Structural anomalies, spin transitions and charge disproportionation in $LnCoO_3$

Karel Knůzek,1 Zdeněk Jirák,1 Jiří Hejtmánek,1 Paul Henry,2 and Gilles André3

1Institute of Physics ASCR, Cukrovarnická 10, 162 53 Prague 6, Czech Republic.
2Institut Laue Langevin, 6, rue Jules Horowitz, 38042 Grenoble Cedex 9, France.
3Laboratoire Léon Brillouin, CEA-CNRS, CEA-Saclay, 91191 Gif-s-Yvette Cedex, France.

The diamagnetic-paramagnetic and insulator-metal transitions in $LnCoO_3$ perovskites ($Ln = La$, $Y$, rare earths) systems show an insulating ground state based on the diamagnetic low spin state of trivalent cobalt (LS, $t^6_{2g}e^0_g$, $S = 0$). With increasing temperature the systems undergo two magnetic transitions connected with excitations either to the intermediate spin (IS, $t^2_{2g}e^2_g$, $S = 1$) or to the high spin state (HS, $t^4_{2g}e^2_g$, $S = 2$).

Both transitions can be easily detected in the magnetic susceptibility in the case of parent compound LaCoO$_3$. The first transition starts at about 50 K and saturated at about 150 K where a new phase is stabilized with insulating character and Curie-Weiss susceptibility. The saturated paramagnetic phase is manifested by a linear dependence of lattice volume and geometry: LS phase, $C_{LS}$, insulating character and Curie-Weiss susceptibility. The second transition of an insulator-metal (I-M) kind starts above 350 K that gives a possibility for a new interpretation of the magnetic susceptibility of LaCoO$_3$ and YCoO$_3$.

The perovskite cobaltites $LnCoO_3$ ($Ln = La$, $Y$, rare earths) systems show an insulating ground state based on the diamagnetic low spin state of trivalent cobalt (LS, $t^6_{2g}e^0_g$, $S = 0$). With increasing temperature the systems undergo two magnetic transitions connected with excitations either to the intermediate spin (IS, $t^2_{2g}e^2_g$, $S = 1$) or to the high spin state (HS, $t^4_{2g}e^2_g$, $S = 2$).

Both transitions can be easily detected in the magnetic susceptibility in the case of parent compound LaCoO$_3$. The first transition starts at about 50 K and saturated at about 150 K where a new phase is stabilized with insulating character and Curie-Weiss susceptibility. The saturated paramagnetic phase is manifested by a linear dependence of lattice volume and geometry: LS phase, $C_{LS}$, insulating character and Curie-Weiss susceptibility. The second transition of an insulator-metal (I-M) kind starts above 350 K that gives a possibility for a new interpretation of the magnetic susceptibility of LaCoO$_3$ and YCoO$_3$.

The second transition of an insulator-metal (I-M) kind starts at about 500 K and is accompanied with another increase of magnetic susceptibility and decrease of electric resistivity to a metallic value $\rho \sim 1$ m$\Omega$cm. Above the I-M transition, another region with quasilinear dependence of inverse susceptibility begins at about 600 K and spreads up to 1000 - 1100 K. There is a clear change of slope with respect to region 150 - 350 K that is traditionally interpreted as an increase of effective moments of $Co^{3+}$ while the strength of AFM interactions is retained (see e.g. Ref. [6]). We infer, however, that the observed susceptibility is a combined effect of a change of AFM interactions towards FM ones and onset of temperature independent Pauli paramagnetism, while the effective moments remain approximately the same.

