Transition from the diamagnetic insulator to ferromagnetic metal in $La_{1-x}Sr_xCoO_3$

(spin transitions of Co^{3+}/Co^{4+} in perovskites $LnCoO_3$ and $(Ln_{1-x}Ae_x)CoO_3$, Ln^{3+}=La,Y,rare-earth, Ae^{2+}=alkali earth)

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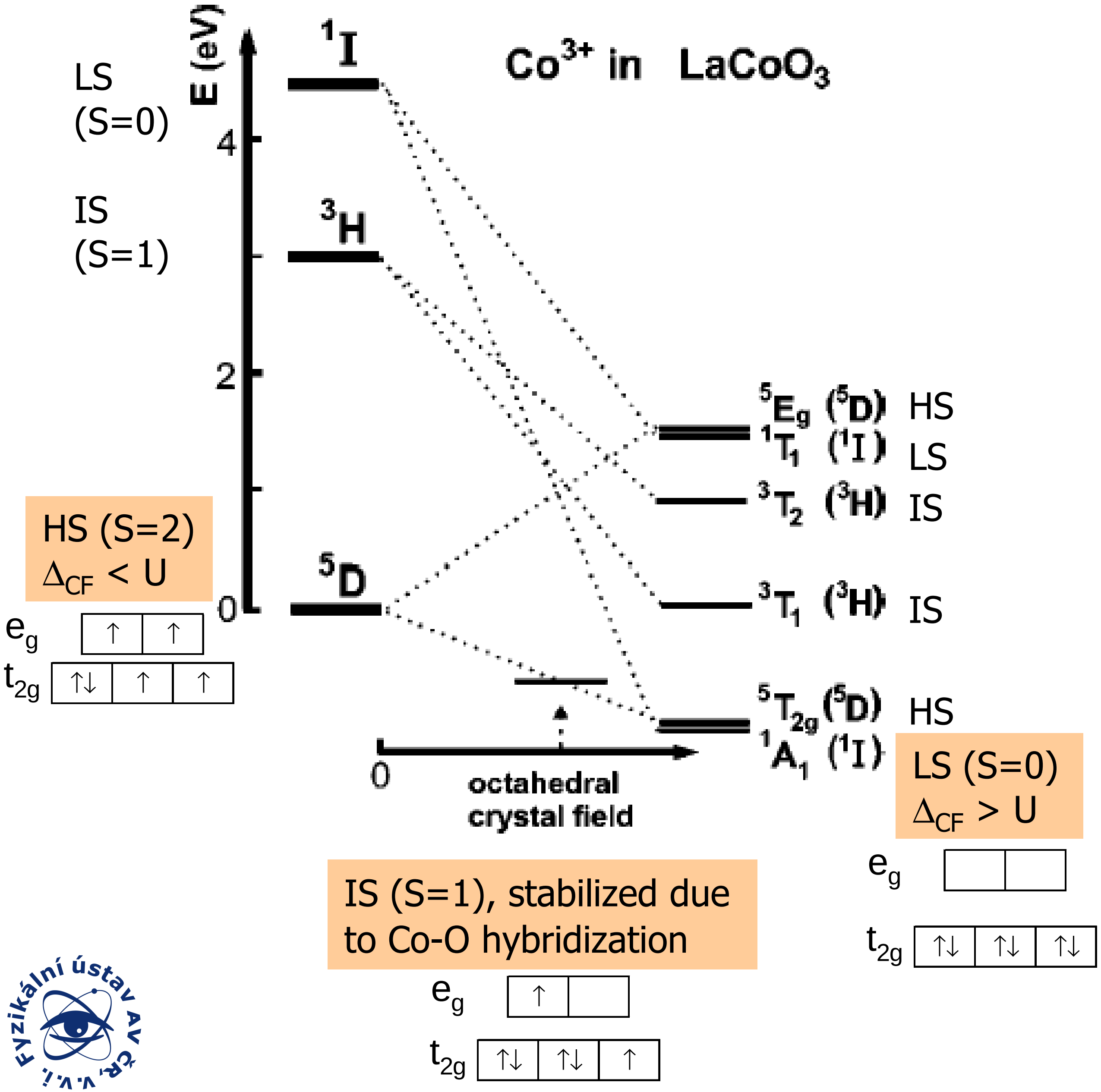
- GGA+U calculation (WIEN2k www.wien2k.at)
- Structural anomalies (X-ray and neutron diffraction)
- Magnetic properties, resistivity, thermopower

Tanabe – Sugano diagram for d^6



HS (S=2)
$\Delta_{CF} < U$

IS (S=1), stabilized due to Co-O hybridization

LS (S=0)
$\Delta_{CF} > U$

Co^{3+} ion in oxides can exists in 3 spin states:

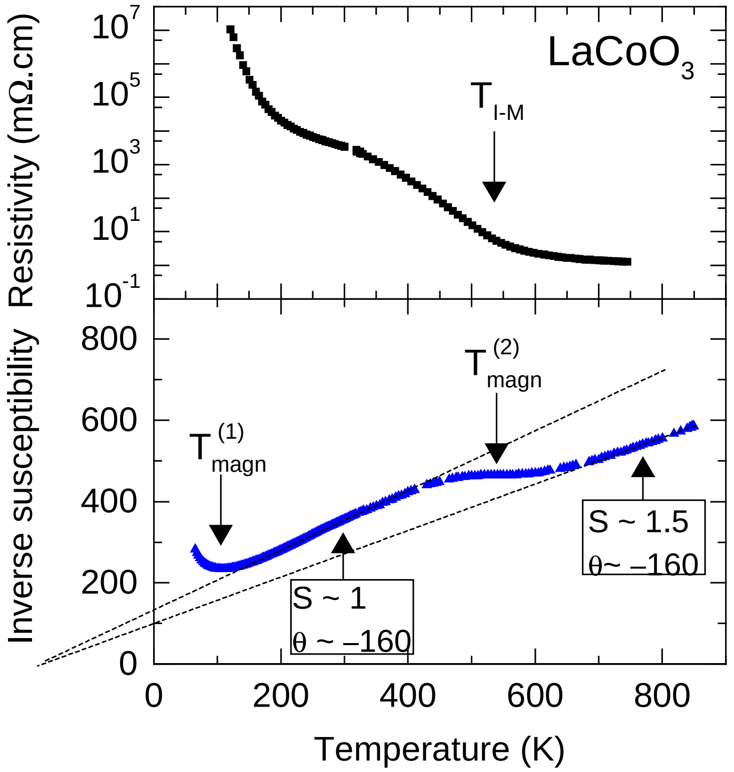
1. Low (LS, S=0, $t_{2g}^6 e_g^0$)
2. Intermediate (IS, S=1, $t_{2g}^5 e_g^1$)
3. High (HS, S=2, $t_{2g}^4 e_g^2$)

due to the subtle balance between:

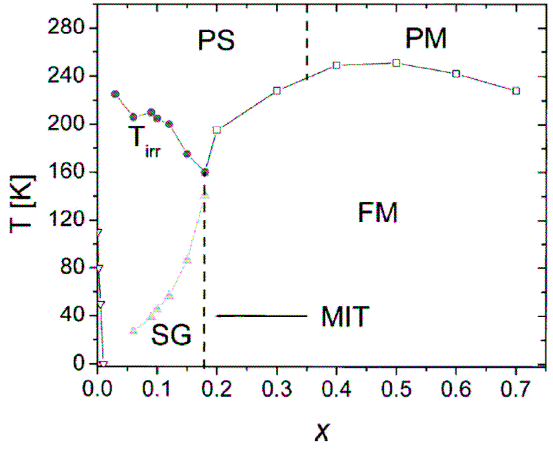
- the crystal field Δ_{CF},
- on-site Coulomb repulsion expressed by Hubbard parameter **U**,
- the energy of charge transfer between Co and oxygen Δ_{Co-O}.

Outline

- ➢ $LaCoO_3$ exhibits diamagnetic-paramagnetic transition around $T^{(1)}_{magn}$ = 80 K. The second magnetic transition coupled with insulator-metal transition occurs around $T^{(2)}_{magn}(T_{I\text{-}M})$ = 540 K.
- ➢ Using GGA+U electronic structure calculations, stability of various configurations of spin states - low (LS), intermediate (IS) and high (HS) - including FM/AFM alignment of spins, was analyzed.
- ➢ We propose a LS-LS/HS-IS model to explain two step magnetic transitions in $LaCoO_3$.
- ➢ The compositional transition in $La_{1-x}Sr_xCoO_3$ from LS phase (x=0) to IS phase (x~0.2) involves the same mechanisms as temperature transition in $LaCoO_3$.



