PHYSICAL REVIEW B **74**, 184420 (2006)

Temperature-induced spin-state transitions in LaCoO$_3$: A two-level model

S. W. Biernacki
Institute of Physics, Polish Academy of Sciences, Aleja Lotnikow 32/46, 02-668 Warsaw, Poland

(Received 6 June 2006; revised manuscript received 14 August 2006; published 16 November 2006)

We investigate the low-spin to high-spin transition of cobalt in LaCoO$_3$. The underlying physics of the transition is related to the large totally symmetric relaxation of ligands accompanying the electron conversion from the t_{2g} to the e_g orbitals of Co^{3+}. The electron distribution function, the electronic entropy, the heat capacity, the susceptibility, and the expansion coefficient are determined using a two-level microscopic model. The gradual low-spin to high-spin transition of Co^{3+} with temperature is calculated, and the results are in good qualitative agreement with known experimental data. In order to explain the observations it is not necessary to invoke an intermediate-spin state.

DOI: 10.1103/PhysRevB.74.184420 PACS number(s): 75.10.Dg, 63.20.Kr, 64.60.−i, 65.20.+w

I. INTRODUCTION

In certain octahedral transition metal compounds, d^4, d^5, d^6, and d^7 configurations can possess two different electronic ground states depending on the temperature. The temperature-induced switching between these two states occurs in crystals with a ligand field strong enough for the Hund's rule determining the ground term to be violated.[1] Among these compounds, Co oxides have been the subject of a number of investigations. The temperature-induced transition can be a gradual function of temperature, but in some cases, it is a very steep function so that the magnetization, magnetic susceptibility, heat capacity, volume, etc., change even discontinuously.

In LaCoO$_3$ two broad transitions in the magnetic susceptibility were observed: around $20\text{ K} < T_1 < 100\text{ K}$ and $400\text{ K} < T_2 < 700\text{ K}$. There are extensive experimental and theoretical investigations of Co oxides (see Refs. 2–11). In LaCoO$_3$ the Co^{3+} ion in each CoO$_6$ octahedron is in its $t_{2g}^6 e_g^0$ configuration. This is the ground state with spin $S=0$—i.e., the low-spin (LS) configuration. The classic interpretation of the transition at T_1 is explained as the appearance of the $t_{2g}^4 e_g^2$ configuration ($S=2$)—i.e., high-spin (HS) state. Later, a different explanation of the T_1 transition was proposed invoking the configuration $t_{2g}^5 e_g^1$ with $S=1$—i.e., intermediate-spin (IS) state. In spite of numerous investigations, the microscopic nature of transitions from the LS state to the excited state is still the subject of debate.

In a recent high-resolution x-ray spectroscopy study Vankó *et al.*[2] using a theoretical analysis based on the charge transfer multiplet model concluded that the first thermal transition is best described by a transition to an orbitally nondegenerate IS state. Another investigation of resonant x-ray absorption in a high-quality LaCoO$_3$ crystal by Medarde *et al.*[3] attributes the low-temperature transition to the existence of a "covalent" IS state. In both papers are shortly reviewed a number of different experiments which include investigations of the thermal expansion, heat capacity, etc. These investigations were interpreted in terms of LS-IS or LS-HS transitions. However, recent electron spin resonance measurements by Noguchi *et al.*[4] and the results of calculations by Ropka and Radwanski[5] support a classical scenario LS-HS electron conversion for the transition.

In this work, we consider the Co^{3+} complex and we investigate the influence of the breathing type distortion of ligands, the oxygen ions. Such a distortion accompanies the thermal excitation of d electrons from the t_{2g} to e_g orbital. The derived electron occupancy of excited states differs remarkably from the Boltzmann occupancy for the same process. We calculate the electronic entropy of the transition, susceptibility, heat capacity, bond length change, and thermal expansion coefficient using only four adjustable parameters which have clear physical meaning. Our calculations are consistent with the LS-HS scenario of phase transitions.

II. TEMPERATURE-INDUCED VOLUME CHANGE

The small energy interval between two electronic configurations may be comparable with the thermal energy of nuclei. In such a case the adiabatic approximation may be violated and the nucleus motion cannot be reduced to simple vibrations in the average field of the electrons. The conventional Tanabe-Sugano diagram[1] shows that the ion with d^6 configuration changes its ground state ${}^5T_{2g} \rightleftharpoons {}^1A_{1g}$ for a specific value of the ratio between the crystal field parameter Dq and the Racah parameter B. The mechanism for the low-spin to high-spin transition is related to the change of electronic configuration $t_{2g}^6 e^0 \rightarrow t_{2g}^4 e^2$. Such a transition is accompanied by a degeneracy increase and, hence, by an entropy increase. In the frame of the adiabatic approximation, the interatomic distance is related to the electronic configuration. As it is quite difficult to estimate the absolute bond length, we shall only estimate the change in bond length caused by the promotion of electrons from the t_{2g} orbital into the e orbital.

