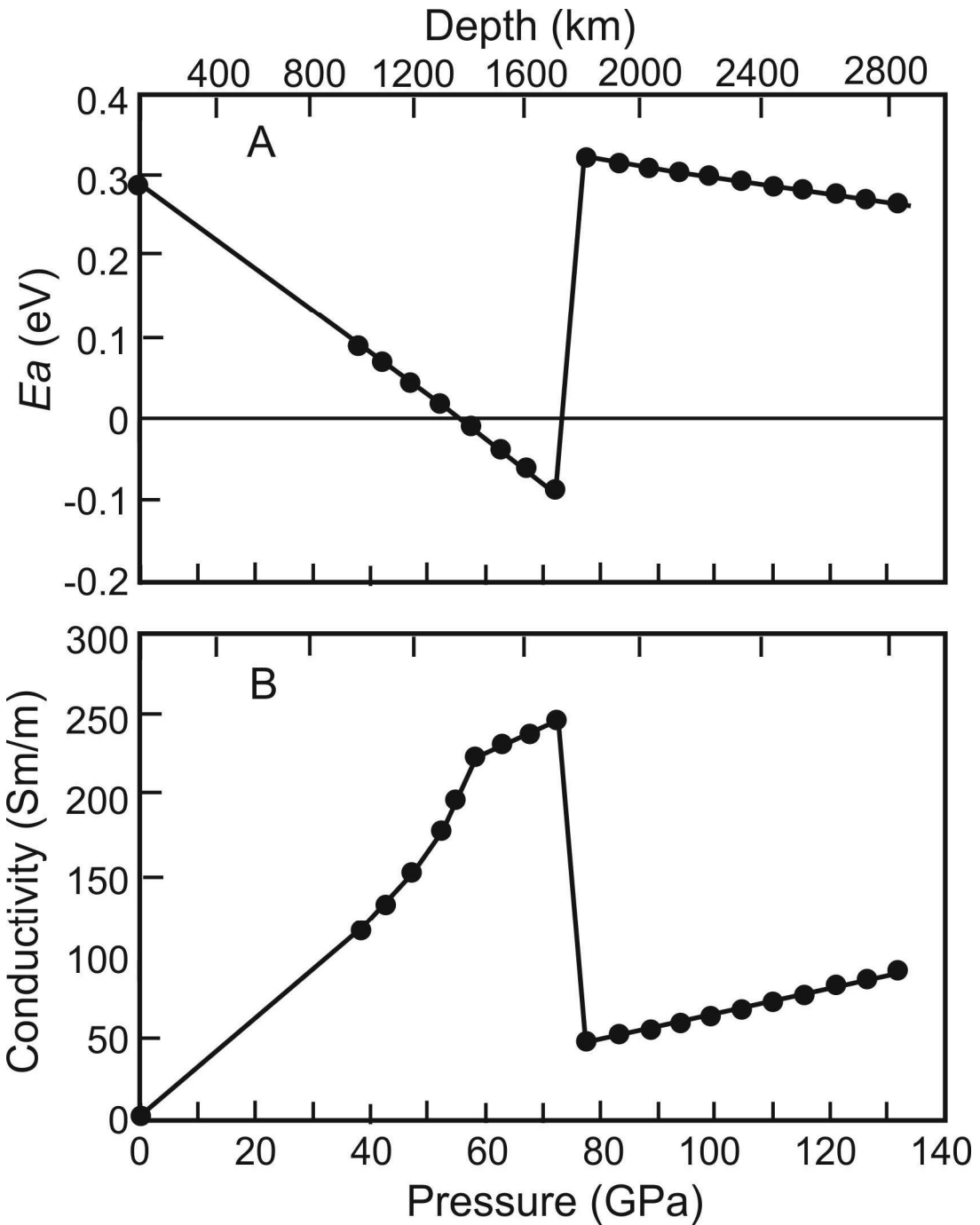
MW phase diagram at high temperature and pressure