PHYSICAL REVIEW B **67**, 174408 (2003)

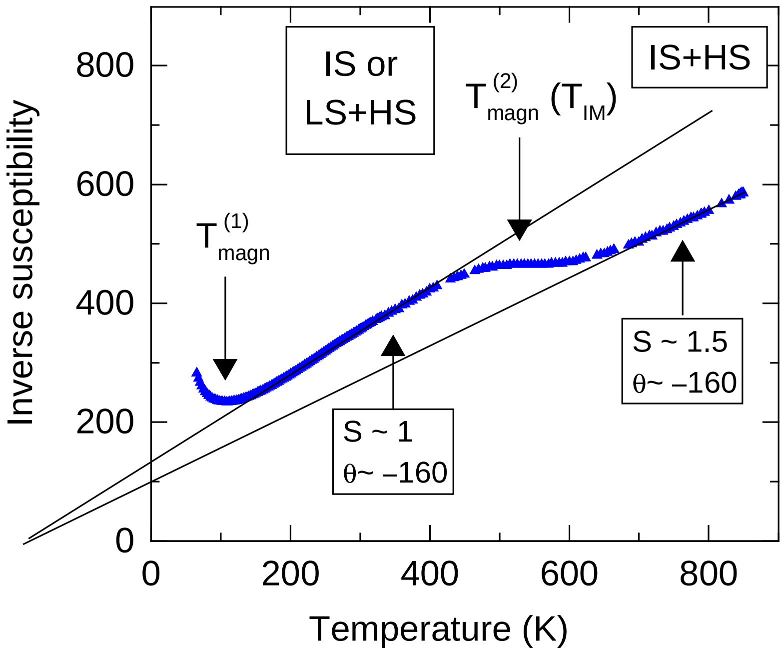


Two principal interpretations

No doubt about the low-spin (LS, $t_{2g}^6e_g^0$) ground state of $LaCoO_3$.
At higher temperatures, magnetic excitations could be either to the intermediate-spin (IS, $t_{2g}^5e_g^1$) or to the high-spin (HS, $t_{2g}^4e_g^2$) states.

1) R.R. Heikes, et al., Physica 30, 1600 (1964).
T = 80 - 350 K: IS Co^{3+};
T > 600 K: IS+HS Co^{3+}
and partial charge disproportionation: $2\ Co^{3+} \rightarrow Co^{2+} + Co^{4+}$

2) P.M. Raccah, J.B. Goodenough, Phys.Rev. 155, 932 (1967).
T = 40 - 150 K: local excitation HS Co^{3+}
T = 150 - 350 K: mixture of LS+HS Co^{3+}, ratio close to 1:1
T > 600 K: IS+HS Co^{3+}

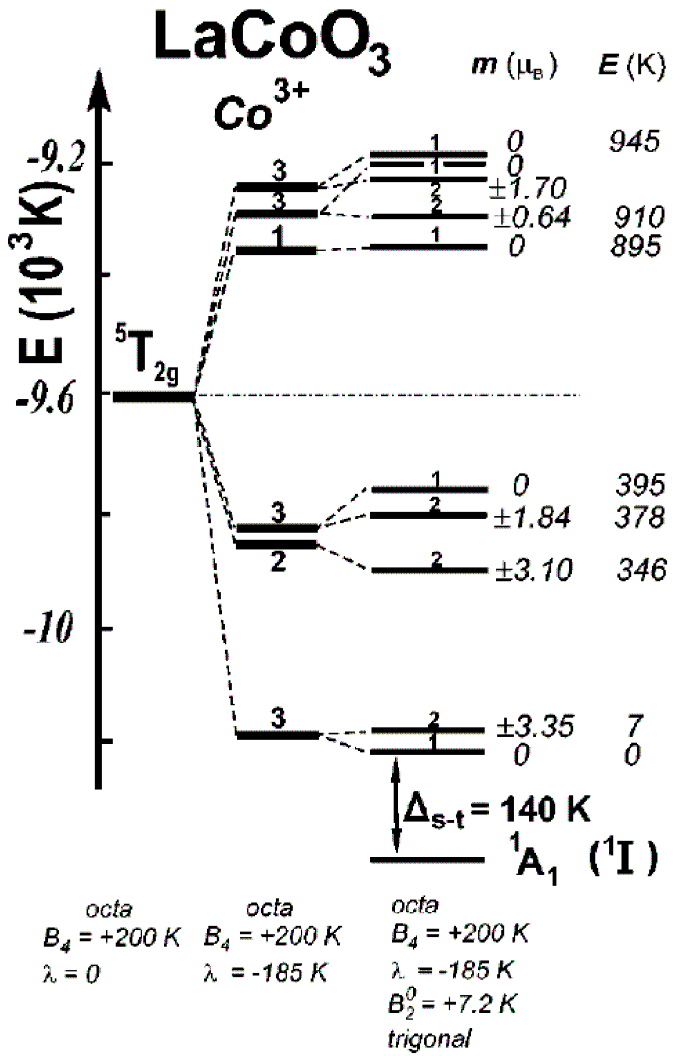


The first excited state: HS

S. Noguchi, S. Kawamata, K. Okuda, et al.,
Evidence for the excited triplet of Co^{3+} in $LaCoO_3$
Phys. Rev. B 66, 94404 (2002).
electron spin resonance (ESR):
g = 3.35 ~ Fe^{2+} (d^6) in HS state.

Z. Ropka, R. J. Radwanski,
^5D term origin of the excited triplet in $LaCoO_3$
Phys. Rev. B 67, 172401 (2003).
HS (^5D): triplet (3+5+7=15)
IS (^3H): singlet (1+3+5=9)

T. Kyômen, Y. Asaka, M. Itoh,
Thermodynamical analysis of spin-state transitions in $LaCoO_3$: Negative energy of mixing to assist thermal excitation to the high-spin excited state
Phys. Rev. B 71, 024418 (2005).
analysis of low-T heat capacity and susceptibility:
LS-LS+HS-IS model.



Aim of the talk

Other experiments/calculations evidencing the first excited magnetic state as HS:

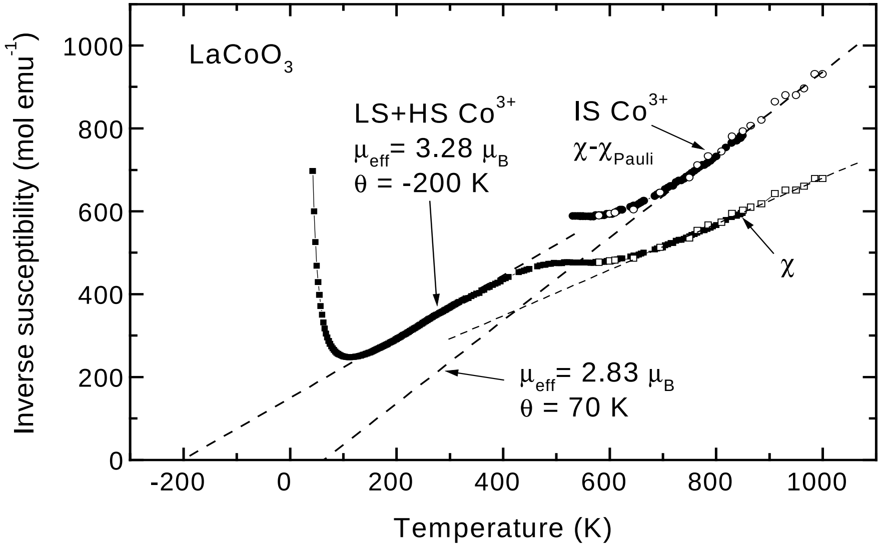
- M. Zhuang, et al., Phys. Rev. B 57, 10705 (1998): Unrestricted Hartree-Fock calculation.
- A. Podlesnyak, et al., Phys. Rev. Lett. 97, 247208 (2006): Inelastic neutron scattering.
- M. W. Haverkort, et al., Phys. Rev. Lett. 97, 176405 (2006): X-ray magnetic circular dichroism (XMCD).

- K. Knížek, et al., J. Phys.-Cond.Mat. 18, 3285 (2006):

GGA+U calculation shows that energy of LS+HS state is comparable or even lower than that of IS state.