In an octahedral field, the potential acting on an ion is of the form $V(O_h) = V(R) = D\left(x^4 + y^4 + z^4 - \frac{3}{5}r^4\right)$, where D is dependent upon the model chosen.[1] In the frame of the model used here $D \propto 1/R^\tau$, where R is the distance between the central atom and its ligands. The exponent τ would be equal to 5 in a classical charge electrostatic model while in the superposition model[12] its value can be smaller. Since $V(O_h) = V(R)$ is a function of the interatomic distance, one can make a first-order expansion of $V(R)$ in terms of the breathing-mode coordinate Q around d-shell equilibrium:

$$V(Q) = V(R) + \left(\frac{\partial V}{\partial Q}\right)_0 Q. \tag{1}$$

$(\partial V/\partial Q)_0$ can be calculated in the frame of the formalism developed by Van Vleck.[13] One finds[14,15]

$$V(Q) = V(R)\left(1 - \frac{\tau Q}{\sqrt{6}R}\right). \tag{2}$$

The average value of the energy of a d electron is expressed in terms of Dq.[1] Usually Dq is considered as a fitting parameter for a comparison with the experimental data. One gets the electronic energies of one electron in the t_2 orbital,

$$E_{t_2} = -4Dq\left(1 - \frac{\tau Q}{\sqrt{6}R}\right), \tag{3}$$

and one electron in the e orbital,

$$E_e = 6Dq\left(1 - \frac{\tau Q}{\sqrt{6}R}\right). \tag{4}$$

Thus, one sees that the electronic energies can be expressed as a function of only Dq before distortion and the totally symmetric distortion Q. Since our purpose is to give a simple explanation of the volume change accompanying the low-spin to high-spin transition, we included only the breathing distortion. The non-totally-symmetric distortions do not involve any increase of volume in the first approximation; they have been omitted.

The wave function of the low-spin term can be approximated by a single Slater determinant $|{}^1A_1, S_z=0\rangle = |\xi\bar{\xi}\eta\bar{\eta}\zeta\bar{\zeta}\rangle$ and the one of the high-spin state by $|{}^5T_2, S_z=2\rangle = |\xi\eta\zeta\bar{\zeta}uv\rangle$ (Ref. 1). The energy of each spin state is obtained by taking the average of $V(Q)$ over the Slater determinant.[14] The energy of each term can be supplemented by the elastic energy $kQ^2/2$, where k is the force constant. One obtains

$$E_{{}^5T_{2g}}(Q) = -5B - 8C + 20Dq - \frac{\tau Q}{\sqrt{6}R}20Dq + \frac{1}{2}kQ^2 \tag{5}$$

and

$$E_{{}^1A_{1g}} = \frac{1}{2}kQ^2, \tag{6}$$

where the energy origin is taken at $E_{{}^1A_{1g}}$ and B and C are the Racah parameters. Seeking the energy minimum of $E_{{}^5T_{2g}}(Q)$ with respect to Q one finds the value of corresponding distortion:

$$\Delta R = \sqrt{6}O_0 = \sqrt{6}[Q({}^5T_{2g}) - Q({}^1A_{1g})] = \frac{\tau 20Dq}{kR}. \tag{7}$$

The energy difference between the ${}^5T_{2g}$ and ${}^1A_{1g}$ terms at $Q=0$ is given by

$$E = E({}^5T_{2g}) - E({}^1A_{1g}) = -5B - 8C + 20Dq, \tag{8}$$

while the energy difference between the same terms at equilibrium minima is lowered by

$$\varepsilon = \frac{25}{2}k\left(\frac{\tau 4Dq}{\sqrt{6}kR}\right). \tag{9}$$

The energy ε is similar to the Jahn-Teller energy when one consider non-totally-symmetric distortion of orbitally degenerate term. Further, we consider the energy ε as an adjustable parameter and we assume that ε includes some portion of the Jahn-Teller energy. Equation (7) shows that the promotion of two d electrons from the t_2 orbital into the e orbital leads to an increase of the interatomic distances ΔR between the cobalt ion and its ligands. In the thermally driven low-spin to high-spin transition the electrons are excited gradually. Hence, this equation should include a multiplier n which is the fraction of excited electrons as a function of temperature. The fraction n will be derived in the next section.