This gives a possibility for a new interpretation of the spin transitions using the LS-HS-IS scenario: The diamagnetic-paramagnetic transition in LaCoO$_3$ originates in thermal population of HS states in LS matrix at about 50 K. Each $Co^{3+}$ thus appears in a mixture of these two states with increasing probability of the HS one that saturates finally in the 1:1 ratio at about 150 K because of strong HS/LS nearest neighbor correlations. The second transition (I-M) starts above 350 - 400 K and should be related to a charge disproportionation [7, 8], in which $t^2_{2g}$ electron transfer between LS/HS $Co^{3+}$ neighbors, LS $Co^{3+}$ $t^2_{2g}e^0_2g + HS$ $Co^{3+}$ $t^4_{2g}e^2_2g \rightarrow LS$ $Co^{4+}$ $t^2_{2g}e^0_2g + HS$ $Co^{2+}$ $t^4_{2g}e^2_2g$, with charge transfer gap $\sim 0.7$ eV (see Fig. 5 in Ref. [6]), is an initial step. With increasing temperature, the probability of the electron exchange increases and new IS $Co^{3+}$ states are gradually populated due to recombination reaction LS $Co^{4+}$ $t^2_{2g}e^0_2g + HS$ $Co^{2+}$ $t^4_{2g}e^2_2g \rightarrow 2 IS$ $Co^{3+}$ $t^2_{2g}e^1_2g$. This opens an $e_g$ conduction channel at about 500 K and leads finally to a formation of metallic phase of IS character that coexists with residual regions of LS/HS kind with fast dynamics. The optical conductivity data reveal indeed that this transition is associated with a collapse of the $e_g$ charge transfer gap (originally $\sim 2$ eV) and the effect of high temperature is thus analogous to the effects of heavy doping in La$_{1-x}$Sr$_x$CoO$_3$ compounds [9]. The transitions temperatures for other $LnCoO_3$ compounds are increasing with decreasing $Ln$ radius [10]. In particular, the onset of magnetic transition in YCoO$_3$ is shifted to 450 - 800 K and it develops concurrently with the I-M transition without reaching

*corresponding author: knizek@fzu.cz
the saturated LS/HS (1:1) phase.

In the present paper we apply the LS-HS-IS model to interpret the thermal expansion of Co-O bonds of $LnCoO_3$ perovskites ($Ln = La$, Pr and Nd) and quantify its parameters. The transitions are treated in a rather formal way as a two-level excitation from LS/LS pairs to LS/HS and IS/IS pairs. Since paramagnetic susceptibility is not sensitive to cobalt moments in systems with magnetic rare earths, the present analysis is primarily based on observed anomalies in thermal expansion that accompany both transitions due to the increasing ionic radius of Co$^{3+}$ with increasing spin state [10, 11, 12, 13].

The thermal expansion data have been obtained by neutron diffraction experiments, performed at low temperature in LLB (Saclay, France) on the G41 diffractometer using a wavelength 2.422 Å and at high temperature in ILL (Grenoble, France) on the D20 diffractometer using a wavelength 1.361 Å. The observed neutron diffraction patterns were analyzed by a Rietveld method with the help of the FULLPROF program (Version 3.30 - Jun2005-LLB JRC). The magnetic susceptibility was measured on a SQUID magnetometer in the range up to 400 K using DC fields 10 kOe. The high temperature data up to 900 K were obtained using a compensated pendulum system MANICS in a field of 10 - 19 kOe.

The thermal expansion $\alpha$ of $LnCoO_3$ is a sum of three contributions: normal lattice expansion $\alpha^{latt}$ and anomalous expansions due to the two spin transitions $\alpha^{mag}_i$.

(1) Lattice term $\alpha^{latt}$ is a weighted sum by populations $p_i(T)$ of thermal expansions of $LnCoO_3$ in individuals magnetic states

$$\alpha^{latt}(T) = \sum_{i=0}^{2} p_i(T) \alpha^{latt}_i(T)$$

where $i = 0$ corresponds to ground state LS pairs, $i = 1$ is the first excited state LS/HS pairs and $i = 2$ means the second excited state IS pairs. Lattice thermal expansion increases with temperature and saturates around Debye temperature $\theta_D$. In our analysis we have used the saturated values $\alpha^{latt}_0 = 14 \times 10^{-6}$K$^{-1}$, $\alpha^{latt}_1 = 18 \times 10^{-6}$K$^{-1}$, and Debye temperatures $\theta_D \sim 300$ K for LaCoO$_3$ and $\theta_D \sim 700$ K for the other $LnCoO_3$.

(2) The anomalous contribution $\alpha^{mag}$ can be expressed as

$$\alpha^{mag}_i(T) = \frac{\partial p_i(T)}{\partial T} d_i^{mag}(T)$$

where $d_i^{mag}$ is related to the difference between the size of ground and excited spin state and their dependence on temperature

$$d_i^{mag}(T) = d_i^{mag}(0) + \int_0^T \alpha_i^{latt}(T) - \alpha_i^{latt}(0) \, dT$$

In our fit we have found $d_1^{mag}(0) = 0.2\%$ and $d_2^{mag}(0) = 0.7\%$ for LaCoO$_3$ and $d_1^{mag}(0) = 0.3\%$ and $d_2^{mag}(0) = 1.0\%$ for the other $LnCoO_3$.