- K. Knížek, et al., J. Appl. Phys. 103, 07B703 (2008):

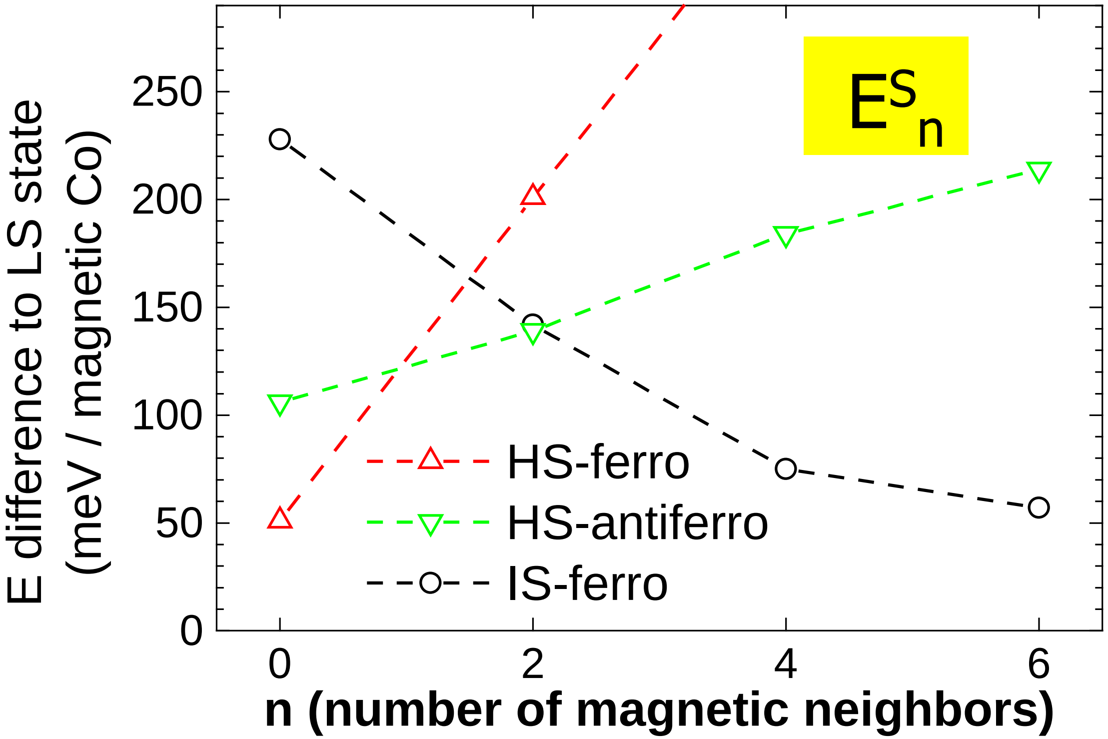
LS/LS-LS/HS-IS/IS model for analysis of thermal dilatation and magnetic susceptibility.



The aim of this presentation is to provide a support for a LS-LS/HS-IS model of the spin transitions thermally induced in $LnCoO_3$ and doping induced in $(Ln_{1-x}^{3+}Ae_x^{2+})CoO_3$ by means of GGA+U electronic structure calculation.

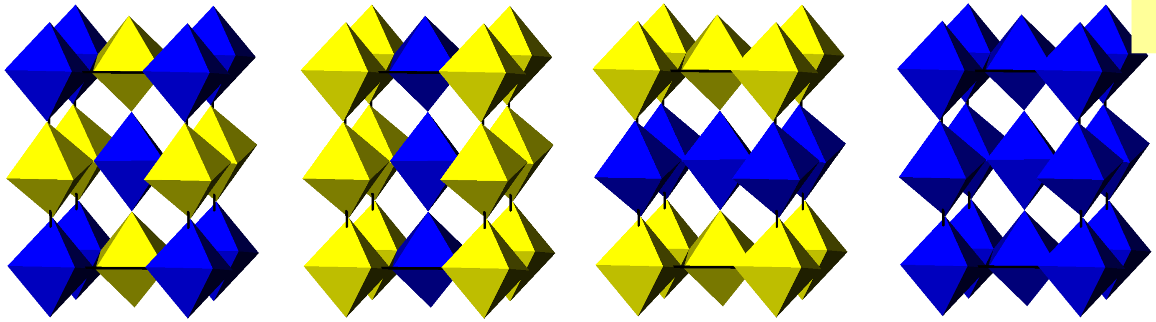
1. Isolated excitations LS ⟶ HS
   AFM interactions
2. LS+HS ⟶ IS
   FM interactions

GGA+U: number of IS or HS neighbours - E^S_n



Dependence of the energy (relative to all Co in LS) of various spin configurations of $LaCoO_3$ on the number (n) of magnetic Co neighbors.

- Stabilization of HS state is is promoted by LS neighbors,
- Stabilization of IS state is promoted by IS neighbors.
- HS: prefers antiferromagnetic interactions
- IS: prefers ferromagnetically aligned neighbors

