Temperature and field dependent electronic structure and magnetic properties of LnCoO3 (La,Gd)

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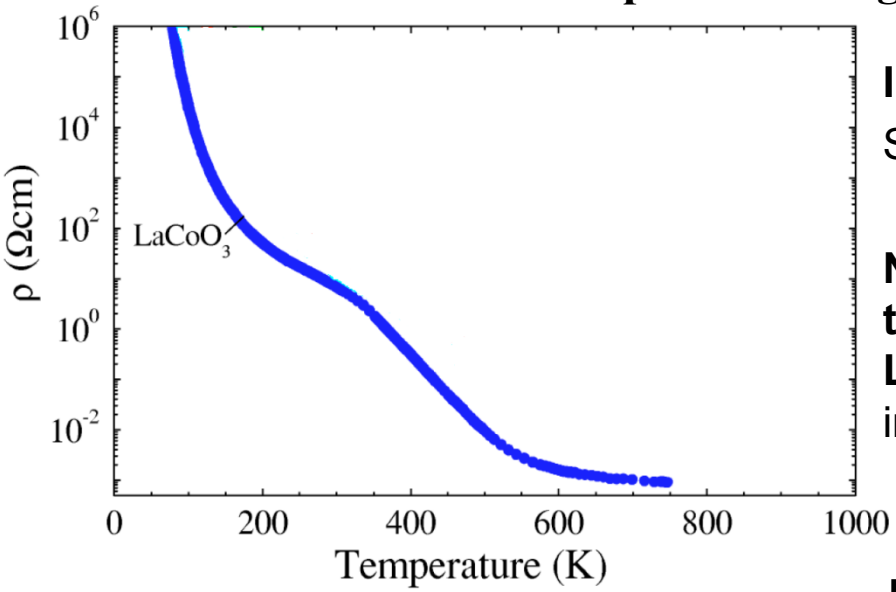
ES&ES Kiev May 2013

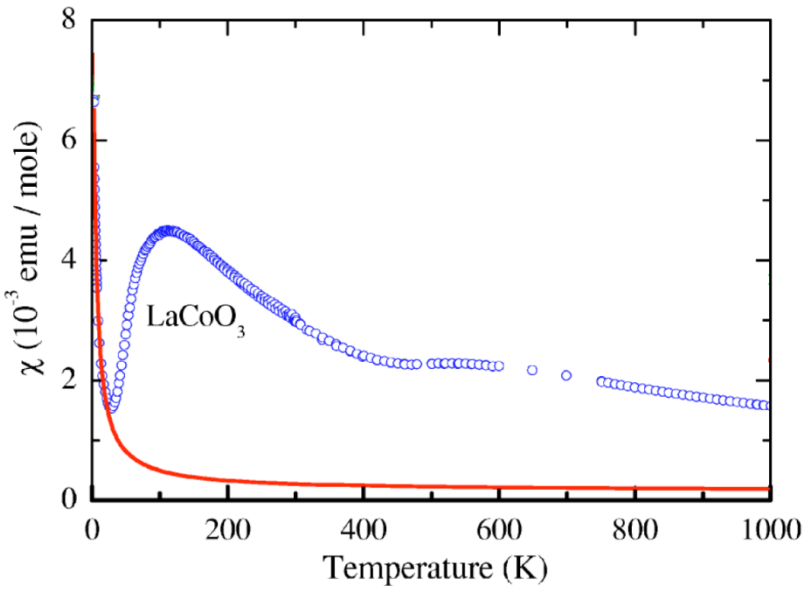
Transport and magnetic properties of $LaCoO_3$



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



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

-**J.B. Goodenough 1958r. 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

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))

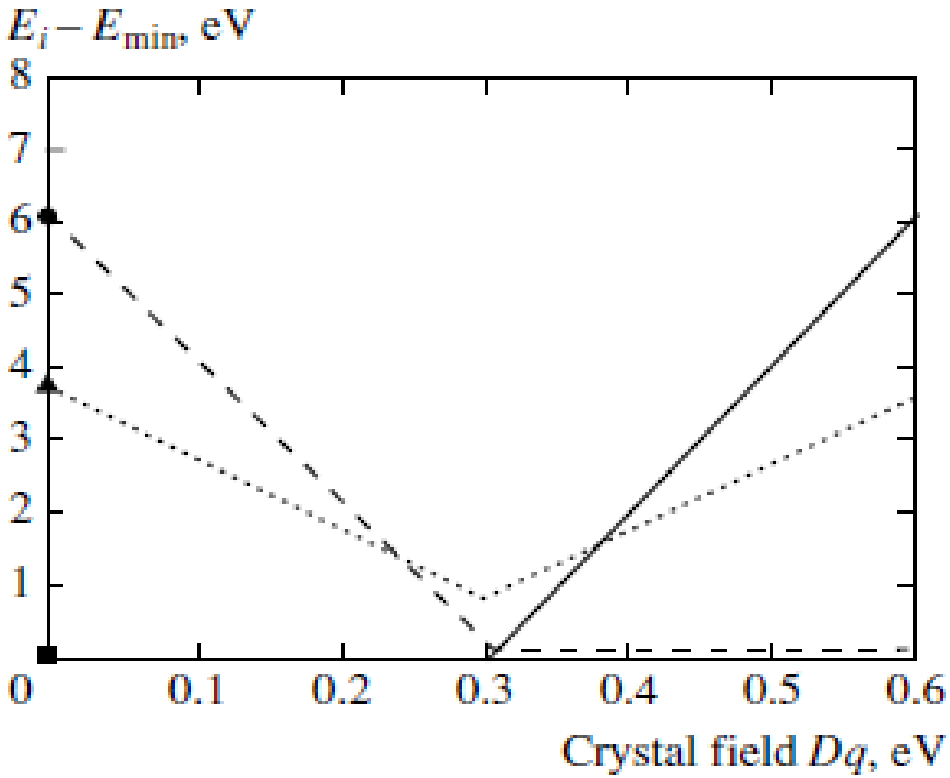


Fig. 1. Tanabe–Sugano diagram for the cobalt ion in a cubic crystal field. The solid line marked by a square stands for the HS state; the dotted line with a triangle, for the IS state; and dashed line with a circle, for the LS state. The calculations were carried out at $U_d = 4$ eV and $V_d = 2.48$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

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

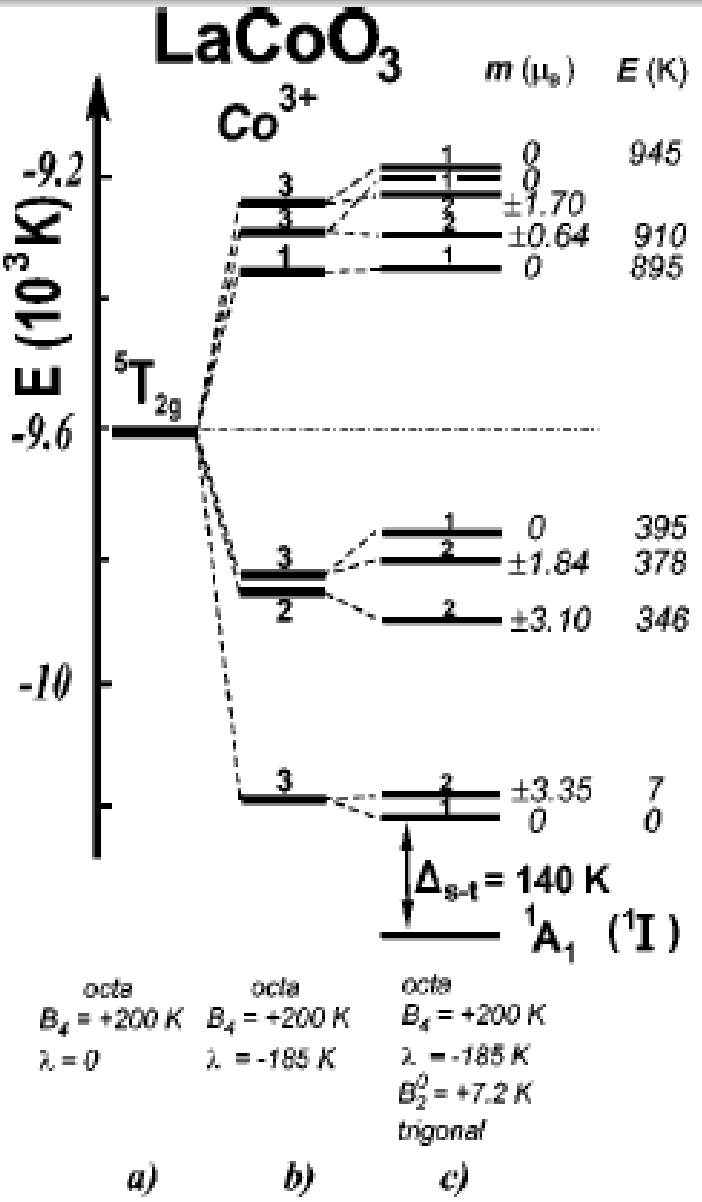


FIG. 6. Calculated low-energy electronic structure of the Co^{3+} ion in $LaCoO_3$ originating from the $^5T_{2g}$ cubic subterm with the $^1A_1$ singlet ground subterm put 140 K below the lowest $^5T_{2g}$ state.

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

LEHMANN REPRESENTATION: electron in strong correlated system as a superposition of Hubbard-type quasiparticles

Single electron GF $G_\sigma = \left\langle\left\langle a_{k\sigma} \middle| a_{k\sigma}^{+} \right\rangle\right\rangle_\omega$ **can be written as**

$$G_\sigma(k,\omega) = \sum_m \left(\frac{A_m(k,\omega)}{\omega - \Omega_m^{+}} + \frac{B_m(k,\omega)}{\omega - \Omega_m^{-}} \right) \qquad (1)$$

where the QP energies are given by

$$\Omega_m^{+} = E_m(N+1) - E_0(N) - \mu, \qquad \Omega_m^{-} = E_0(N) - E_m(N-1) - \mu,$$

and the QP spectral weight is equal to

$$A_m(k,\omega) = \left| \langle 0, N \middle| a_{k\sigma} \middle| m, N+1 \rangle \right|^2, \qquad B_m(k,\omega) = \left| \langle m, N-1 \middle| a_{k\sigma} \middle| 0, N \rangle \right|^2.$$

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Review of the Generalized Tight-Binding (GTB) method

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

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

$$H = H_0 + H_1.$$

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

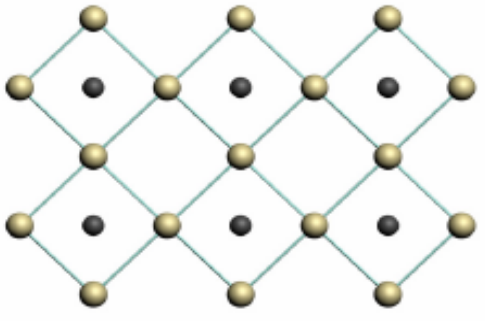
Cluster perturbation theory:

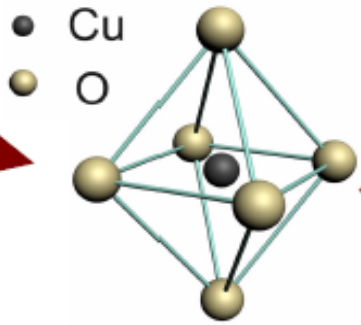
Synthesis of local quasiparticles exact treatment and

Hubbard perturbation from the atomic limit

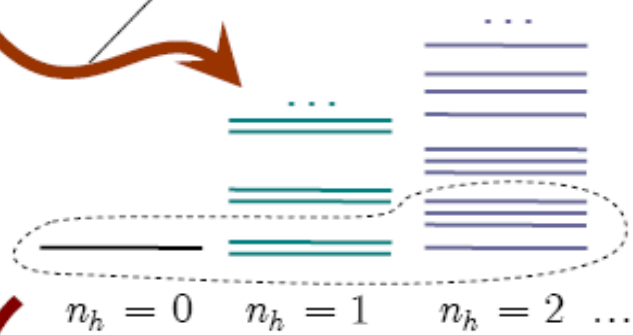
Generalized tight binding method as a perturbative realization of Lehmann view

