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

(spins 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
Co$^{3+}$ ion in oxides can exist in 3 spin states:

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

due to the subtle balance between:

- the crystal field $\Delta_{CF}$,
- on-site Coulomb repulsion expressed by Hubbard parameter $U$,
- the energy of charge transfer between Co and oxygen $\Delta_{Co-O}$.
LaCoO$_3$ exhibits diamagnetic-paramagnetic transition around $T^{(1)}_{\text{magn}} = 80 \text{ K}$. The second magnetic transition coupled with insulator-metal transition occurs around $T^{(2)}_{\text{magn}}(T_{\text{I-M}}) = 540 \text{ K}$.

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$_x$CoO$_3$ from LS phase ($x=0$) to IS phase ($x\sim0.2$) involves the same mechanisms as temperature transition in LaCoO$_3$.
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.

   \(T = 80 - 350\) K: IS Co\(^{3+}\);
   \(T > 600\) K: IS+HS Co\(^{3+}\)
   and partial charge disproportionation: \(2\) Co\(^{3+}\) → Co\(^{2+}\) + Co\(^{4+}\)

   \(T = 40 - 150\) 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


Electron spin resonance (ESR): $g = 3.35 \sim$ Fe$^{2+} (d^6)$ in HS state.


HS ($^5$D): triplet (3+5+7=15)
IS ($^3$H): singlet (1+3+5=9)


Analysis of low-T heat capacity and susceptibility: LS-LS+HS-IS model.
Other experiments/calculations evidencing the first excited magnetic state as HS:


- 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.

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 $\rightarrow$ HS
   AFM interactions
2. LS+HS $\rightarrow$ IS
   FM interactions
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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 promoted by LS neighbors,
- Stabilization of IS state is promoted by IS neighbors.
- HS: prefers antiferromagnetic interactions
- IS: prefers ferromagnetically aligned neighbors

Tilting of CoO$_6$ octahedra as in LaCoO$_3$ at 5 K (PRB 66, 094408) $U \sim 3$ eV
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 $E_n^S$ 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.

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

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

Tilting of CoO_6 octahedra as in LaCoO_3 at 5 K (PRB 66, 094408) \( U \sim 3 \text{ eV} \)
LaCoO$_3$ - DOS

Transition from the diamagnetic insulator to ferromagnetic metal in La$_{1-x}$Sr$_x$CoO$_3$

- LS: gap $t_{2g^{-}}e_g \sim 0.8$ eV
- LS/HS: gap $t_{2g}^{LS} - t_{2g}^{HS} \sim 0.5$ eV
- IS: half-metal

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IS: half-metal

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

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

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

LS/HS: \( \text{gap } t_{2g}^{LS} - t_{2g}^{HS} \sim 0.5 \text{ eV} \Rightarrow \) charge disproportionation:

\[
\text{LS Co}^{3+} (t_{2g}^6e_g^0) + \text{HS Co}^{3+} (t_{2g}^4e_g^2) \rightarrow \\
\rightarrow \text{LS Co}^{4+} (t_{2g}^5e_g^0) + \text{HS Co}^{2+} (t_{2g}^5e_g^2) \rightarrow \\
\]

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

- 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$_x$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 ($\rho$) and low (metallic-like) value of thermoelectric power.
- The transition temperature $T_{IM}$ ($T^{(2)}_{mag}$) depends linearly on Ln ionic radius.

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 $T^{(1)}_{\text{mag}}$ also depends linearly on Ln ionic radius.

Fits of lattice thermal expansion and the three contributions:

\[\alpha_{\text{latt}} (\cdots), \alpha_{\text{mag}} (\text{---}), \alpha_{\text{I-M}} (- - -)\]

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 $\theta$.

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.

$$E(p) = E^0 - E^p p^{1/3}$$


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**Approximation of excited pairs**

(LS/LS $\rightarrow$ LS/HS $\rightarrow$ IS/IS)


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 \(\text{La}_{1-x}\text{Sr}_x\text{CoO}_3\) on the electron or hole doping (virtual atom approximation for \(\text{La}_{1-x}\text{Sr}_x\)). The energy is relative to configuration with all Co in LS state.
The compositional transition in La$_{1-x}$Sr$_x$CoO$_3$ 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.
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$_x$CoO$_3$ 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!

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The susceptibility $\chi_{\text{obs}}$ can be separated into two components:

1. Magnetic background of pure LaCoO$_3$ with 2 magnetic transitions.
2. Curie type contribution, $\chi_C = C/T$.

This observation is in agreement with previous conclusion that carriers present in lightly doped La$_{1-x}$Sr$_x$CoO$_3$ ($x=0.001-0.010$) 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.