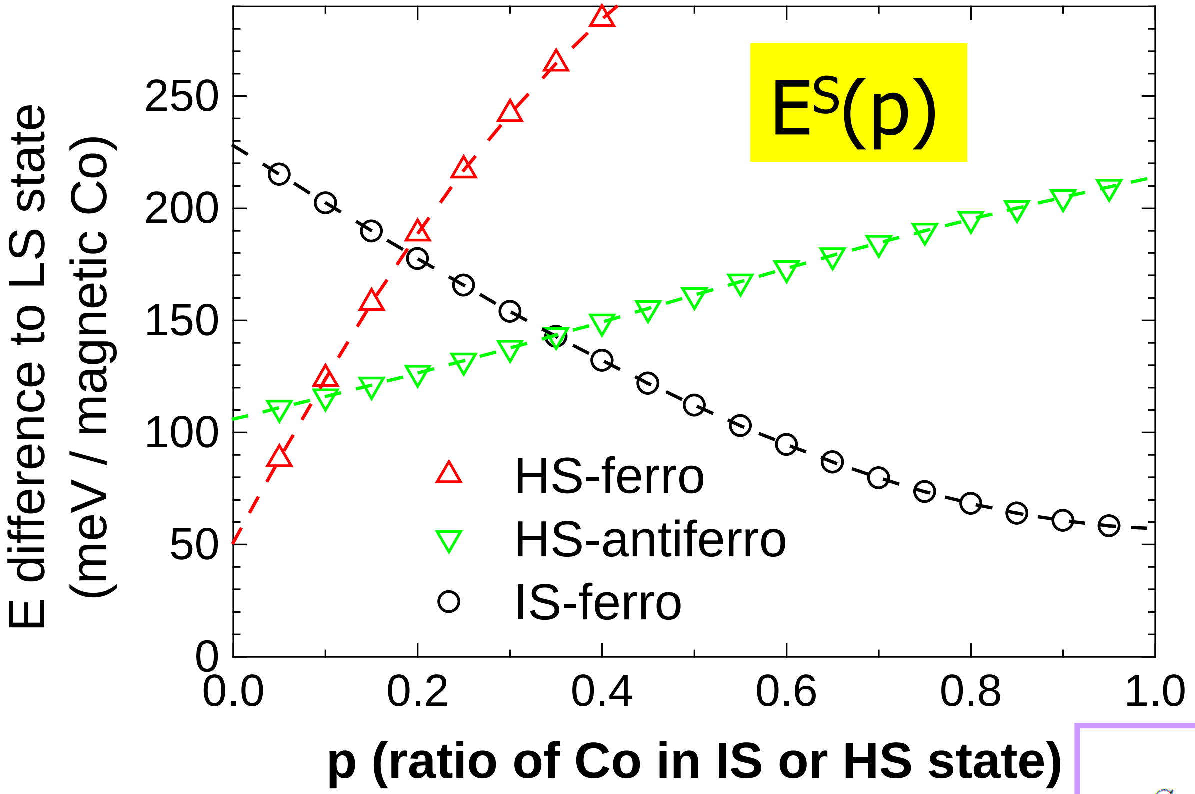


🔷 IS or HS

🔶 LS

Tilting of CoO_6 octahedra as in $LaCoO_3$ at 5 K (PRB 66, 094408) U ~ 3 eV

GGA+U: number of Co in IS or HS - $E^S(p)$

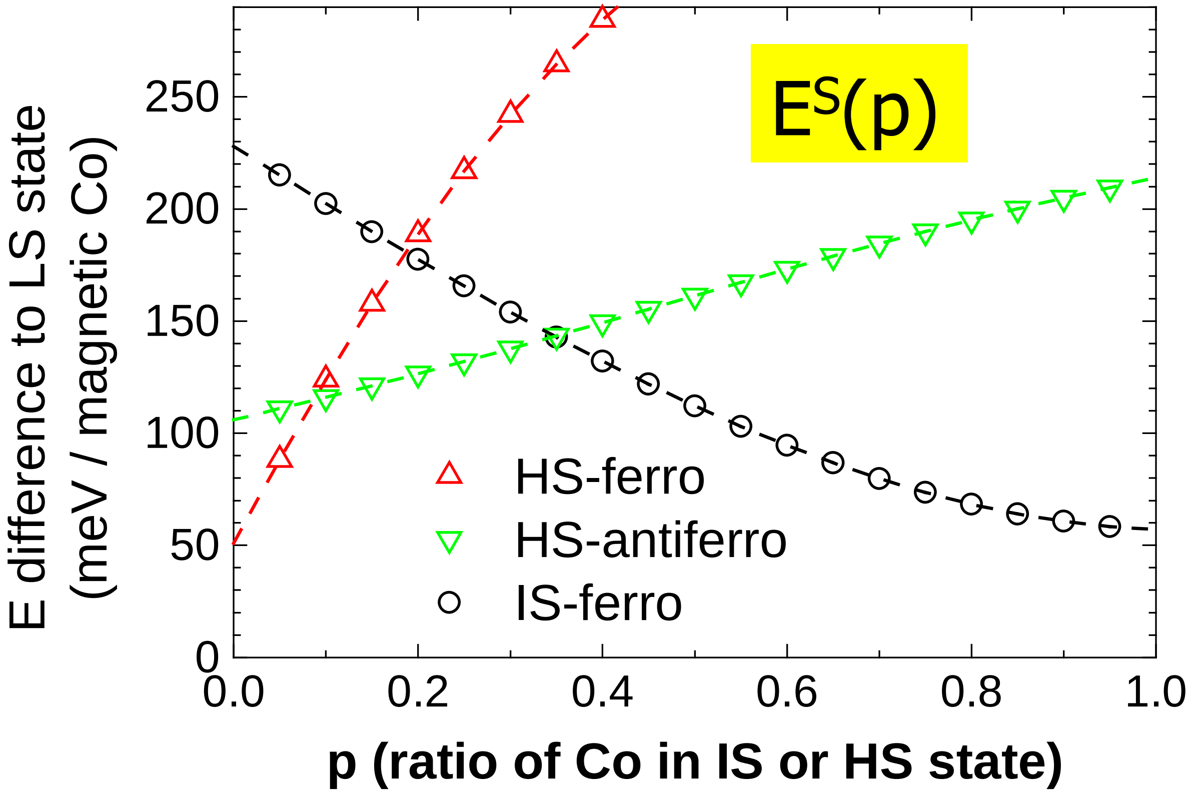


Dependence of the energy (relative to all Co in LS) of various spin configurations of $LaCoO_3$ on the concentration (p) of magnetic Co ions.

$$E^S(p) = \sum_{n=0}^{6} E_n^S \binom{6}{n} p^n (1-p)^{6-n}$$

Supposing random distribution of the excited species, their energy E^S is governed by kind of ionic states in the nearest-neighbor positions and can be calculated using the above equation, where E^S_n is an energy of the spin configuration with *n* neighbors in the same spin state (IS or HS) and 6-*n* neighbors in LS state and *p* is a concentration of the excited magnetic ions.

GGA+U: number of Co in IS or HS - $E^S(p)$



$$E^S(p) = \sum_{n=0}^{6} E_n^S \binom{6}{n} p^n (1-p)^{6-n}$$

- For a small amount of excited Co ions the HS state is the only probable magnetic state.
- The spins of diluted HS states are FM aligned, but with increasing number of excited magnetic ions AFM alignment becomes preferable.
- When p is getting near 0.4, the repulsion between HS neighbors makes this state unfavorable and the IS state becomes the preferred spin state
- For p = 1, IS is the only probable magnetic state.

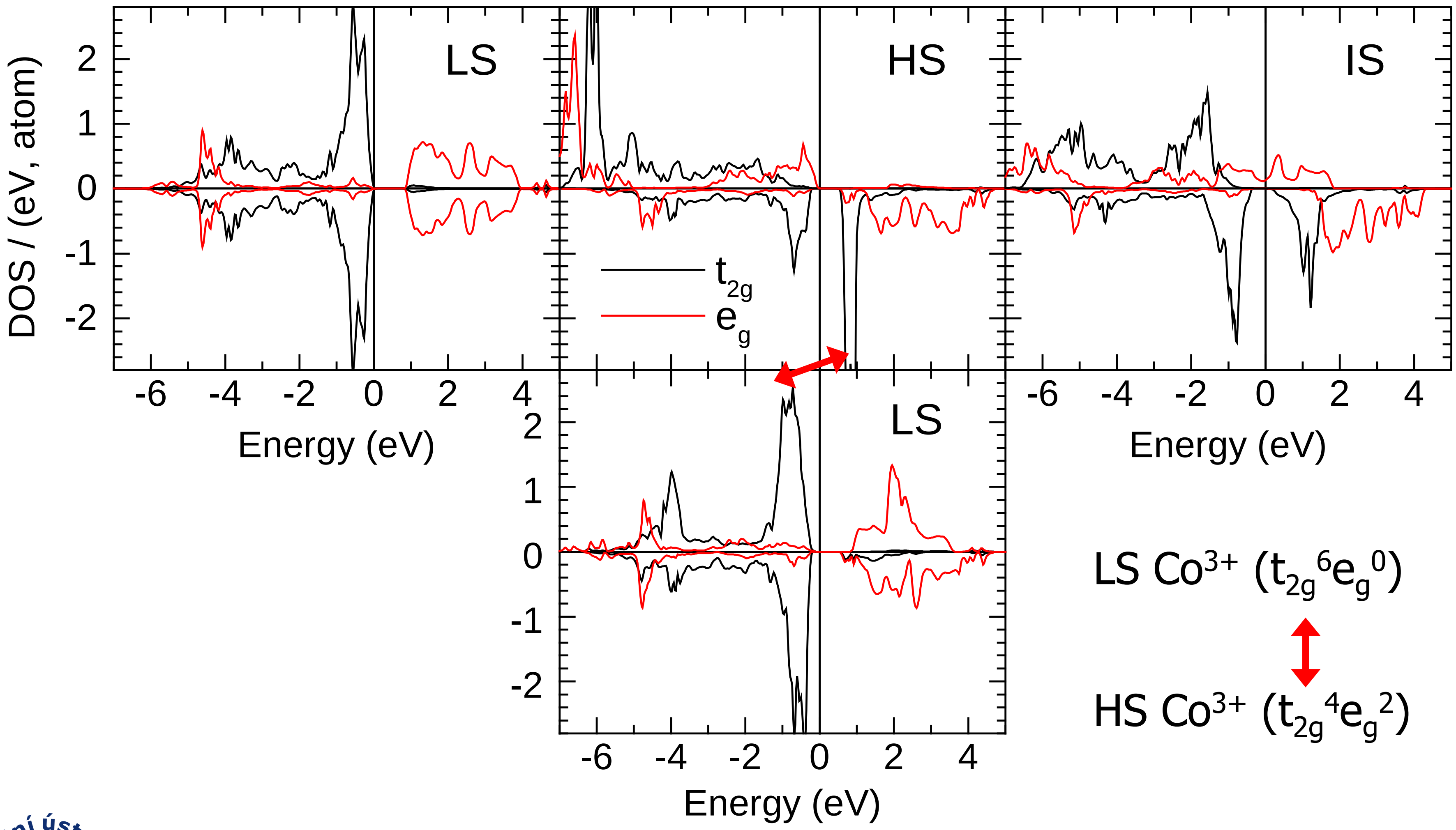
Tilting of CoO_6 octahedra as in $LaCoO_3$ at 5 K (PRB 66, 094408) U ~ 3 eV

$LaCoO_3$ - DOS

LS: gap t_{2g}-e_g ~0.8 eV

LS/HS: gap t_{2g}^{LS} -t_{2g}^{HS} ~0.5 eV

IS: half-metal



LS Co^{3+} ($t_{2g}^6 e_g^0$)

↕

HS Co^{3+} ($t_{2g}^4 e_g^2$)

→

p (ratio of Co^{3+} in IS or HS state)

Charge disproportionation

LS/HS: gap t_{2g}^{LS} -t_{2g}^{HS} ~0.5 eV => charge disproportionation:

$$\text{LS Co}^{3+}\ (t_{2g}^{6}e_g^{0}) + \text{HS Co}^{3+}\ (t_{2g}^{4}e_g^{2}) \rightarrow$$