The GTB method consists of 3 steps:





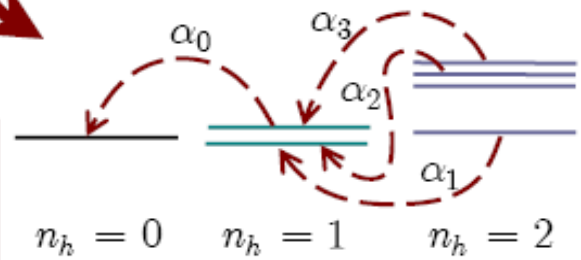
I. Exact diagonalization of $H_c(i) \rightarrow |p\rangle = |m, n_h\rangle,\ \varepsilon_p$

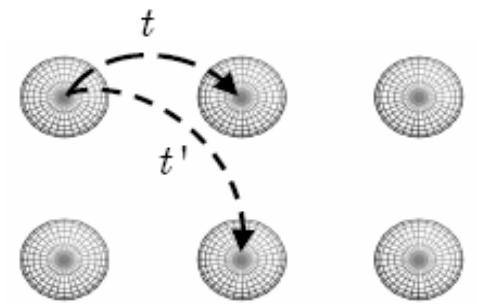


II. The intracell X-operators are constructed:

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

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





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:

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

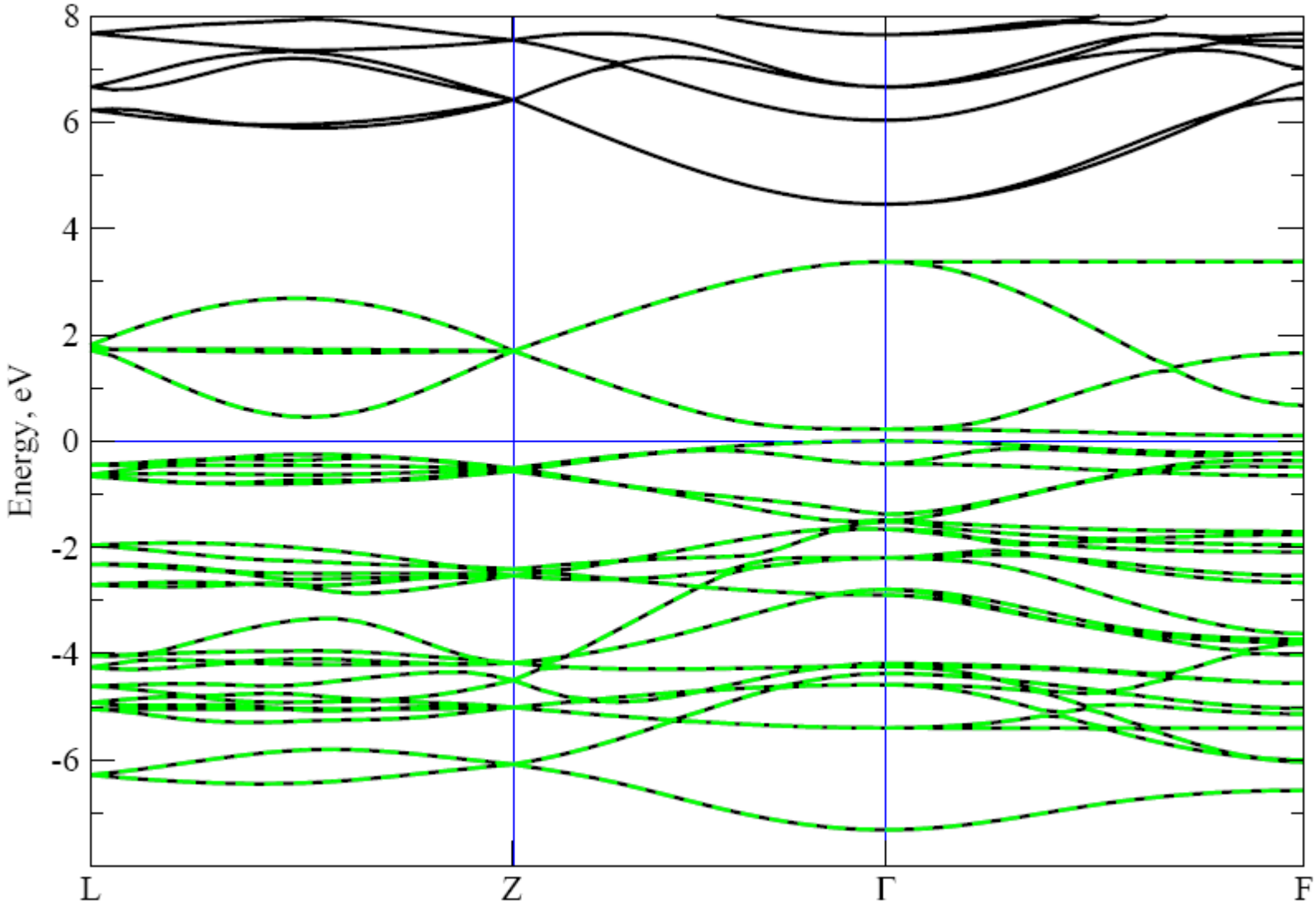
$$F(m) = \left\langle X^{pp}\right\rangle + \left\langle X^{qq}\right\rangle, \quad m = m(p,q)$$

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)

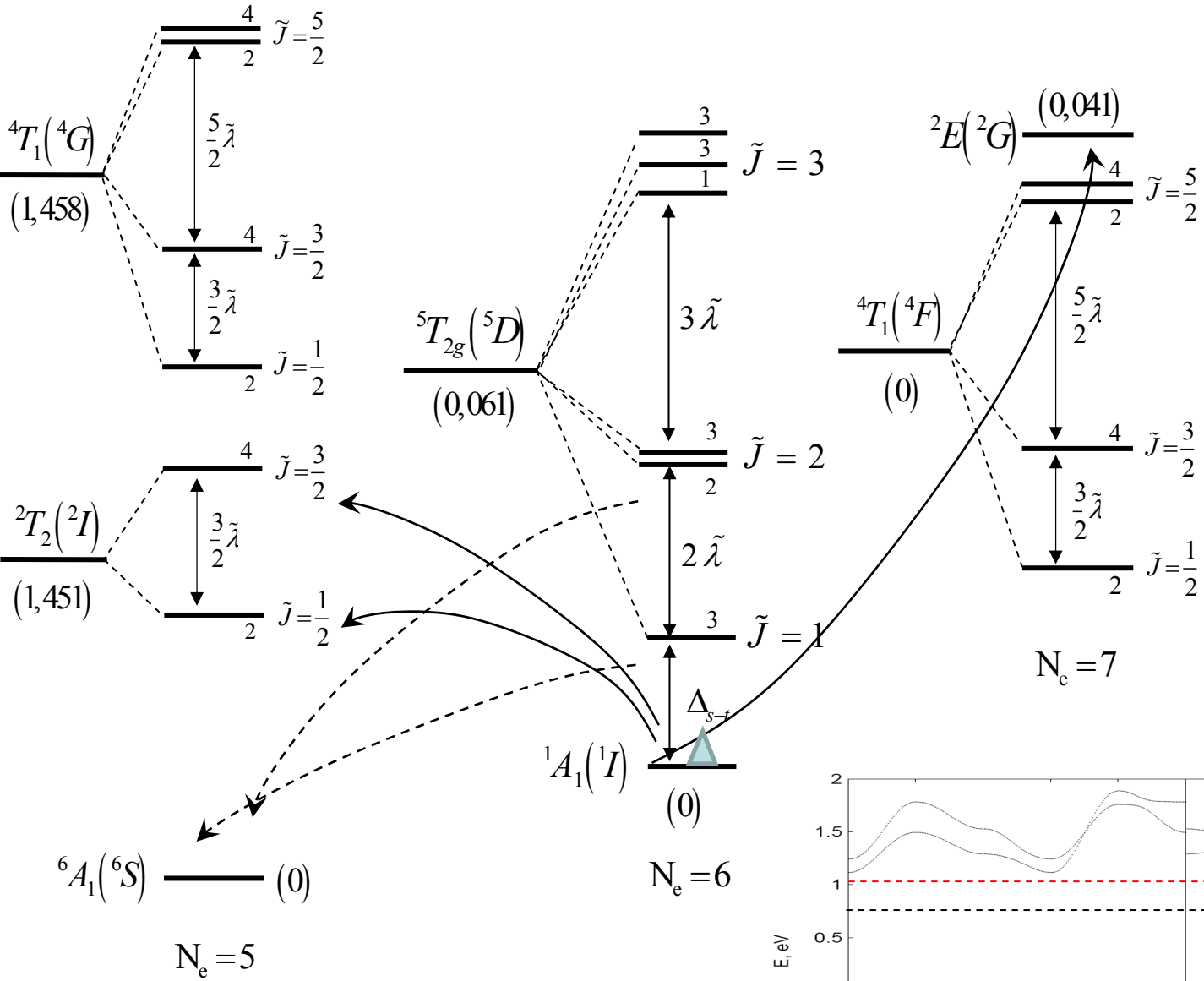


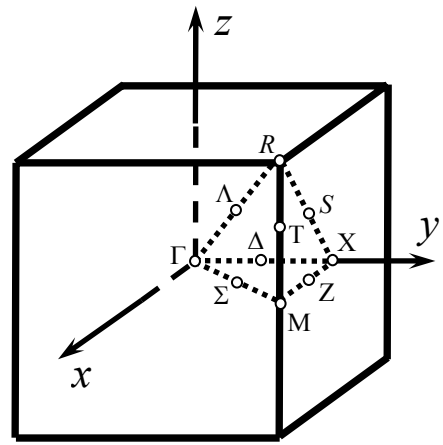
Exact diagonalization of MeO6 cluster

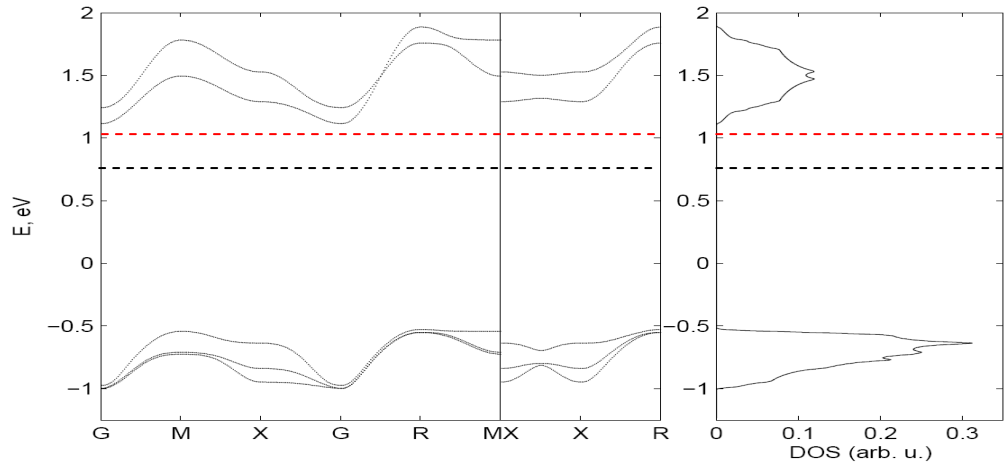
- For ionic bonding (d^n ion in a crystal field) the multielectron states have been found by Tanabe and Sugano in 1954
- For ionic +covalence bonding

$d^n \rightarrow d^n + d^{n+1}L$ (L is an ligand hole)

The exact diagonalization has been done by Orlov and Ovchinnikov, JETP 109, 322 (2009)