Population of excited states $p_i$ ($i = 1, 2$) is calculated for each temperature point by solving the set of 2 equations

$$p_i(T) = \frac{\nu_i e^{-E_i/T}}{1 - \sum_{j=1}^{2} p_j(T)}$$

where $E_i$ is the energy difference between the ground and excited states in units of $T$, and $\nu_i$ is degeneracy of the

![FIG. 1: Experimental (symbols) and fitted (lines) thermal expansion of Co-O bond for LaCoO$_3$, PrCoO$_3$ and NdCoO$_3$. The three contributions $\alpha^{latt}$, $\alpha^{mag}_1$ and $\alpha^{mag}_2$ of the fitted thermal expansion are also displayed.](image1)

![FIG. 2: Upper: Population of ground and excited states. Middle: Weiss evolution for excited states. Lower: Molar $\theta$ for excited states. The solid line is fit based on our model (see Eq. 4).](image2)
TABLE I: Ionic radii \( r_{Ln} \) for 9-fold coordination and the parameters of the thermal expansion fit for \( Ln = \text{La}, \text{Pr} \) and \( \text{Nd} \) (see Eq. 6 and 8 for description of the parameters) and of the susceptibility fit for \( Ln = \text{La} \) and \( \text{Y} \).

| \( Ln \)  | \( r_{Ln} \) (Å) | \( E_1^0 \) (K) | \( T_o \) (K) | \( n \) | \( E_2^p \) (K) | \( E_2^g \) (K) |
|----------|------------------|------------------|---------------|-----|----------------|------------------|
| \( \text{LaCoO}_3 \) | 1.216 | 160 | 100 | 3.00 | 2 460 | 2 500 |
| \( \text{PrCoO}_3 \) | 1.179 | 970 | 500 | 3.11 | 2 700 | 2 600 |
| \( \text{NdCoO}_3 \) | 1.163 | 1 200 | 500 | 3.17 | 2 800 | 2 650 |
| \( \text{YCoO}_3 \) | 1.075 | 2 875 | 860 | 3.50 | 3 600 | 3 300 |

excited state. The ground state has \( \nu_0 = 1 \). For the first excited state \( \nu_1 = 3 \) can be anticipated for spin-orbit split state of HS Co\(^{3+} \) that is isolated in diamagnetic matrix while the spin degeneracy \( \nu_1 = 2S + 1 = 5 \) is more appropriate for concentrated LS/HS pairs. For the second excitation \( \nu_2 = 2\nu_1 \) was used.

The energy difference for the first excited state \( E_1(T) \) depends on the structure changes induced by temperature \( \Delta E \) or by pressure \( \Delta P \). In our analysis the dependence of energy \( E_1(T) \) on temperature was arbitrarily fitted by a power function \( \text{[10]} \)

\[
E_1(T) = E_1^0 \left[ 1 - \left( \frac{T}{T_o} \right)^n \right] \quad \text{(5)}
\]

where \( E_1^0 \) is the energy splitting at \( T = 0 \) K, \( T_o \) is the temperature where \( E_1(T_o) = 0 \) and \( n \) is a fitting parameter that describes the curvature.

Since the stability of IS state is promoted by neighbors of the same kind, the energy \( E_2(p) \) was set to depend on the concentration \( p_2 \) by the equation \( \text{[6, 8]} \)

\[
E_2(p) = E_1(T) + E_2^p - E_2^g p_2^{1/3} \quad \text{(6)}
\]

where \( E_2^p \) is the energy splitting for \( p = 0 \) and \( E_2^g \) describes the dependence on \( p_2 \).

The experimental and calculated thermal expansion of Co-O bond for PrCoO\(_3\) and NdCoO\(_3\), completed with data on LaCoO\(_3\) taken from Ref. \([11]\), are displayed in Fig. 1.