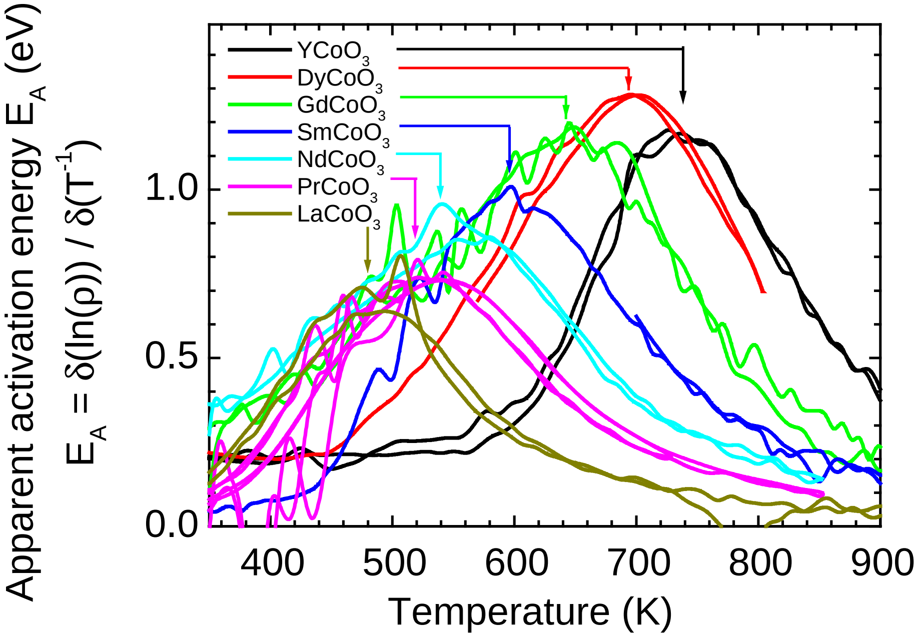
$$\rightarrow \text{LS Co}^{4+}\ (t_{2g}^{5}e_g^{0}) + \text{HS Co}^{2+}\ (t_{2g}^{5}e_g^{2}) \rightarrow$$

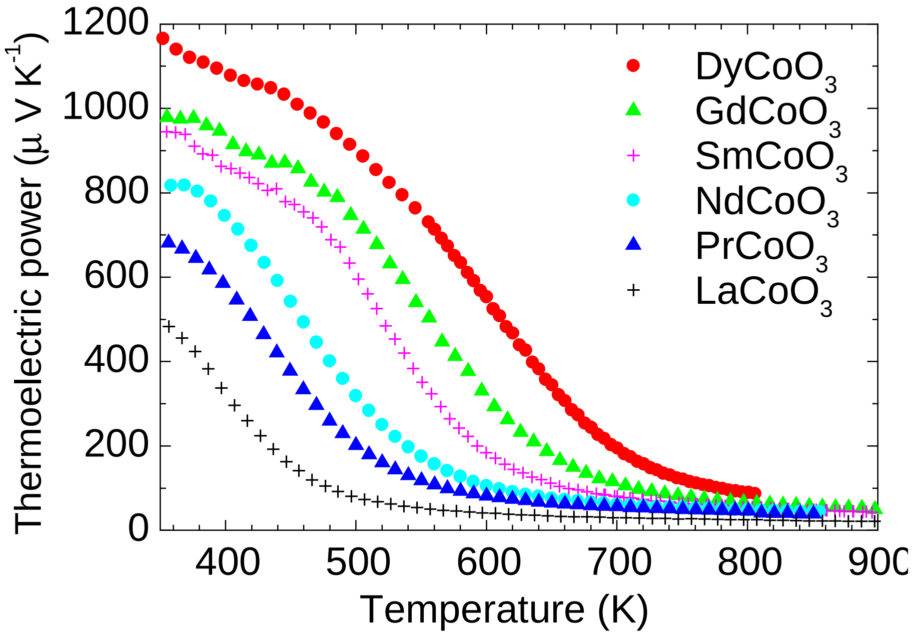
reverse charge equalization: $\rightarrow 2\ \text{IS Co}^{3+}\ (t_{2g}^{5}e_g^{1})$

- The second magnetic transition is based on a reversal of thermally populated HS/LS pairs into IS states.

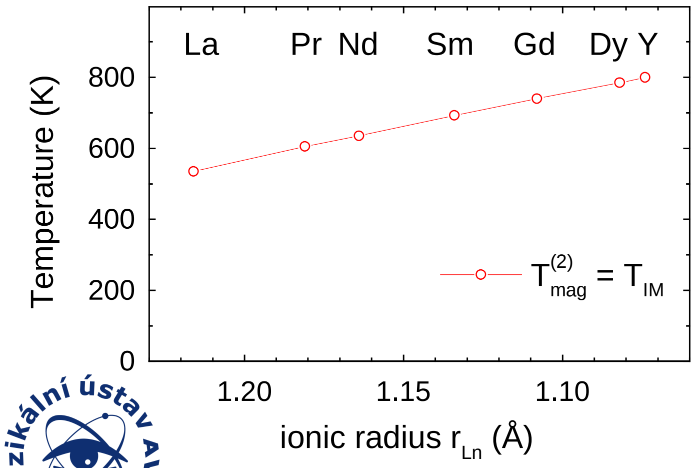
$LnCoO_3$: Electrical transport

Transition from the diamagnetic insulator to ferromagnetic metal in $La_{1-x}Sr_xCoO_3$





Transition temperatures in *Ln*CoO_3

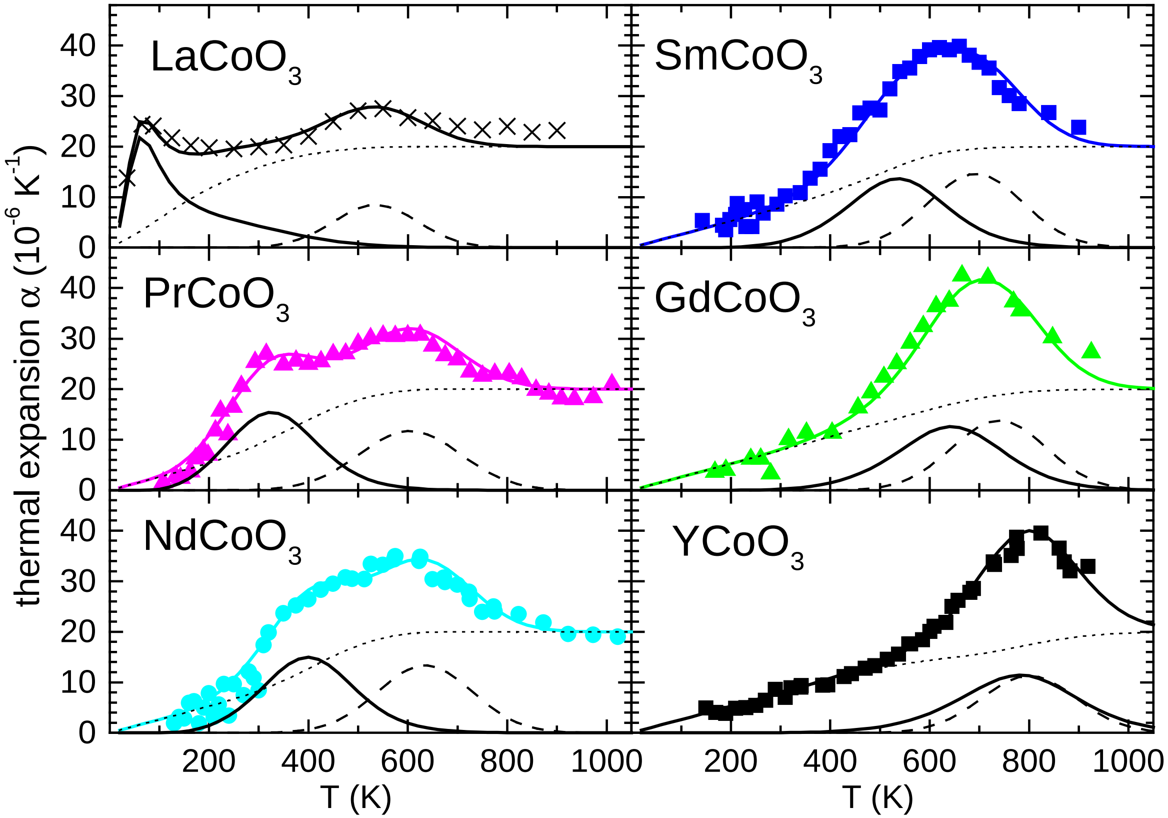


- ➢ Magnetic measurement of other $LnCoO_3$ is complicated by large mag. moment of Ln (≠La,Y,Lu).
- ➢ T_{IM} is manifested by maximum in activation energy (E_A) of resistivity (ρ) and low (metallic-like) value of thermoelectric power.
- ➢ The transition temperature T_{IM} ($T^{(2)}_{mag}$) depends linearly on Ln ionic radius.

S. Yamaguchi, et al., Phys. Rev. B 54, 11022(R) (1996).
K. Knížek, et al., Eur. Phys. J. B 47, 213 (2005).

$LnCoO_3$: Thermal expansion anomalies

- ➢ The spin transitions are reflected in anomalous thermal expansion due to the different ionic radius of Co^{3+} in LS, IS or HS
- ➢ The transition temperature $T^{(1)}_{mag}$ also depends linearly on Ln ionic radius.