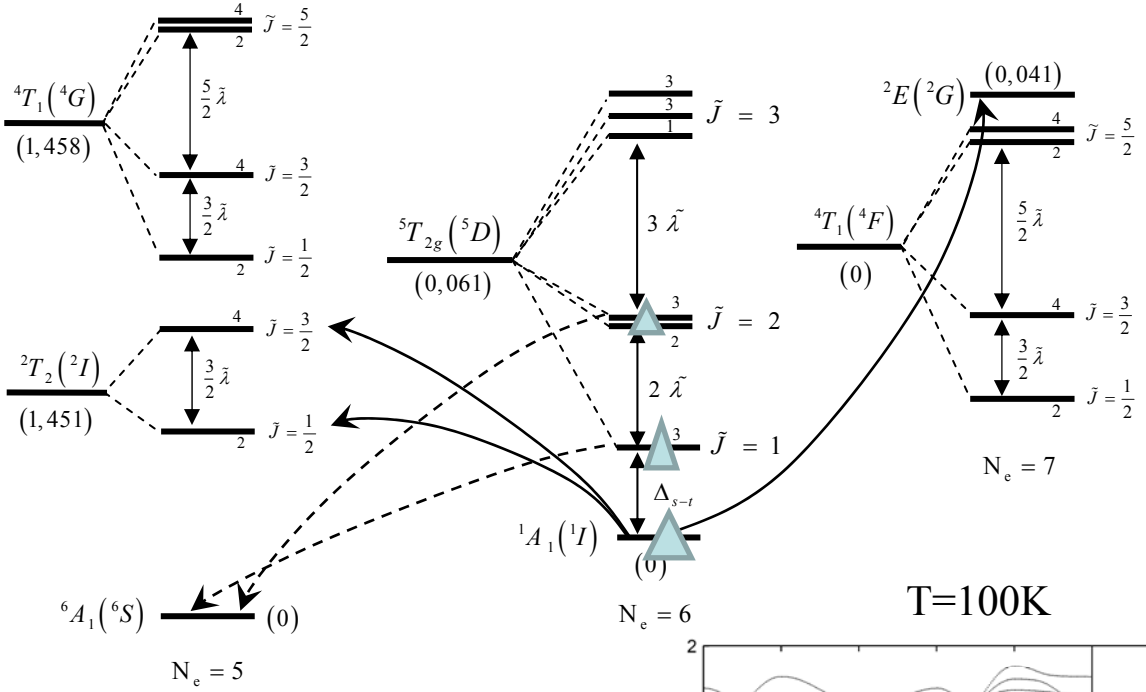






LaCoO3 band structure at T=0

LaCoO3 band structure at finite T



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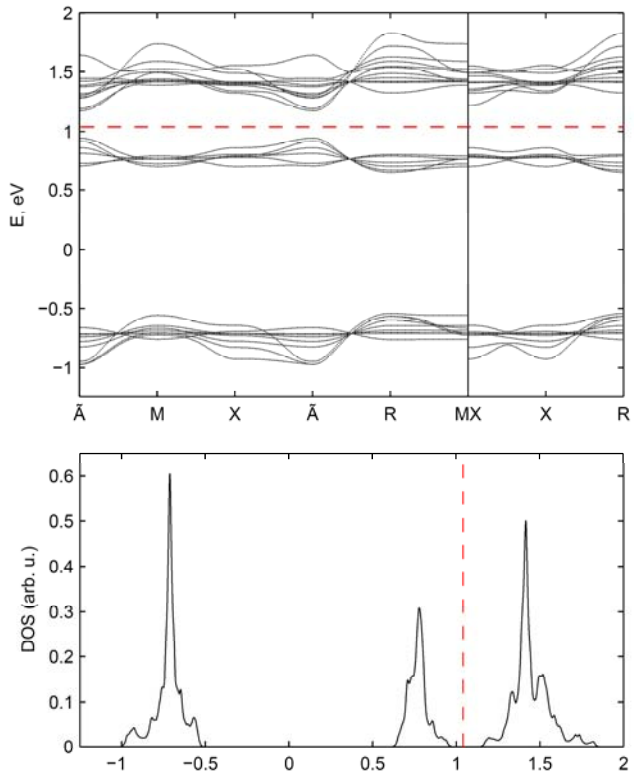
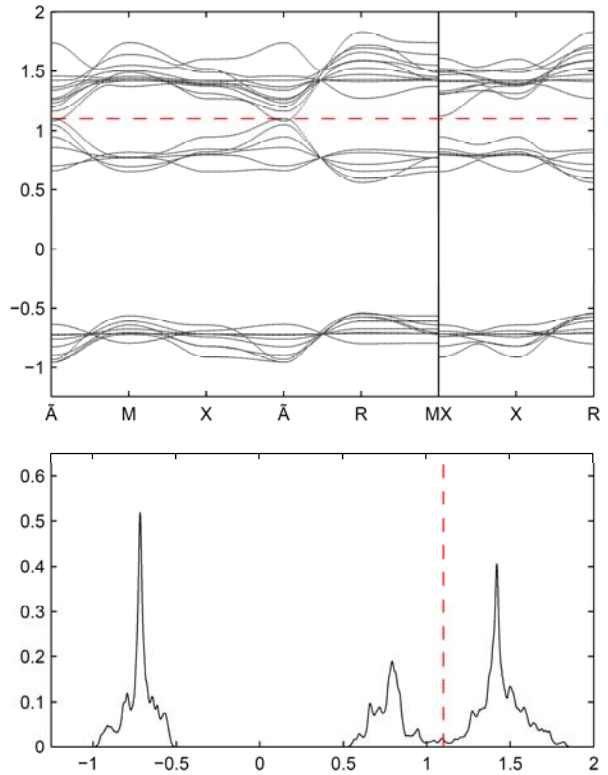
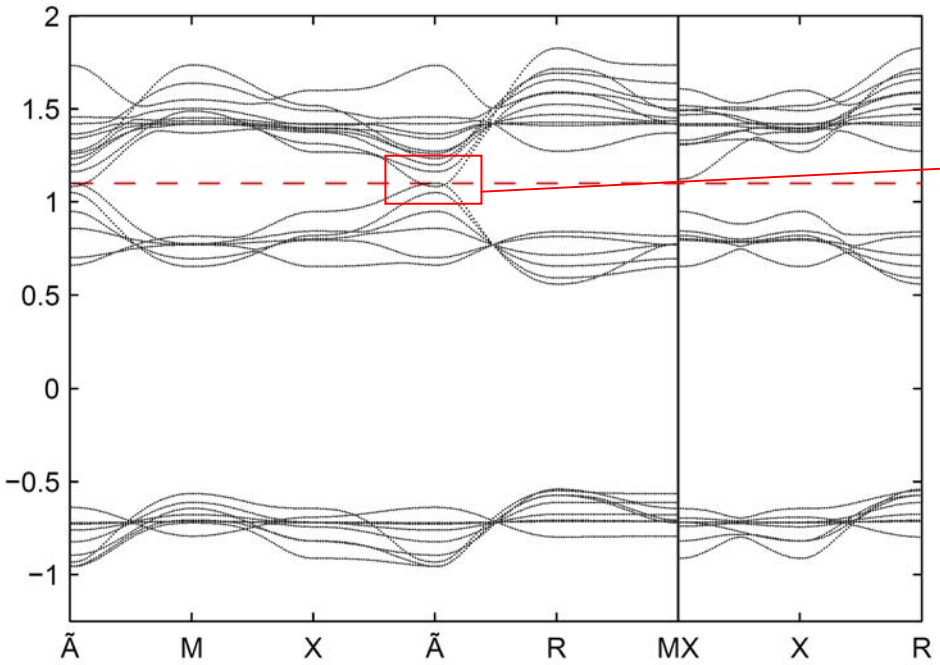
Z.V.Pchelkina
JETP 2011