The susceptibility was fitted by an equation

\[
\chi(T) = \frac{N_A \mu_B^2}{3k_B} \sum_{i=1}^{2} \frac{\mu_i^2 p_i(T)}{T - \theta_i(T)} \quad \text{(7)}
\]

where \( N_A \) is the Avogadro number, \( \mu_B \) the Bohr magneton, \( k_B \) the Boltzmann constant and \( \mu_i \) is the effective moment of corresponding excited state. The Weiss temperature \( \theta \) was set to depend on the population of excited states \( \theta_i(T) = \theta_i^0 p_i(T) \). In our fit we have found \( \theta_1^0 = -200 \) K, \( \theta_2^0 = +200 \) K, \( \mu_1 = \mu_2 = 3.25 \) for LaCoO\(_3\) and 2.93 for YCoO\(_3\).

The temperature dependence of \( p_i \) and \( \theta_i \) for LaCoO\(_3\) and the experimental and calculated molar susceptibility for LaCoO\(_3\) and YCoO\(_3\) are shown in Fig. 2. The parameters of the thermal expansion fit (La, Pr, Nd) and of the susceptibility fit (La, Y) are summarized in Table 1.

In conclusion, the diamagnetic-paramagnetic and insulator-metal transitions in \( LnCoO_3 \) can be successfully explained within a model of two-level excitation. The first level is the excitation of HS Co\(^{3+} \) species in the LS matrix. The steep temperature decrease of the excitation energy close to the LS-HS crossover \( (T_o) \) is a signature that the local excitations lead finally to a global phase transition. The second excitation is based on the interatomic electron transfer and stabilization of IS Co\(^{3+} \) states. The present interpretation can be characterized as a LS-HS-IS scenario that is distinct from LS-IS-HS (or LS-LS/H-S/HS/H/S) models previously used.

This work was supported by the Project No. 202/06/0051 of the Grant Agency of the Czech Republic. The Institut Laue Langevin (Grenoble, France) and the Laboratoire Leon Brillouin (Saclay, France) are thanked for providing access to the neutron beams and for all technical support during the experiments.

[1] S. Noguchi, S. Kawamata, K. Okuda, H. Nojiri, and M. Motokawa, Phys. Rev. B 66, 94404 (2002).
[2] A. Podlesnyak, S. Streule, J. Mesot, M. Medarde, E. Pomjakushina, K. Conder, A. Tanaka, M. W. Haverkort, and D. I. Khomskii, Phys. Rev. Lett. 97, 247208 (2006).
[3] M. W. Haverkort, Z. Hu, J. C. Cezar, T. Burnus, H. Hartmann, M. Reuther, C. Zobel, T. Lorenz, A. Tanaka, N. B. Brookes, H. H. Hsieh, H.-J. Lin, C. T. Chen, and L. H. Tjeng, Phys. Rev. Lett. 97, 176405 (2006).
[4] M. Zhuang, W. Zhang, and N. Ming, Phys. Rev. B 57, 10705 (1998).
[5] K. Knížek, Z. Jirák, J. Hejtmánek, and P. Novák, J. Phys.-Condens. Matter 18, 3255 (2006).
[6] R. R. Heikes, R. C. Miller, and R. Mazelsky, Physica 30, 1600 (1964).
[7] V. L. Kozehevnikov, I. A. Leonidov, E. B. Mitberg, M. V. Patrakeev, A. N. Petrov, and K. R. Poeppelmeier, J. Solid State Chem 172, 296 (2003).
[8] S. R. Sehlin, H. U. Anderson, and D. M. Sparlin, Phys. Rev. B 52, 11681 (1995).
[9] Y. Tókura, Y. Okimoto, S. Yamaguchi, H. Taniguchi, T. Kimura, and H. Takagi, Phys. Rev. B 58, R1699 (1998).
[10] K. Knížek, Z. Jirák, J. Hejtmánek, M. Veverka, M. Maryško, G. Maris, and T. T. M. Palstra, Eur. Phys. J. B 47, 213 (2005).
[11] P. G. Radaelli and S.-W. Cheong, Phys. Rev. B 66, 094408 (2002).
[12] C. Zobel, M. Kriener, D. Bruns, J. Baier, M. Grüniger, T. Lorenz, P. Reuter, and A. Revcolevschi, Phys. Rev. B 66, R020402 (2002).
[13] J. Baier, S. Jodlauk, M. Kriener, A. Reichl, C. Zobel, H. Kierspel, A. Freimuth, and T. Lorenz, Phys. Rev. B 71, 14443 (2005).

[14] T. Vogt, J. A. Hriljac, N. C. Hyatt, and P. Woodward, Phys. Rev. B 67, R140401 (2003).