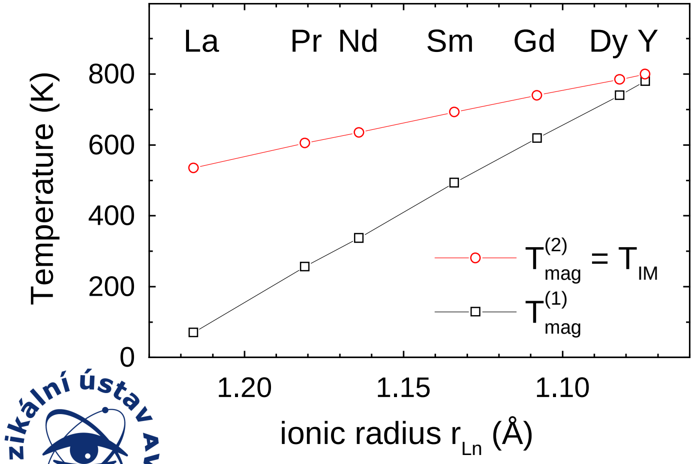


Fits of lattice thermal expansion and the three contributions:

α_{latt} (···), α_{mag} (—), $\alpha_{I\text{-}M}$ (- - -)

K. Knížek, *et al.*, Eur. Phys. J. B 47, 213 (2005).

Transition temperatures in *Ln*CoO$_3$

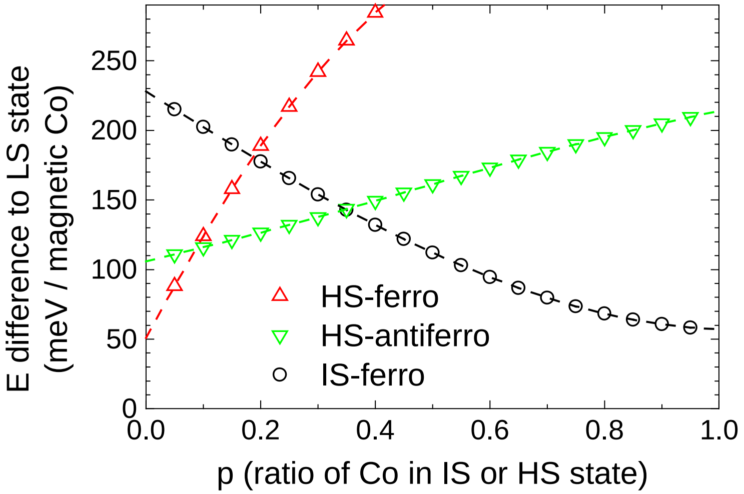


$LnCoO_3$ - summary

The magnetic susceptibility can be analyzed as excitations from ground LS state to magnetic states with 2 energy levels: (1) HS (2) IS.

However, the thermodynamic model is complex and must take into account:

1. **Dependence of the excitation energy of one Co-site on the spin state of the neighboring Co-sites (dependence of the excitation energy on the number of corresponding excited states).**
2. Varying ferro/antiferro-magnetic interactions in dependence on the population of HS state (AF) of IS states (FM) manifested in the temperature dependence of Weiss θ.
3. Dependence of the excitation energy on the temperature or pressure induced structural changes.
4. Insulating or metallic character of the spin state - possibility of Pauli susceptibility contribution.
5. HS multiplet instead of single excitation energy.



$$E(p) = E^o - E^p\, p^{1/3}$$

S. R. Sehlin, et al., Phys.Rev.B 52, 11681 (1995).

K. Knížek, et al., J. Appl. Phys. 103, 07B703 (2008):
ad 1.-3.) included in LS/LS-LS/HS-IS/IS model for analysis of thermal dilatation and magnetic susceptibility.

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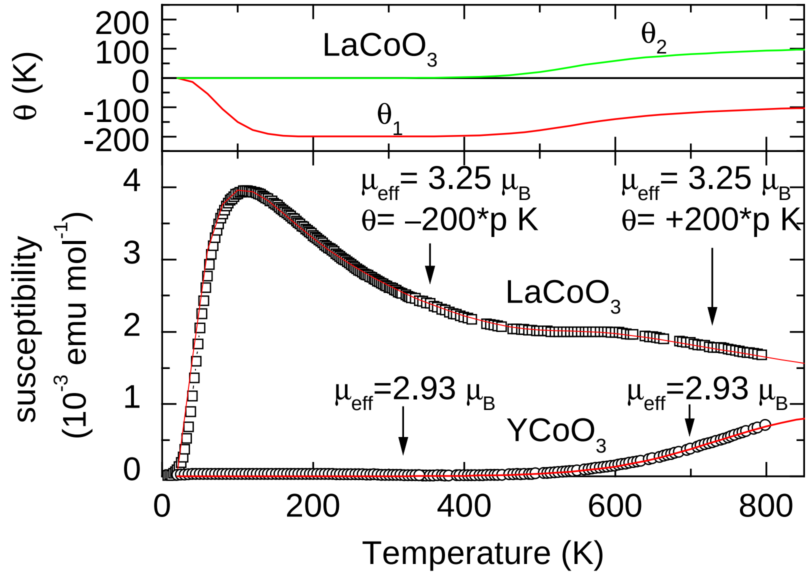

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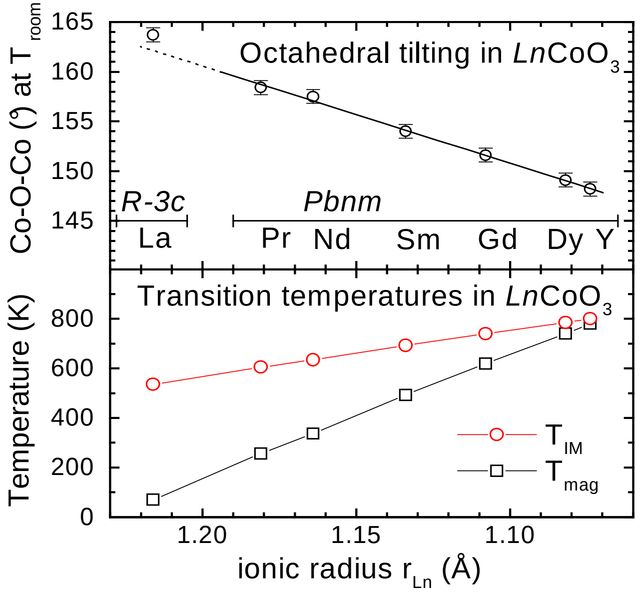

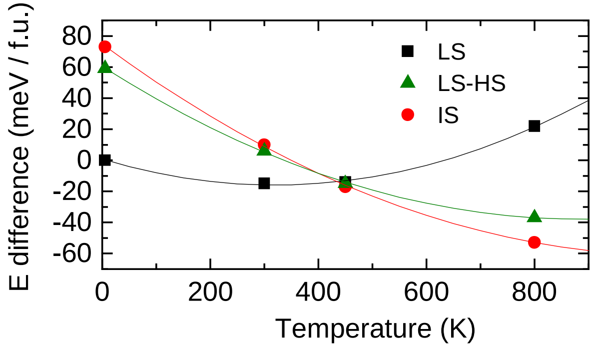

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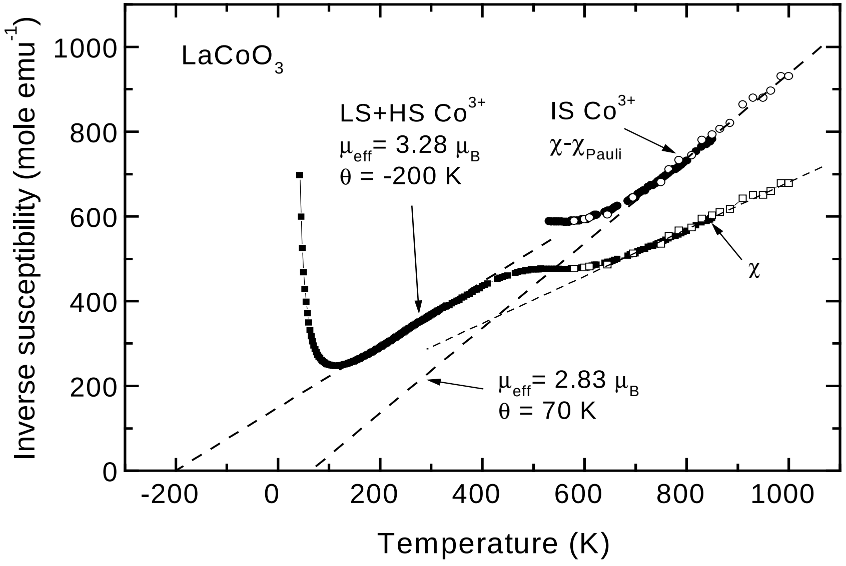