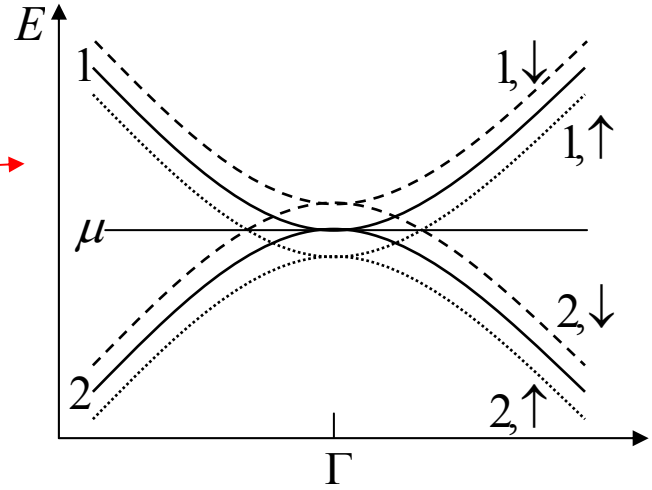
T=100K



T=585K

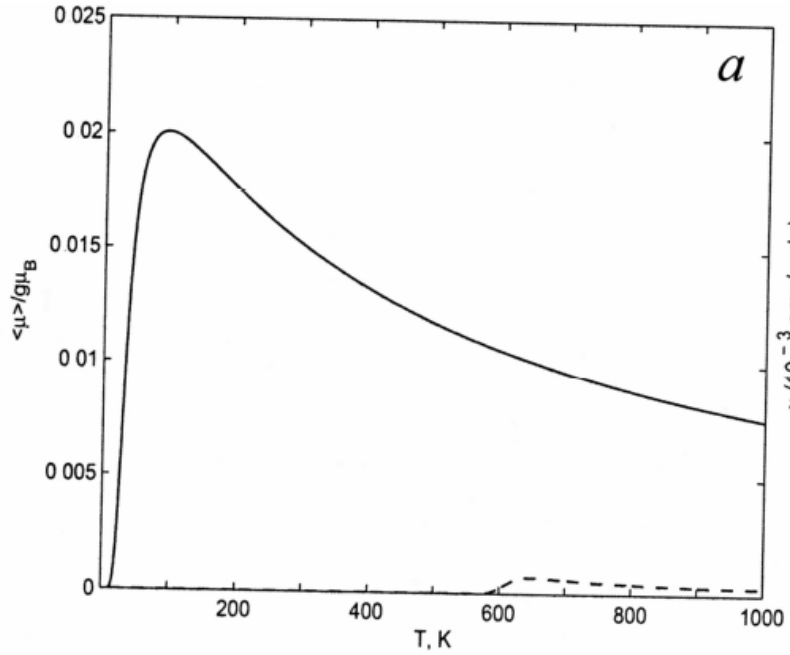


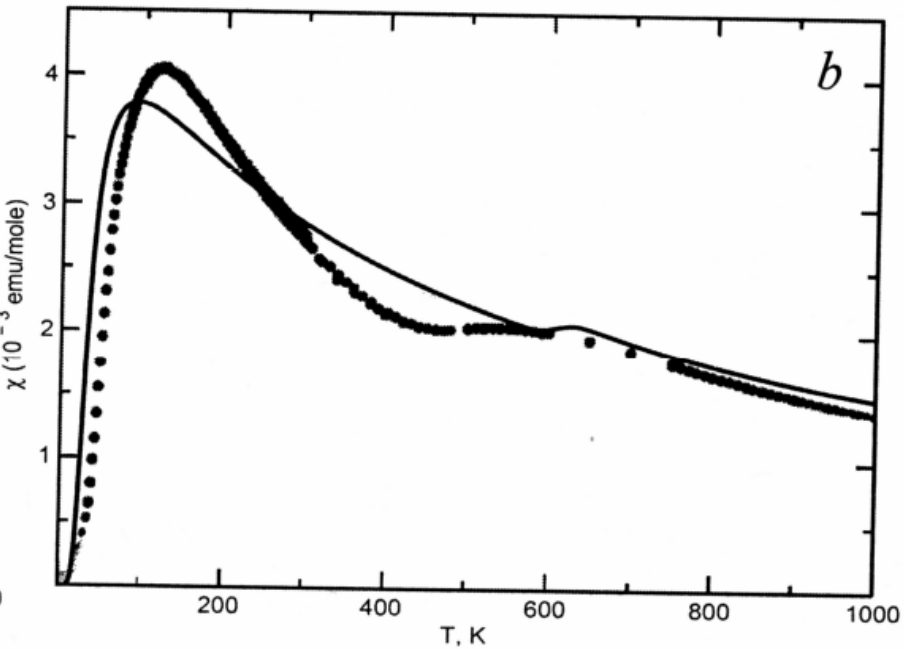




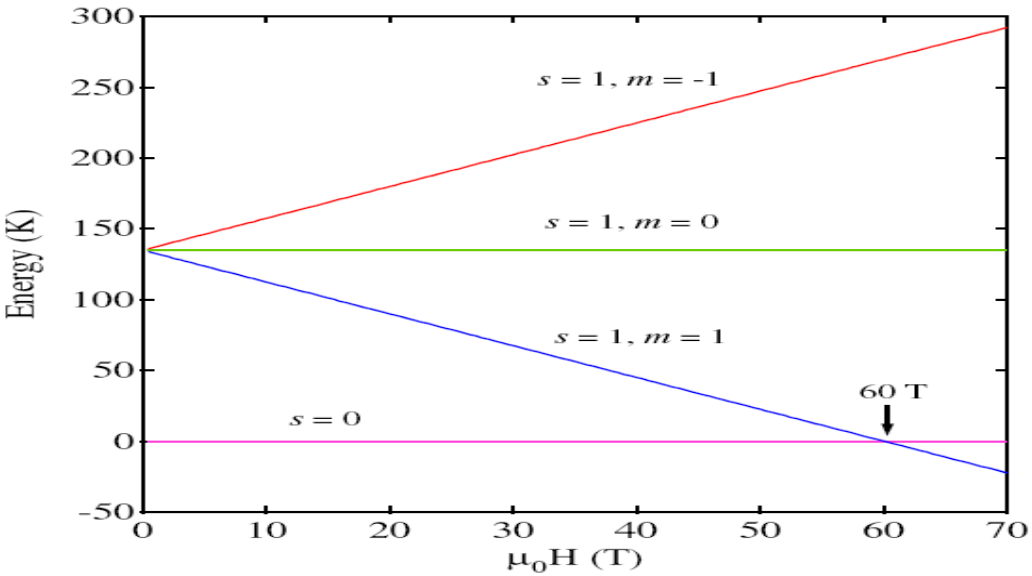
$$\varepsilon_k = \frac{\hbar^2}{2m^*}\left(k_x^2 + k_y^2 + k_z^2\right) = \frac{\hbar^2}{2m^*}k^2 \qquad m^* = 4.8\ m_e$$

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



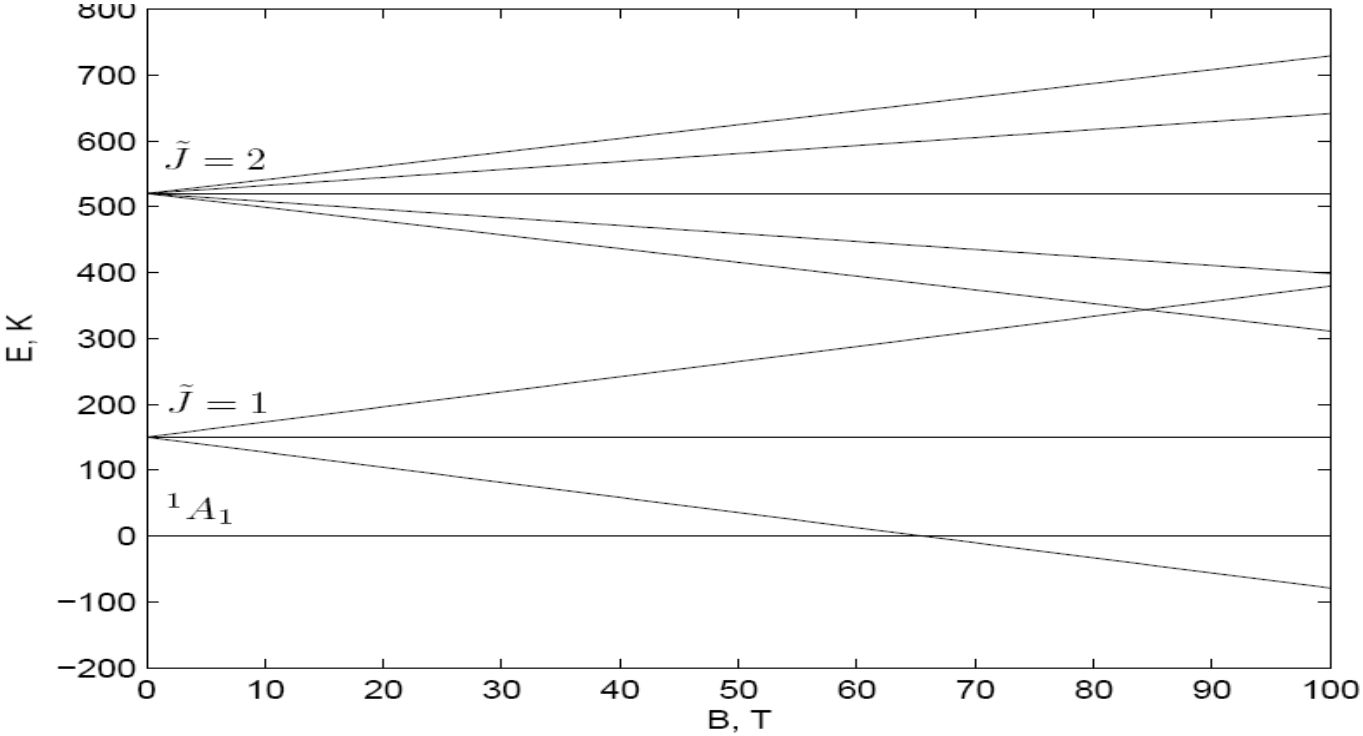


K. Sato et al., J. Phys. Soc. Jpn. 78, 093702 (2009)



Spin crossover and insulator-metal transition in strong magnetic field

(Ovchinnikov, Orlov, JETP Lett.2010)



Metal LaCoO3 above critical field, T=0

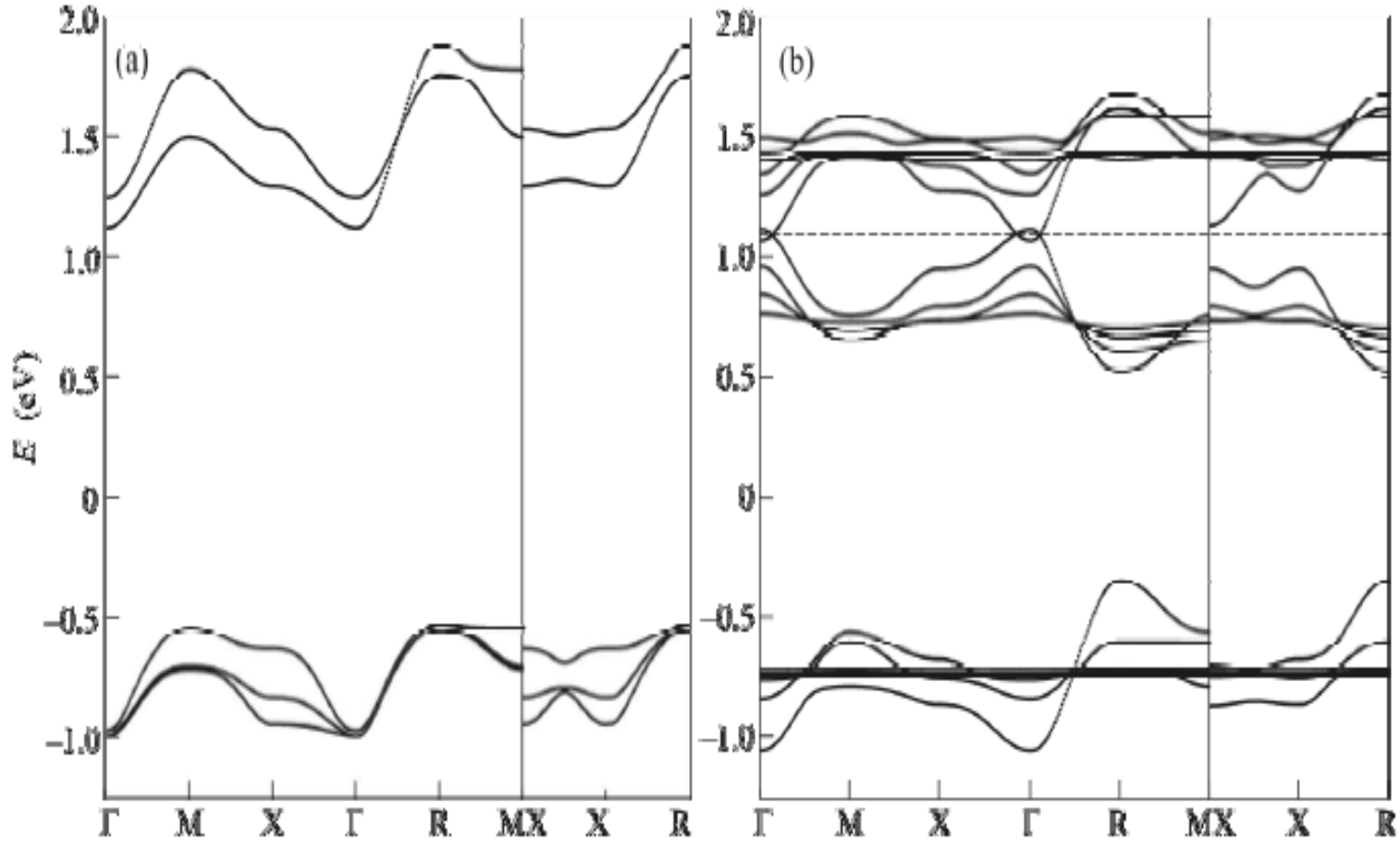
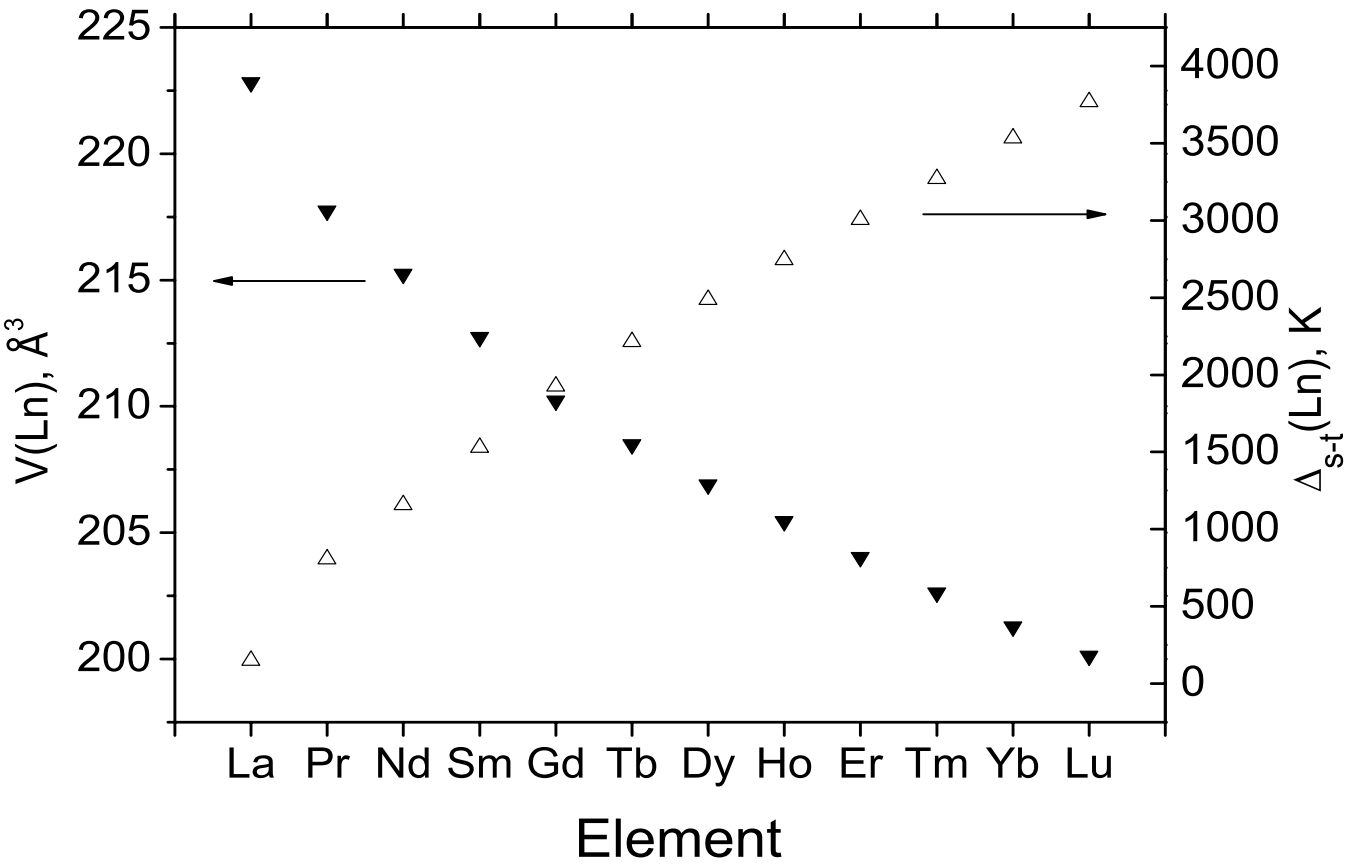