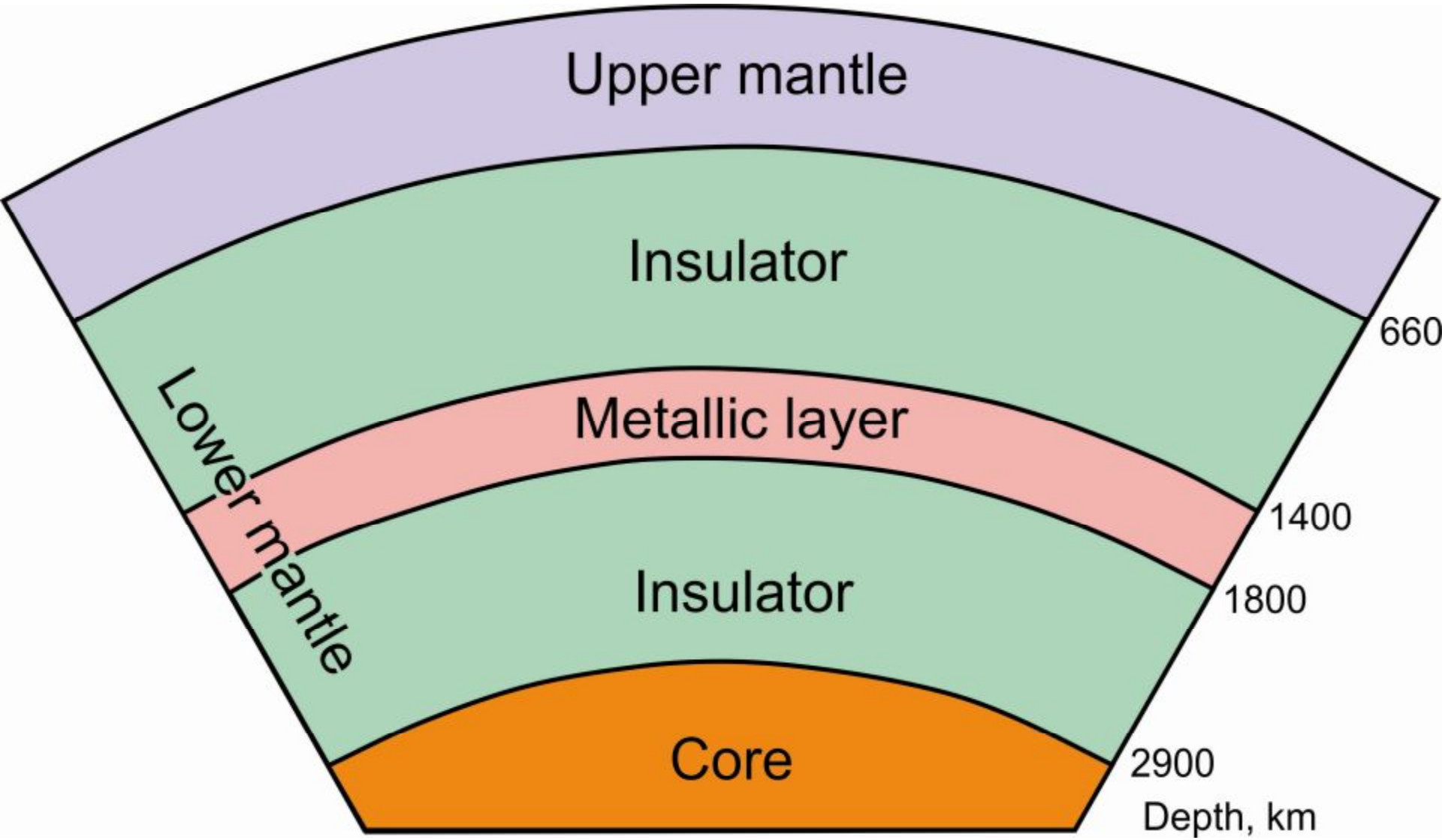
(Ovchinnikov, JETP Lett. 2011)



Energy gap and conductivity vs pressure and depth.

Experimental estimation for conductivity from the geophysical satellite data (Constable etal 2004): Jump of conductivity to 200 S/m at the depth of 1300 km




Upper mantle
Insulator
660
Lower mantle
Metallic layer
1400
Insulator
1800
Core
2900
Depth, km

Conclusions

- Electronic structure of Mott insulator with singlet ground term and small spin gap is strongly temperature dependent with smooth metallization at high temperature
- For magnesiowustite a metal state is predicted at the Earth's mantle conditions T~ 2000-2500 K and pressure 60-80 ГПа resulting in 400 km metal belt at the depth 1400-1800 km

$\mathcal{C}$ of integration is chosen as $\theta = \text{const}$. Then the geometric phase related to the ground state is

$$\gamma = \pi(1 - \cos\theta) = \pi\left(1 - \frac{\varepsilon}{\sqrt{\varepsilon^2 + \rho^2}}\right). \qquad (16)$$

The lost of analyticity occurs at the diabolic point located at the origin of the parameter space $(\Re\lambda, \Im\lambda, \varepsilon)$. In vicinity of the diabolic point the geometric phase behaves as a step function

$$\gamma = \begin{cases} 0, \text{ for } \rho = 0,\ \varepsilon \to +0\ (\theta \to 0) \\ 2\pi, \text{ for } \rho = 0,\ \varepsilon \to -0\ (\theta \to \pi) \end{cases} \qquad (17)$$

Geometric phase is the order parameter, its change is 2pi in the QPT

Spin crossover is a quantum phase transition at T=0 (Nesterov, Ovchinnikov, arXiv 0907.1310, JETP Lett.90, 580 (2009)

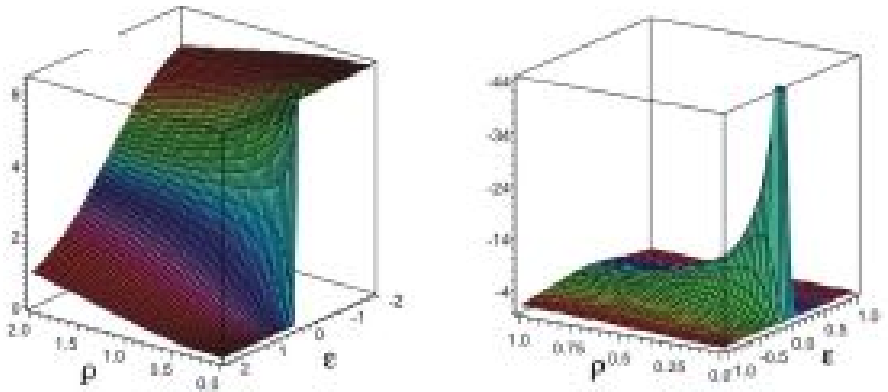


Fig. 2. Geometric phase γ (left) and its derivative $\partial\gamma/\partial\varepsilon$ (right) as a function of the Hamiltonian parameters ρ and ε. There is clear step-function behavior at