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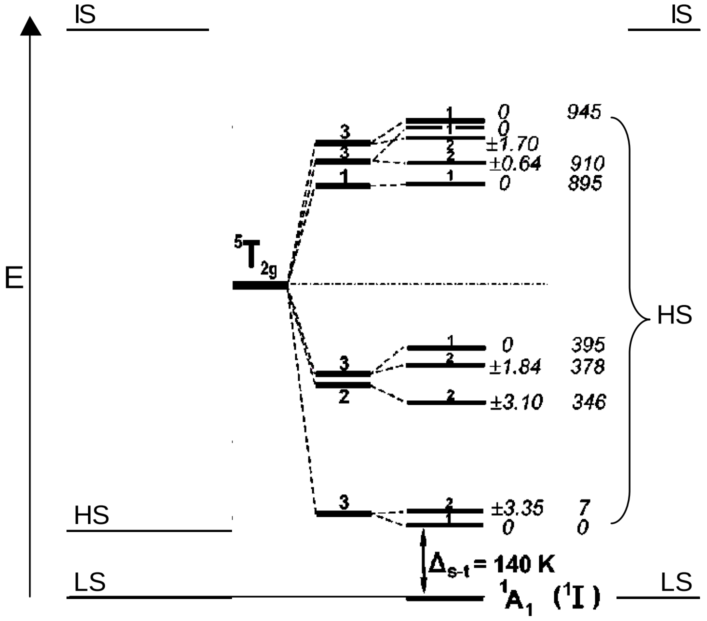

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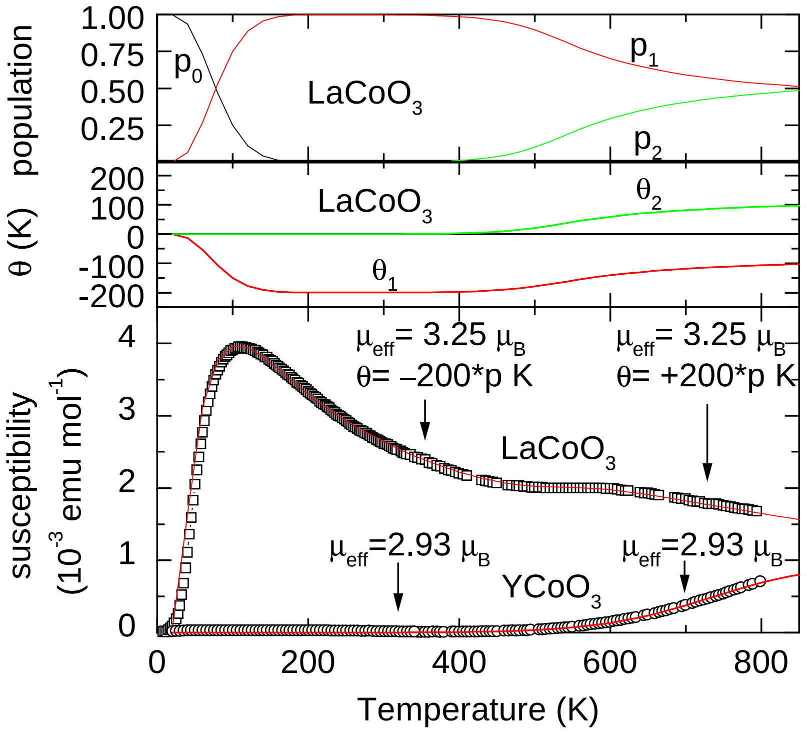
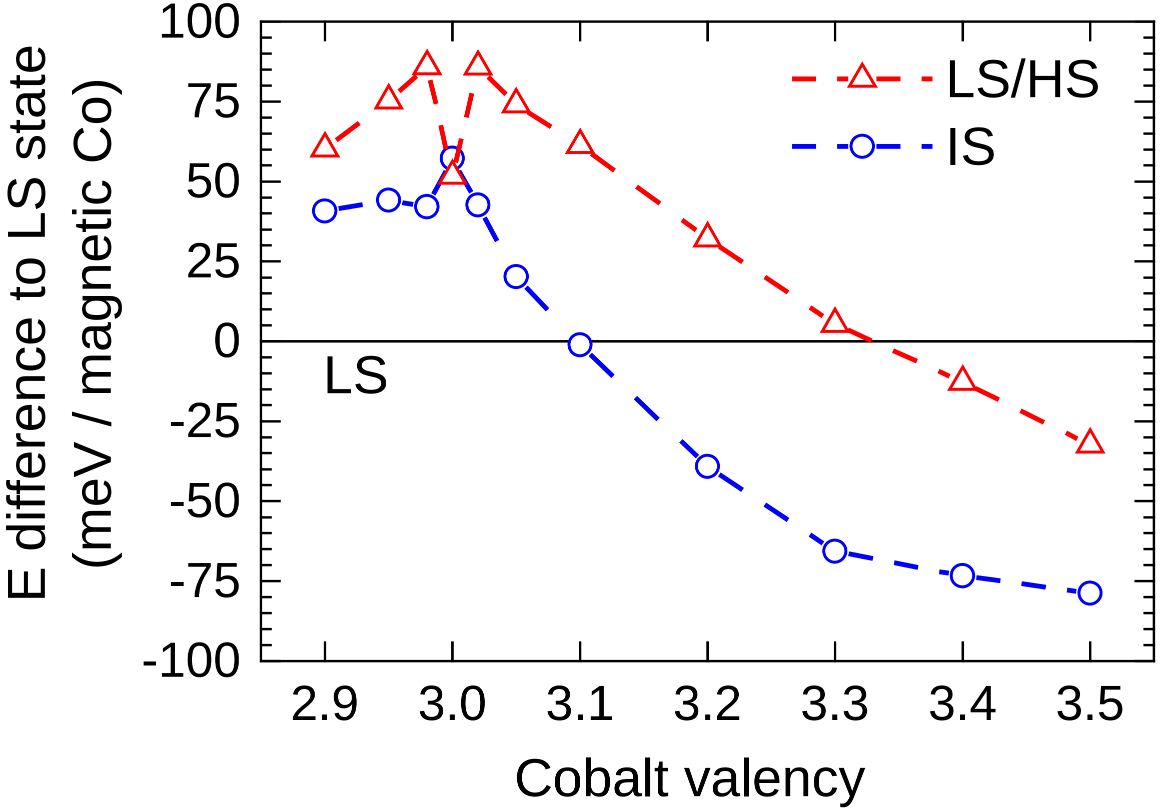


Approximation of excited pairs
(LS/LS → LS/HS → IS/IS)

K. Knížek, et al., J. Appl. Phys. 103, 07B703 (2008):
ad 1.-3.) included in LS/LS-LS/HS-IS/IS model for analysis of thermal dilatation and magnetic susceptibility.

GGA+U: dependence on doping

- Favorable energy of the mixed LS/HS state is restricted to a narrow region around the integer valence Co^{3+}, where the LS/HS state can be stabilized due to forming a gap in density of states
- In the mixed valence region, the itinerant character of IS state is more favorable.
- With increasing doping the IS state becomes ground state for x > 0.1.



Dependence of the energy of various spin configurations in $La_{1-x}Sr_xCoO_3$ on the electron or hole doping (virtual atom approximation for $La_{1-x}Sr_x$). The energy is relative to configuration with all Co in LS state.

Schematic phase diagram $La_{1-x}Sr_xCoO_3$

Transition from the diamagnetic insulator to ferromagnetic metal in $La_{1-x}Sr_xCoO_3$

Schematic phase diagram of $La_{1-x}Sr_xCoO_3$.