Рис.3. Квазичастичный спектр при $T = 0\,\mathrm{K}$ и магнитном поле (a) $B < B_C$ и (b) $B > B_C$. Пунктирной линией показано положение химического потенциала

Electronic structure and spin crossover in GdCoO3

Chemical pressure from Berch-Murnagan equation of states and spin gap for all Ln

(Dudnikov, Ovchinnikov, Orlov etal JETP 2011**) for GdCoO3 Es~2000K**



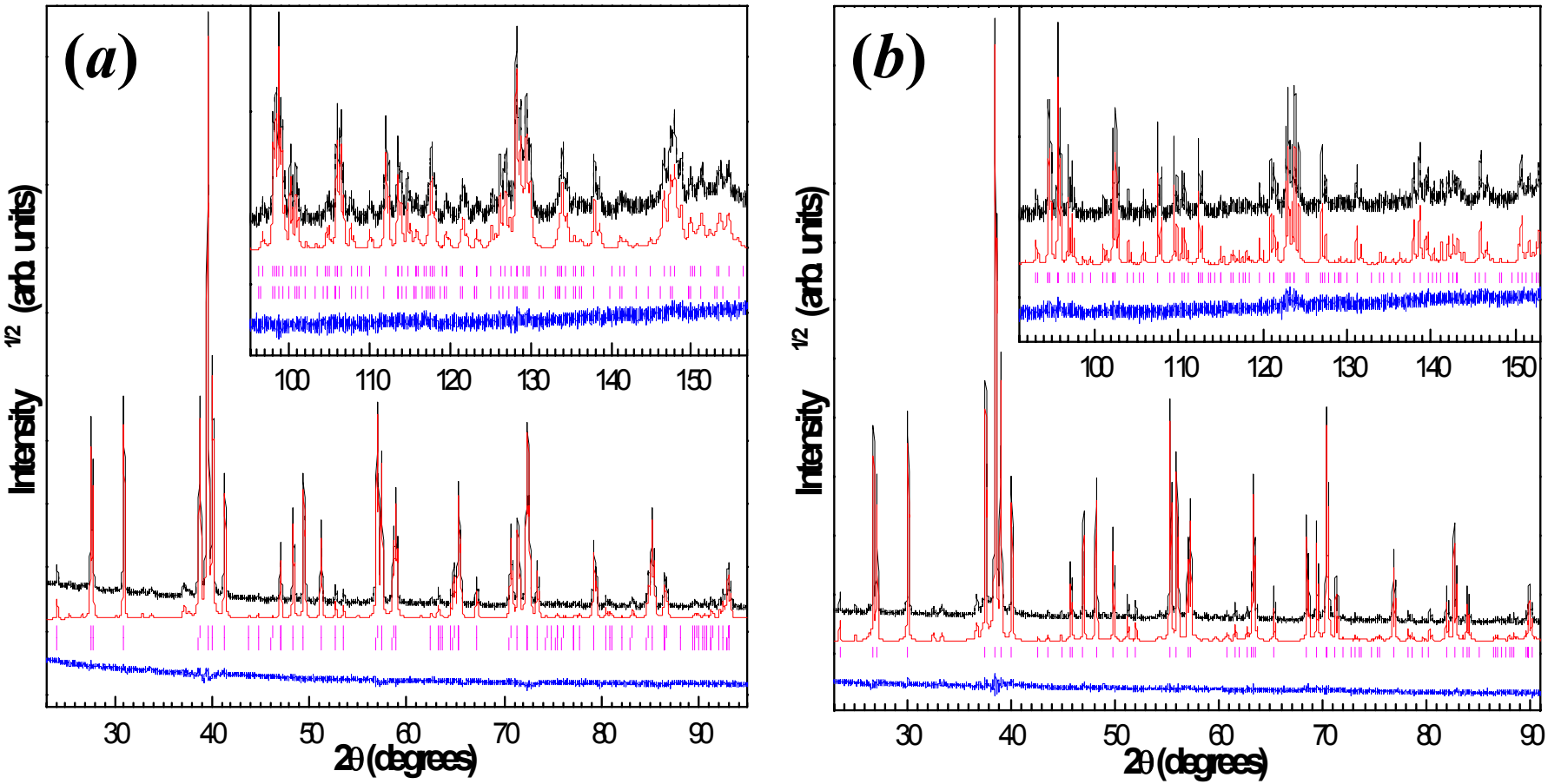
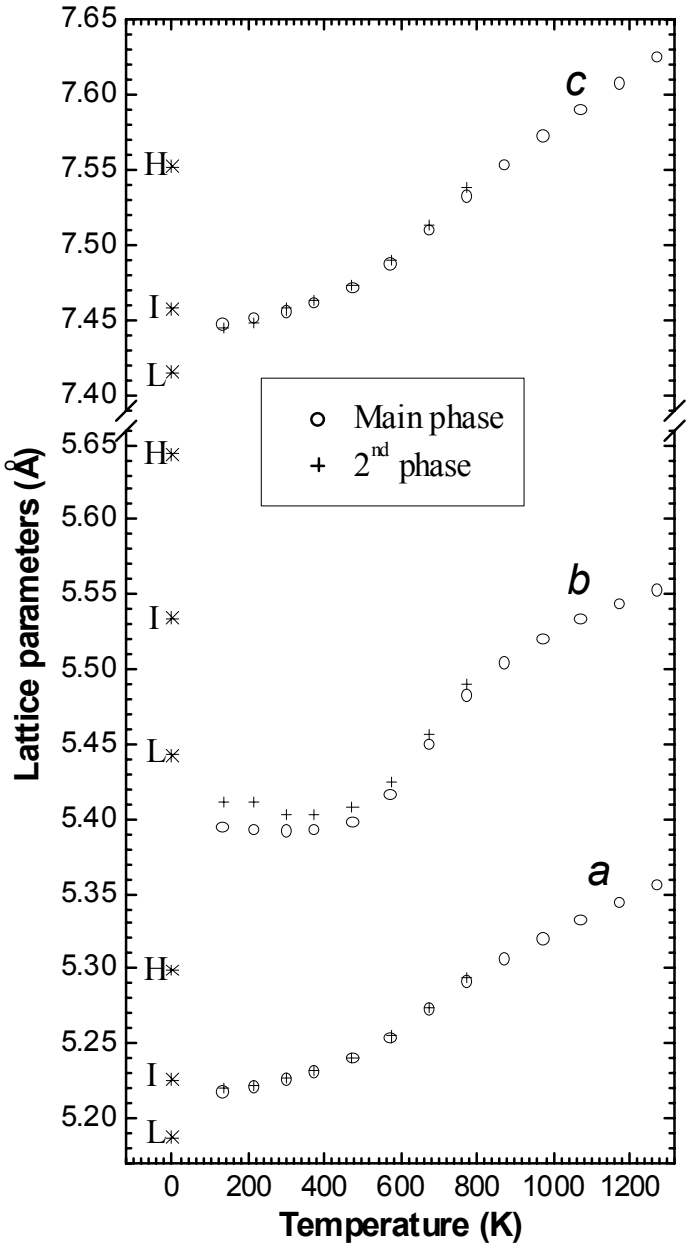
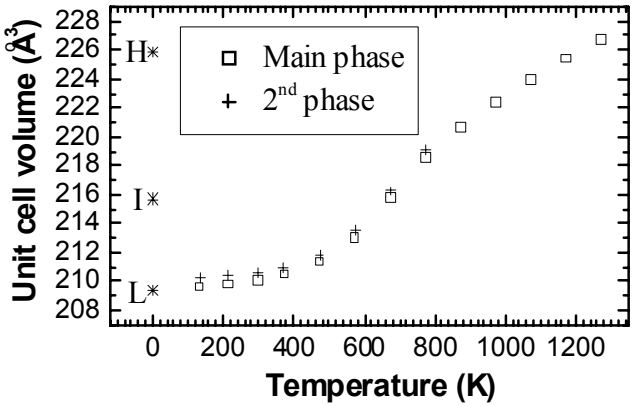


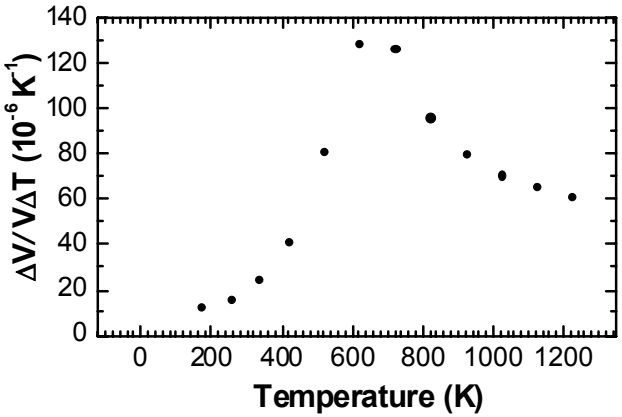
Fig. 2. The observed, calculated, and difference PXRD profiles after the DDM refinement of the $GdCoO_3$ crystal structure at 298K and 1273K. The vertical bars show the positions of the peaks for the first and second phases. Two type of polycrystalline samples: solid state and sol-gel synthesis.

