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

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Transport and magnetic properties of LaCoO$_3$

**Insulator at** $T < 100$ K the energy gap $E_g \approx 0.2$ eV.

*Narrow-gap semiconductor* with gap $E_g$ smoothly transforms into metal with heating at $T \sim E_g$, in LaCoO$_3$ $E_g = 2300$K, experiment reveals smooth insulator metal transition at $T_{PMT} = 550 – 600$K

- J.B. Goodenough 1958r. $T=0$ LS (S=0), $T\neq0$ HS (S=2)
- $S_{eff} \approx 1$ from Curie law, HS vs IS?
- Small gap between LS and HS states results in one maximum at $T\sim 150$K, the second peak is unclear


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

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 $U_d = 4\text{ eV}$ and $V_d = 2.48\text{ eV}$. 
Full atomic multiplet calculations reproduce well the ESR experiment


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

$$G_{\sigma}(k,\omega) = \sum_{m} \left( \frac{A_{m}(k,\omega)}{\omega-\Omega_{m}^+} + \frac{B_{m}(k,\omega)}{\omega-\Omega_{m}^-} \right)$$

(1)

where the QP energies are given by

$$\Omega_{m}^+ = E_{m}(N+1) - E_{0}(N) - \mu, \quad \Omega_{m}^- = E_{0}(N) - E_{m}(N-1) - \mu,$$

and the QP spectral weight is equal to

$$A_{m}(k,\omega) = \left| \left\langle 0,N | a_{k\sigma} | m,N+1 \right\rangle \right|^2, \quad B_{m}(k,\omega) = \left| \left\langle m,N-1 | a_{k\sigma} | 0,N \right\rangle \right|^2.$$
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
\[ H_{\text{c}}(\hat{\varepsilon}) \rightarrow |p\rangle = |m, n_{h}, \varepsilon_{p}\rangle \]

II. The intracell X-operators are constructed:
\[ X_{f}^{n} \leftrightarrow X_{f}^{p,q} \equiv |p\rangle \langle q| = |m, n_{h}, \varepsilon_{p}, n_{h}'\rangle |m, n_{h}, \varepsilon_{p}, n_{h}'\rangle\]
\[ a_{f,\lambda,\sigma} = \sum_{n} \gamma_{\lambda,\sigma}(n)X_{f}^{n} \]

III. Hamiltonian in the X-representation:
\[ H = \sum_{f,p} (\varepsilon_{p} - N\mu)X_{f}^{pp} + \sum_{f \neq g, n,n'} t_{fg}^{nn'}X_{f}^{n}X_{g}^{n'} \]

\[ n_{h} = 0 \quad n_{h} = 1 \quad n_{h} = 2 \quad \ldots \]
Dyson equation in the X-method

\[ \alpha_{k\lambda} = \sum_{m} \gamma_{\lambda} (m) X_{k}^{m} \quad X_{k}^{m} \equiv X_{k}^{p,q} \]

Single-electron GF:
\[ G_{\lambda\lambda'} (k, \omega_n) = \sum_{m,m'} \gamma_{\lambda} (m) \gamma_{\lambda'} (m') D_{m,m'}^{m'} (k, \omega_n) \]

\[ D_{m,m'}^{m'} (k, \omega_n) = \left\langle \langle X_{k}^{m} | X_{k}^{m'} \rangle \right\rangle_{\omega_n} \]

Dyson equation:
\[ \hat{D} (k, \omega_n) = \left[ \hat{G}_{0}^{-1} (\omega_n) - \hat{P} (k, \omega_n) t_{k} + \hat{\Sigma} (k, \omega_n) \right]^{-1} \hat{P} (k, \omega_n) \]

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

"Hubbard I" approximation:
\[ \hat{\Sigma} = 0, \quad P_{m,m'}^{m'} \rightarrow F (m) \delta_{m,m'}, \quad G_{0}^{m,m'} (\omega_n) = \delta_{m,m'} / \left\{ i\omega_n - (\varepsilon_p - \varepsilon_q) \right\}, \]
\[ F (m) = \langle X_{pp}^{m} \rangle + \langle X_{qq}^{m} \rangle, \quad m = m(p,q) \]
Hybrid LDA+GTB scheme without fitting parameters
(in collaboration with prof. V.I. Anisimov group, Ekaterinburg,

- 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
LaCoO$_3$ band structure at finite T

S.G.Ovcinnikov, Yu.S.Orlov, I.A.Nekrasov, Z.V.Pchelkina
JETP 2011
\[ \varepsilon_k = \frac{\hbar^2}{2m^*} \left( k_x^2 + k_y^2 + k_z^2 \right) = \frac{\hbar^2}{2m^*} k^2 \quad m^* = 4.8 \, m_e \]

\[ \langle S_z \rangle = \frac{1}{2} \left( n_{1\uparrow} - n_{1\downarrow} + n_{2\uparrow} - n_{2\downarrow} \right) \]
Spin crossover and insulator-metal transition in strong magnetic field

(Ovchinnikov, Orlov, JETP Lett. 2010)
Metal LaCoO3 above critical field, T=0
Electronic structure and spin crossover in GdCoO$_3$

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

(Dudnikov, Ovchinnikov, Orlov et al. JETP 2011) for GdCoO$_3$ $E_s \sim 2000$K
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 $b_{HS} > b_{LS}$
Anomalously large thermal expansion in GdCoO$_3$ (dashed line) and LaCoO$_3$ (solid) (a), and spin crossover scheme with crystal field increasing under external pressure or decreasing under negative pressure of large thermal expansion

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

$E_0=2300$K, $T_S=800$K, $n=4$ by fitting the Co$^3+$ susceptibility, $E_0=2260$K, $T_S=717$K, $n=3.39$ by Knizek et al 2005
Effect of spin crossover on the magnetic susceptibility and thermal expansion

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

\[ C_{eff} = g^2 \mu_B^2 S(S + 1)n_{HS} \quad \Theta_{eff} = \frac{J_{Co-Co}zS(S + 1)}{3k_B}n_{HS} \]

\[ n_{HS} = \frac{g_{HS}\exp(-\Delta_S/k_BT)}{1 + g_{HS}\exp(-\Delta_S/k_BT)} \]

\[ \alpha_{LS} \approx 10^{-5} K^{-1} \quad \alpha_{HS} \approx 5 \cdot 10^{-5} K^{-1} \]
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 et al., Donetsk)
Quasiparticle spectrum at $T = 0$, GdCoO$_3$ is the insulator with charge transfer gap $E_g \approx 0.5$ 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 Brillouin zone.
Quasiparticle spectrum for two values of temperature. (a) At $T = 750 \text{ K}$, the increase in the gap states is observed, while (b) at $T = 800 \text{ K}$, the band structure is of the metal type.
GdCoO$_3$: Temperature dependence of the measured heat capacity and the calculated dielectric band gap $E_g$; $E_g = 0$ at $T = T_{\text{IMT}} \approx 780$ K.
Quantum critical point and spin fluctuations in the lower-mantle ferropericlase

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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

- LnCoO$_3$ 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 temperature $T_s$
- 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 Co$^{+3}$ 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