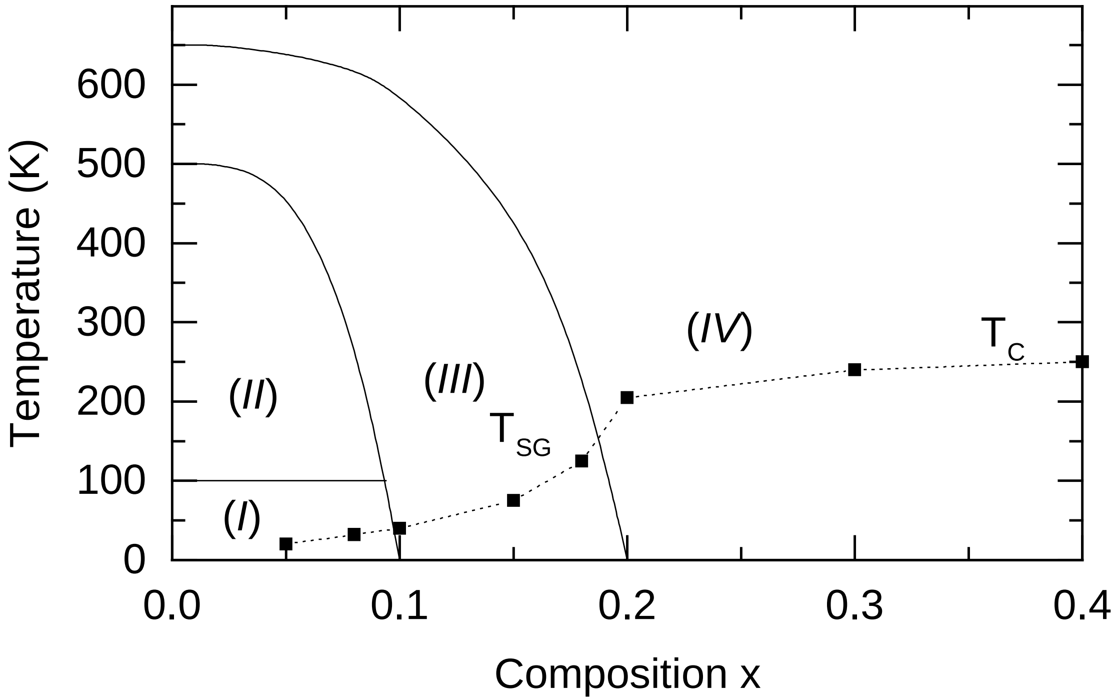
(*I*): LS Co^{3+} + polarons

(*II*): LS+HS Co^{3+} + polarons

(*III*): phase separated state (from 20% to 80% IS)

(*IV*): IS Co^{3+}/Co^{4+}.

The dotted line shows the experimentally observed spin-glass and FM critical temperatures.

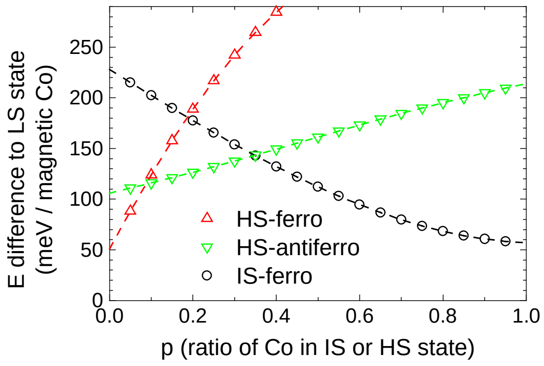


- The compositional transition in $La_{1-x}Sr_xCoO_3$ from LS phase (x=0) to IS phase (x>0) involves the same mechanisms as temperature transition in $LaCoO_3$.
- This transition occurs via a phase-separated state, where metallic IS domains coexist with the Co^{4+} poor regions in the LS ground state (low-T) or in mixed LS/HS state (higher-T).
- This phase separation vanishes when x~0.2, and a uniform IS phase is established, analogous to that in pure $LaCoO_3$ in the high-T limit.

Z. Jirák, et al., Phys. Rev. B 78, 014432 (2008)
J. Hejtmánek, et al., J. Magn.Magn.Mat. 320, e92 (2008)

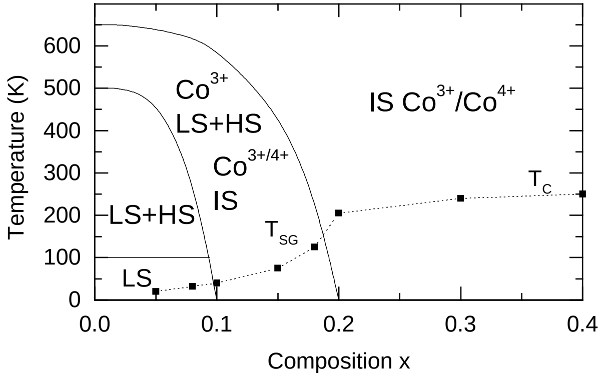
Conclusions

- ➢ The GGA+U calculation, and structural and magnetic data are consistent with the LS-LS/HS-IS model of spin transitions in $LaCoO_3$ and its rare earth analogs.
- ➢ The first step of this model consists of a local excitation of HS states in the LS matrix. With increasing number of HS states a strong HS-HS nearest neighbor correlations make further excitation less favorable and alternative configurations based on clustering of IS states become competing.
- ➢ The second step of the model is a reversal of thermally populated HS/LS pairs into IS states.
- ➢ Interactions between HS states are antiferromagnetic, whereas between IS states are ferromagnetic.
- ➢ The increase of susceptibility at the second spin transitions is due to a change of AFM interactions towards FM ones and/or onset of temperature independent Pauli paramagnetism, while the effective moments remain approximately the same.
- ➢ The hole doping in $La_{1-x}Sr_xCoO_3$ leads to a steep decrease of the LS-IS excitation energy while the LS-HS one is increased. Finally, the uniform IS ground state is stabilized.



Thank you for your attention !

www.fzu.cz/~knizek/JEMS2008.pdf



Related publications

1. K. Knížek, P. Novák, Z. Jirák, Spin state of LaCoO3; dependence on CoO6 octahedra geometry, Phys. Rev. B 71, 054420 (2005).
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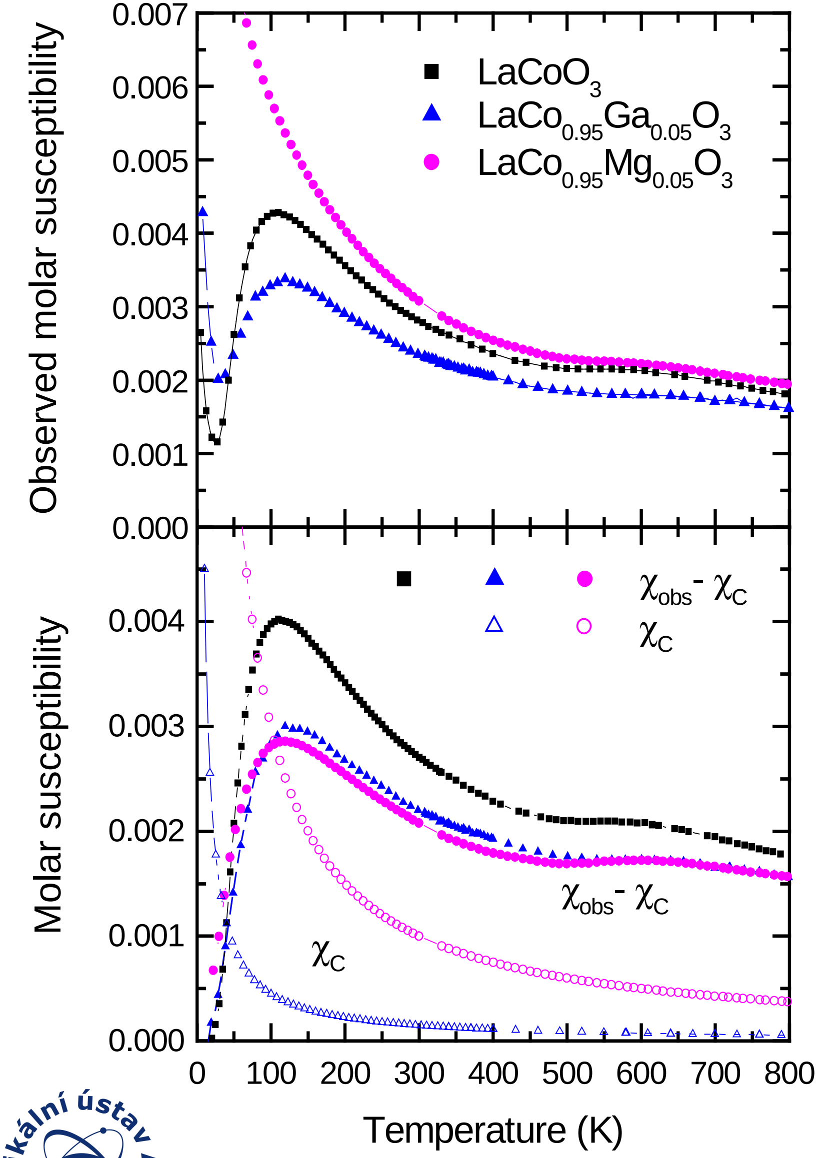
Magnetic polarons

Transition from the diamagnetic insulator to ferromagnetic metal in $La_{1-x}Sr_xCoO_3$



The susceptibility χ_{obs} can be separated into two components:

1. Magnetic background of pure $LaCoO_3$ with 2 magnetic transitions.
2. Curie type contribution, χ_C=C/T.

This observation is in agreement with previous conclusion that carriers present in lightly doped $La_{1-x}Sr_xCoO_3$ (x=0.001-0.010) generate magnetic polarons of large total spin.

When the Curie type contribution is related to the concentration of mobile holes, an estimation for size of the magnetic polarons *S* = 7 - 10 is obtained, consistent with results in the previous reports.

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