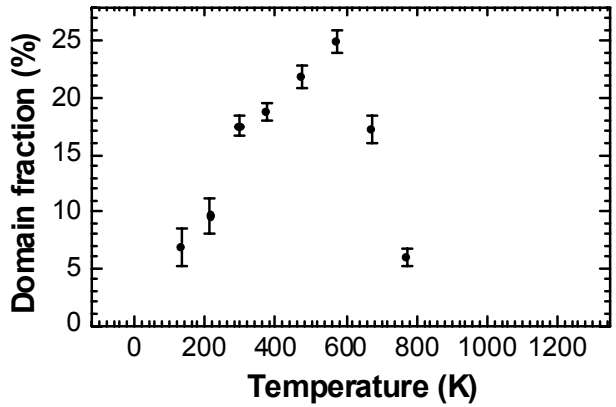
The line width at 1200K is less then at 300K

Phase separation of the HS and LS states with different unit cell volumes and b parameter





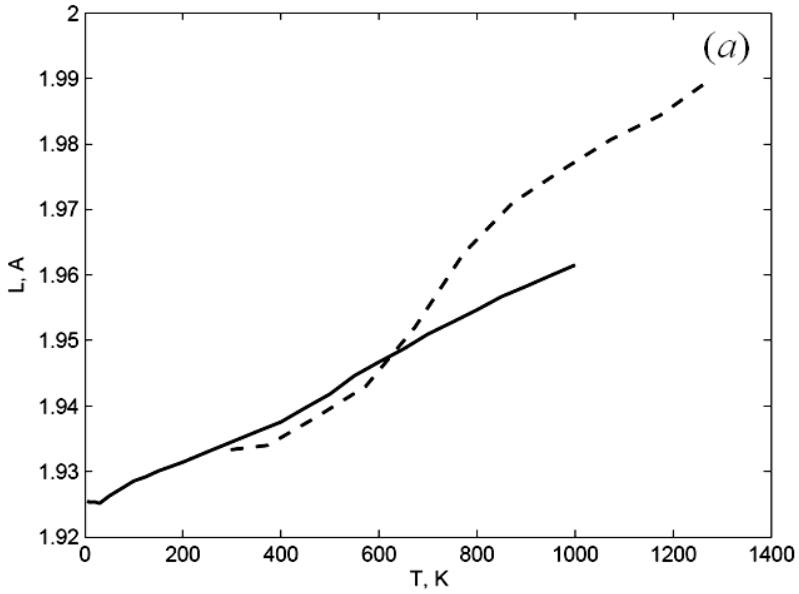


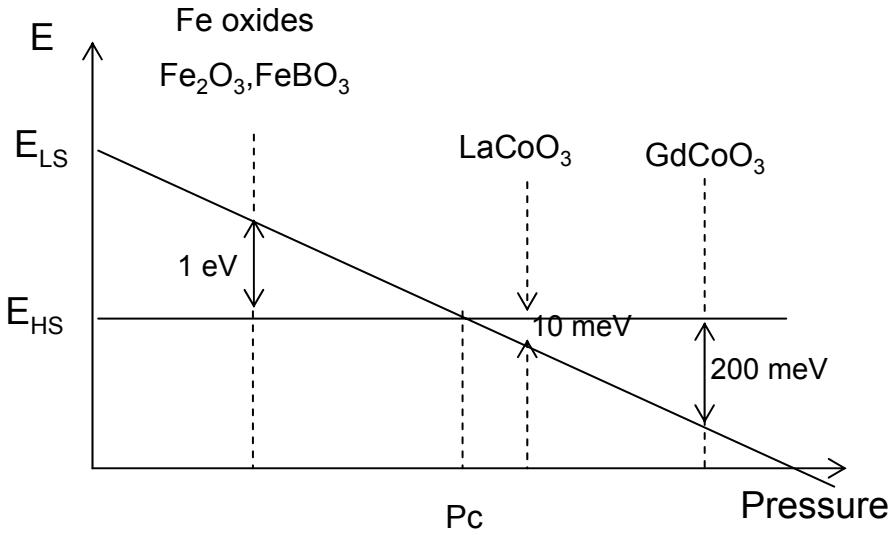


Ab initio GGA-total energy calculations for LS, IS, and HS results in $V_{HS}>V_{LS}$

Parameters a and c almost the same, while $b_{HS}>b_{LS}$

Spin crossover induced by large thermal expansion



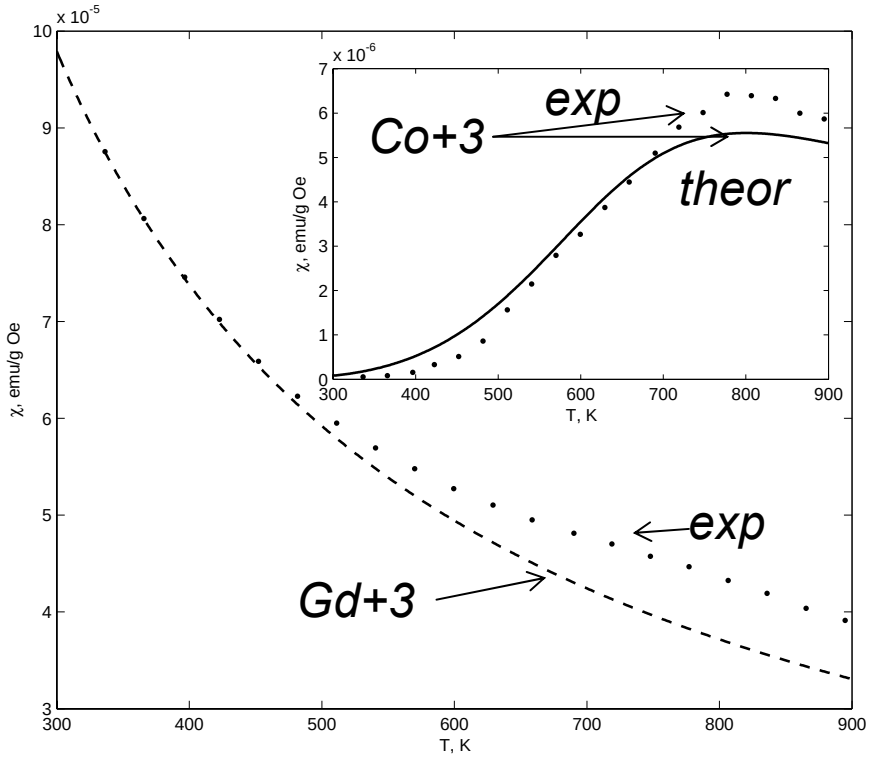


Anomalously large thermal expansion in GdCoO3 (dashed line) and LaCoO3 (solid) (a), and spin crossover scheme with crystal field increasing under external pressure or decreasing under negative pressure of large thermal expansion

$$\Delta_S(T) = E_0\left[1-\left(\frac{T}{T_S}\right)^n\right]$$

E0=2300K, Ts=800K, n=4 by fitting the Co+3 susceptibility, *E0=2260K, Ts=717K, n=3.39 by Knizek etal 2005*

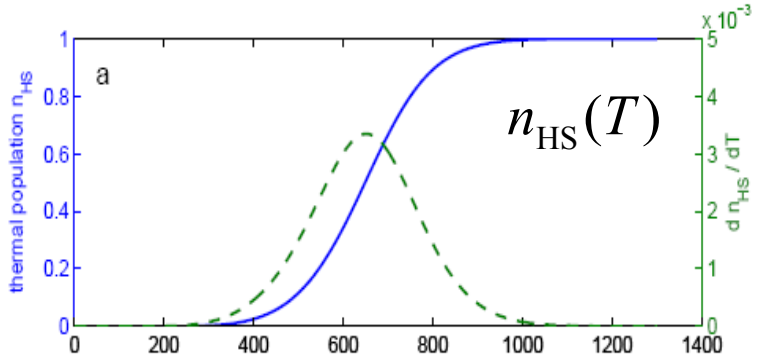
Effect of spin crossover on the magnetic susceptibility and thermal expansion

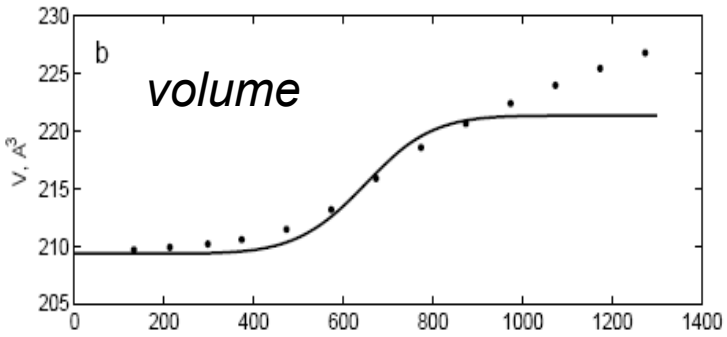


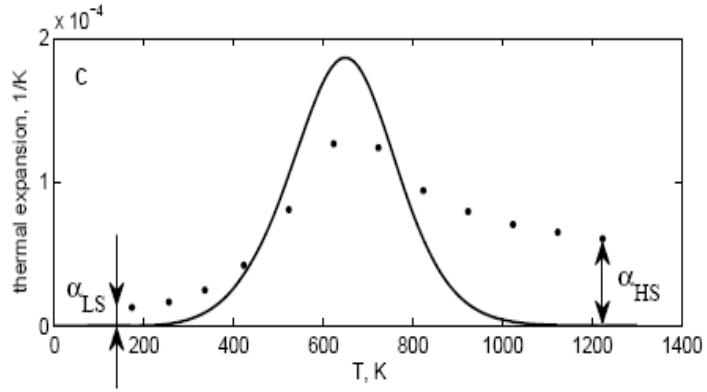
$$\chi_{Co} = N_A \frac{\partial \langle \mu \rangle}{\partial B} = N_A \frac{C_{eff}}{3k_B \left(T - \Theta_{eff} \right)}$$

$$C_{eff} = g^2 \mu_B^2 S(S+1) n_{HS} \qquad \Theta_{eff} = \frac{J_{Co-Co} z S(S+1)}{3k_B} n_{HS}$$

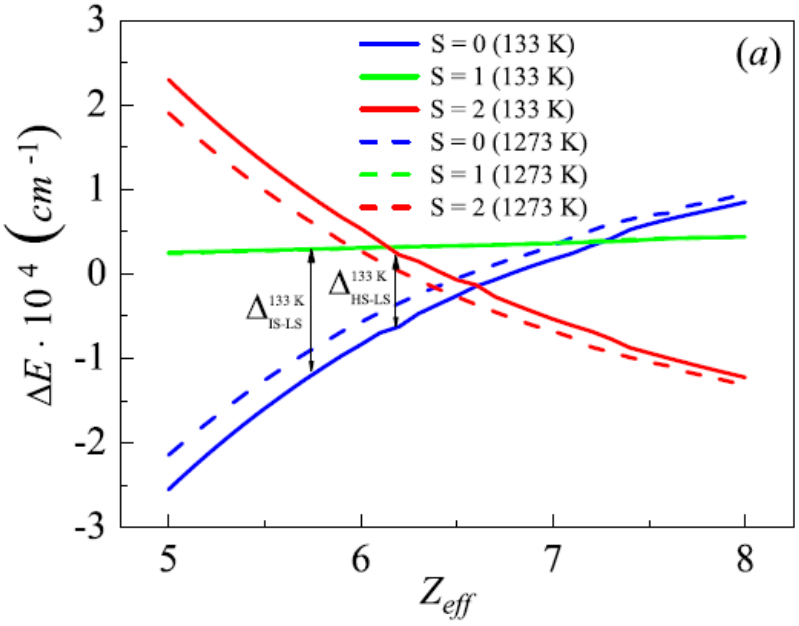
$$n_{HS} = \frac{g_{HS} \exp(-\Delta_S / k_B T)}{1 + g_{HS} \exp(-\Delta_S / k_B T)}$$

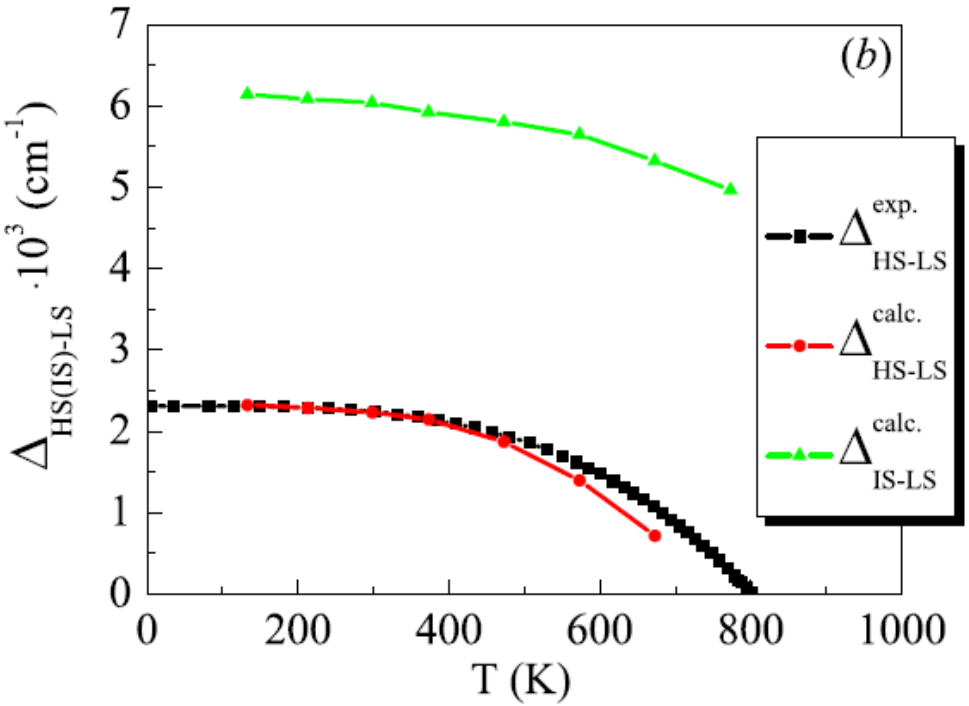






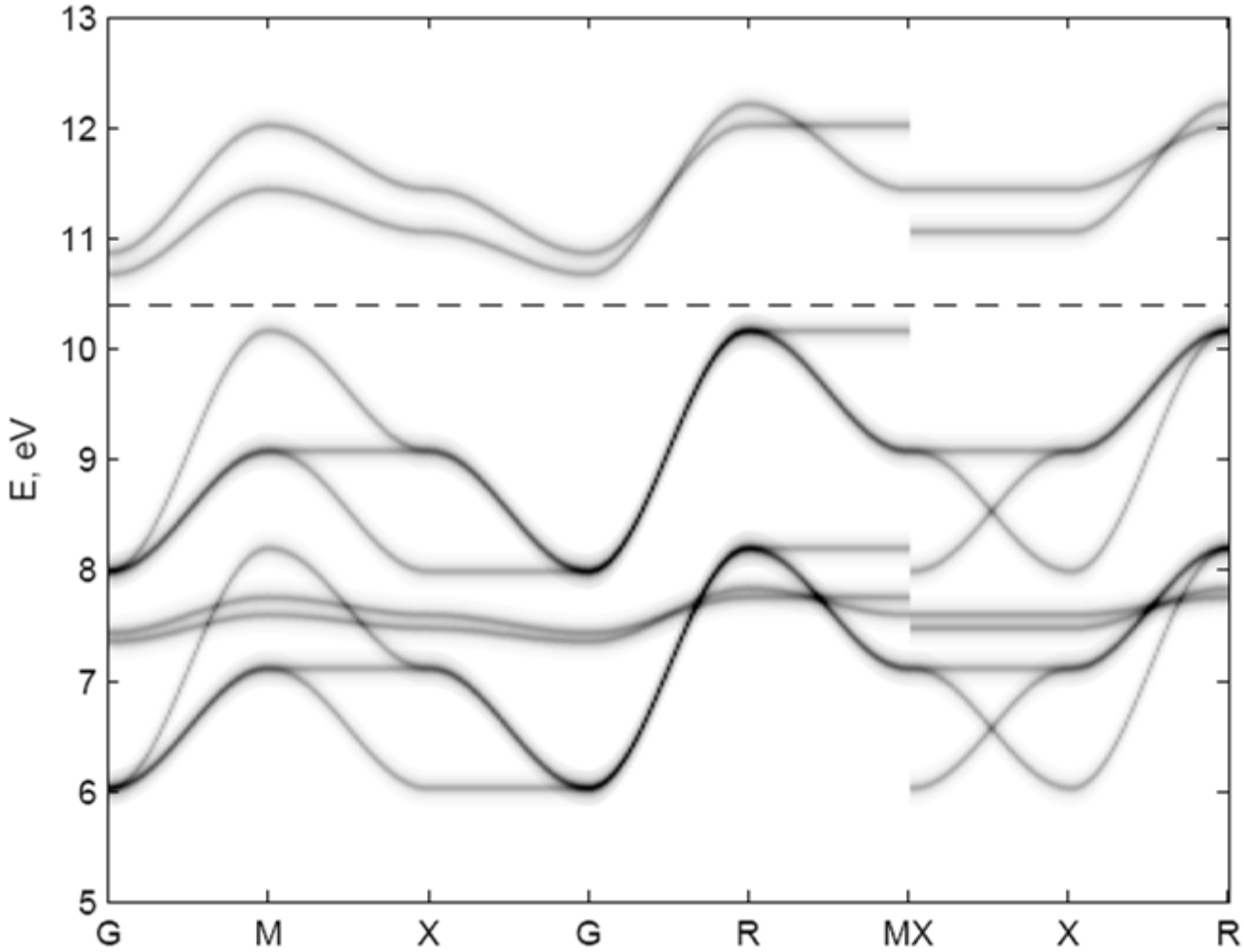
$\alpha_{\mathrm{LS}} \approx 10^{-5} K^{-1}$ $\alpha_{\mathrm{HS}} \approx 5 \cdot 10^{-5} K^{-1}$



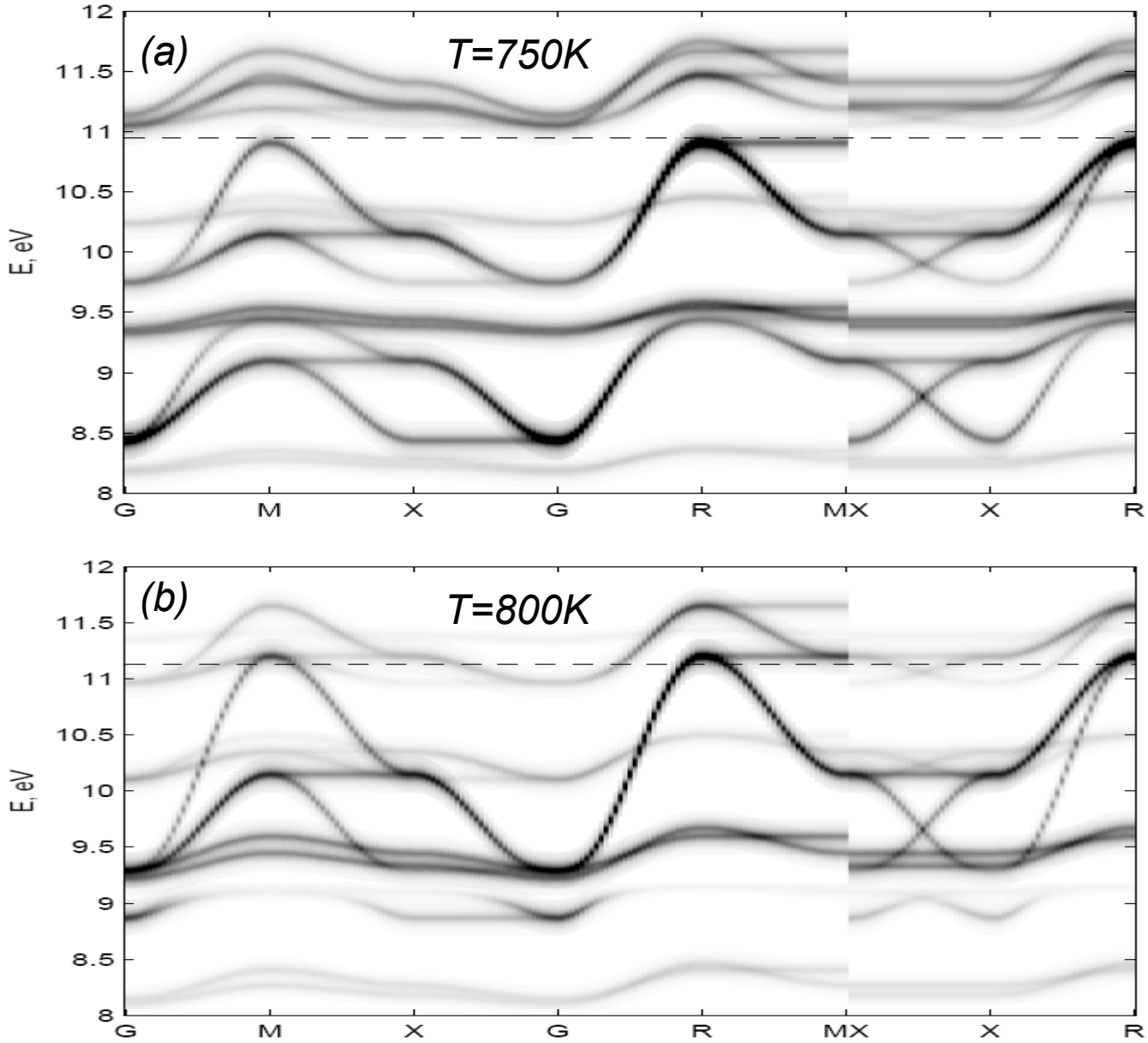


Energy levels of HS, IS, and LS as function of the cation effective charge (a) and temperature dependence of the spin gap and the IS-LS gap (b) calculated within the modified crystal field theory (Lamonova, Pashkevich etal, Donetsk)

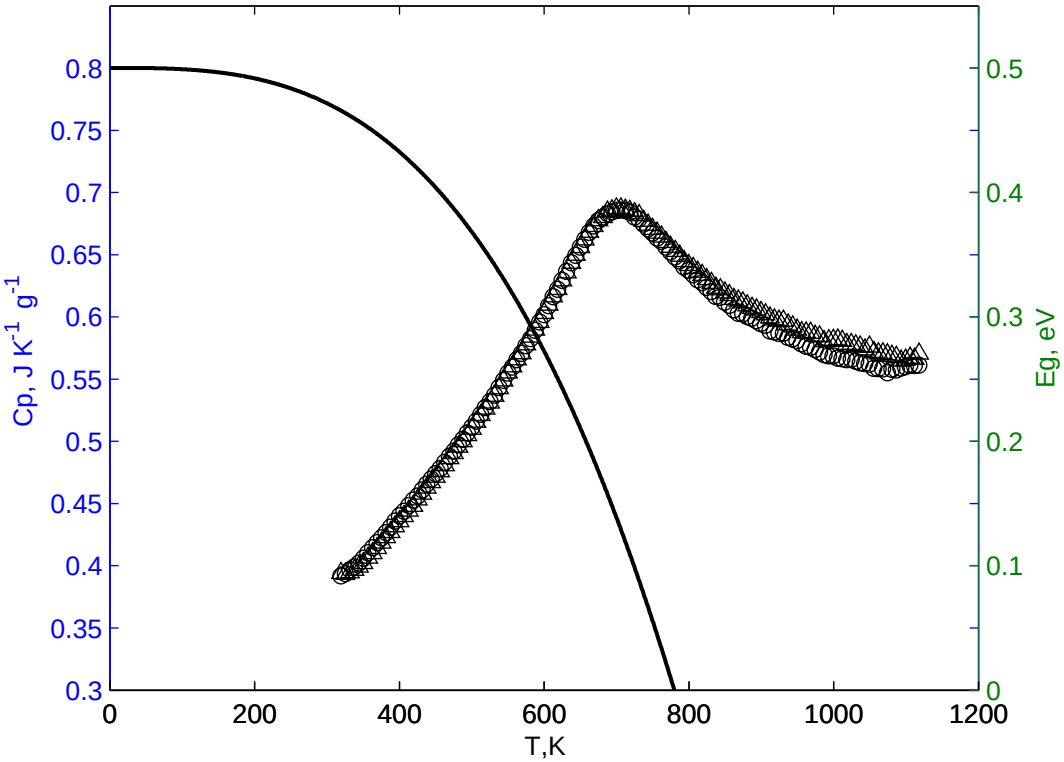
Quasiparticle spectrum at $T = 0$, $GdCoO_3$ is the insulator with charge transfer gap Eg ≈ 0.5 eV. $G(0, 0, 0)$, $M(\pi, \pi, 0)$, $X(\pi, 0, 0)/(0, \pi, 0)$, $R(\pi, \pi, \pi)$ are symmetric points of the Brillouein zone



Quasiparticle spectrum for two values of temperature. (a) At T = 750 K, the increase in the gap states is observed, while (b) at T = 800 K, the band structure is of the metal type.



GdCoO3: Temperature dependence of the measured heat capacity and the calculated dielectric band gap Eg; Eg = 0 at T = T_{IMT} ≈ 780 K.



Quantum critical point and spin fluctuations in the lower-mantle ferropericlase

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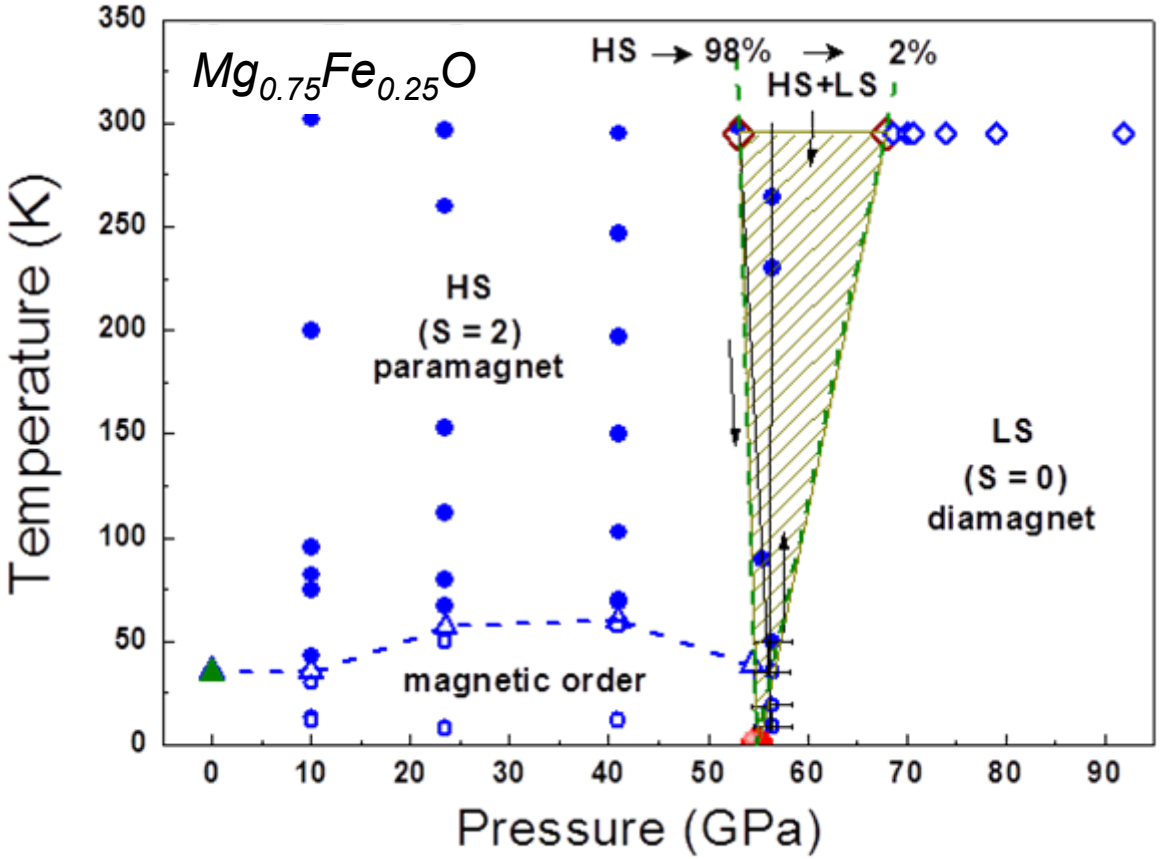

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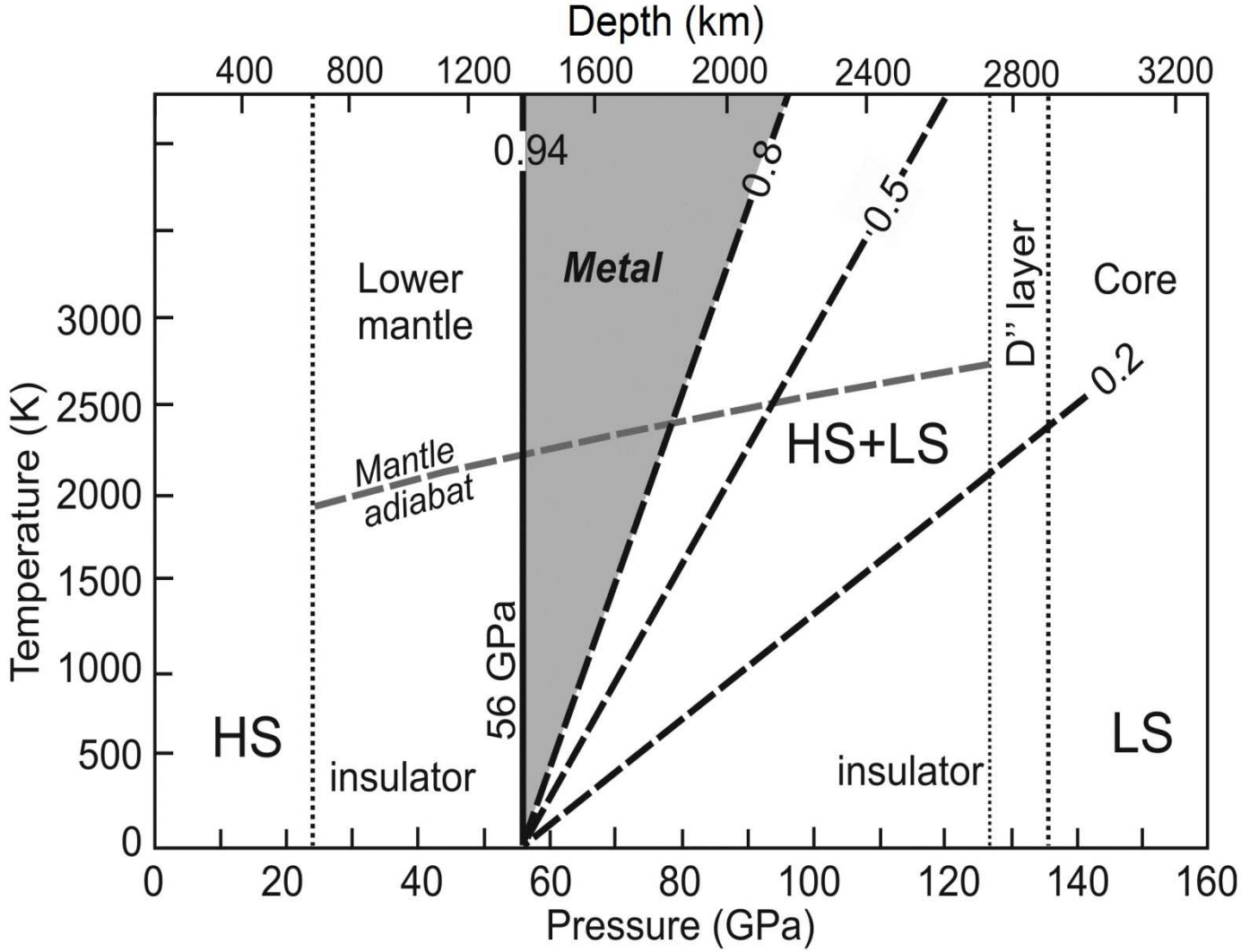
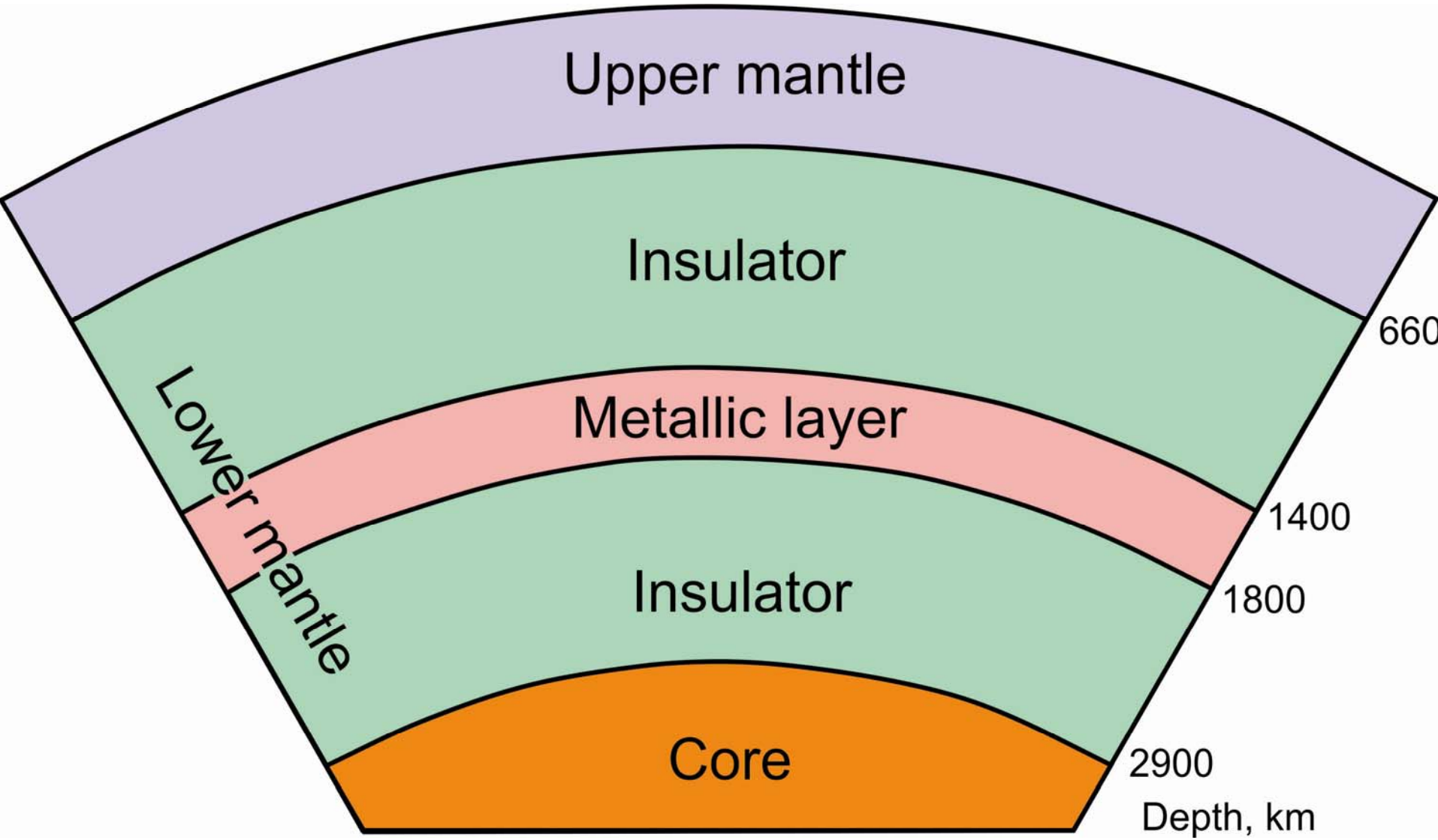
MW phase diagram at high temperature and pressure

S.G.Ovchinnikov, T.M.Ovchinnikova, P.G.Dyad'kov, V.V.Plotkin, K.D.Litasov, JETP Lett 2012



Predicted metallic layer in the Earth's low mantle at depth 1400-1800km

S.G.Ovchinnikov, T.M.Ovchinnikova, P.G.Dyad'kov, V.V.Plotkin, K.D.Litasov, JETP Lett 2012



Conclusions

- LnCoO3 is a class of strongly correlated oxides with spin singlet Co+3 term and S=2, L=1, J=1 excited magnetic term
- Peculiar magnetic and electric properties can be described by LDA+GTB method with temperature dependent spin gap and band structure
- A spin gap is minimal for La and sharply increases for other Ln due to chemical pressure, large thermal expansion results in spin crossover at temperatureTs
- Coexistence of the HS and LS states with different lattice parameters is revealed by XRD as the phase separation
- The volume expansion is large due to different unit cell volumes of the HS and LS phases, the main contribution is given by HS/LS fluctuations instead of lattice anharmonism
- Thermal excited HS C0+3 term determines the width of the in-gap state band and results in the insulator-metal transition
- Insulator-metal-insulator transition is predicted under high pressure and high temperature for the Earth’s low mantle