III. LOW-SPIN TO HIGH-SPIN THERMAL TRANSITION

The two-level semiempirical model which includes the ground and first excited crystal terms accounts for gross aspects of the thermal transition. The free energies of the ${}^1A_{1g}$ and ${}^5T_{2g}$ crystal field states in terms of coordinate Q can be written as follows [see Eqs. (5) and (6)]:

$$f_{{}^1A_1} = \frac{1}{2}kQ^2,$$

$$f_{{}^5T_2} = E - aQ + \frac{1}{2}kQ^2 - k_BT \ln g, \tag{10}$$

where $a=\tau 20Dq/\sqrt{6}R$ is the electron-lattice coupling constant and $g=15$ is the total degeneracy of the ${}^5T_{2g}$ term. Using Eqs. (10), the statistical sum Z for the system consisting of ${}^1A_{1g}$ and ${}^5T_{2g}$ states is written as

$$\begin{aligned} Z &= \exp\left(-\frac{f_{{}^1A_{1g}}}{k_BT}\right) + \exp\left(-\frac{f_{{}^5T_{2g}}}{k_BT}\right) \\ &= \exp\left(-\frac{kQ^2}{2k_BT}\right)\left[1 + g\exp\left(-\frac{E-aQ}{k_BT}\right)\right]. \end{aligned} \tag{11}$$

At temperature 0 K, the Co^{3+} ion is in the ground state and $Q=0$. At higher temperatures the excited state with the minimum at $Q=Q_0=a/k$ is admixed to the ground state. Therefore the equilibrium coordinate is in the range $0 \leqslant Q < Q_0$. The equilibrium displacement Q for a given temperature T can be found by minimizing the free energy F which, for separate metal ions, is given as

$$F = -k_BT \ln Z = \frac{1}{2}kQ^2 - k_BT \ln\left[1 + g\exp\left(-\frac{E-aQ}{k_BT}\right)\right]. \tag{12}$$

We define high-spin distribution function n as the dimensionless coordinate $n=Q/Q_0$. At the deformation coordinate Q_0 the electron energy gain in the state ${}^5T_2$ is $\varepsilon=a^2/2k$ $=kQ_0^2/2$. Noting that $a/k=Q_0$ and $a=2\varepsilon/Q_0$ the last equation can be rewritten as

$$F = \varepsilon n^2 - k_B T \ln\left[1 + g \exp\left(-\frac{E - 2\varepsilon n}{k_B T}\right)\right]. \tag{13}$$

The condition $(\partial F/\partial n)=0$ gives the self-consistent equation for the high-spin fraction n:

$$n = \frac{1}{\frac{1}{g}\exp\left(\frac{E - 2\varepsilon n}{k_B T}\right) + 1}. \tag{14}$$

The electron occupancy of the excited term can be also obtained in an equivalent way as

$$n = \frac{\exp\left(-\frac{f_{^5T_2}}{k_B T}\right)}{Z} = \frac{1}{\frac{1}{g}\exp\left(\frac{E - 2\varepsilon \frac{Q}{Q_0}}{k_B T}\right) + 1}. \tag{15}$$

If $\varepsilon=0$, i.e., the energy separation between terms is E and n is the Boltzmann occupancy. $n \to 1$ corresponds to the high-temperature limit (well below the melting point of the material). $n \to 0$ indicates the low-temperature limit—i.e., the $(t_{2g})^6 e_g^0$ electron configuration.

The dependence of the transition-metal—ligand distance vs temperature is now given as

$$\Delta R(T) = n\frac{\tau 20Dq}{\sqrt{6}kR}. \tag{16}$$

At the critical temperature T_C the low-spin and high-spin fractions are at equilibrium—i.e., $n=1-n=1/2$. Using this condition, it follows from Eq. (14) that

$$T_C = \frac{E - \varepsilon}{k_B \ln g}. \tag{17}$$

Using expression (14) for the fraction n we derive in the next section the formula for the calculation of such functions as the heat capacity and magnetization at the crossover of the electron transition.

IV. ENTROPY, HEAT CAPACITY, SUSCEPTIBILITY, AND THERMAL EXPANSION

Now, we are going to calculate the entropy and heat capacity due to the phase transition. The corresponding entropy S is given by a standard thermodynamic equation: namely, $S=-(\partial F/\partial T)$. A straightforward derivation using Eq. (13) gives

$$S = -k_B[-n \ln g + n \ln n + (1-n)\ln(1-n)]. \tag{18}$$

The electronic heat capacity is given by

$$C_V = T\frac{\partial S}{\partial T}. \tag{19}$$

Using Eq. (19), it can be written as

$$C_V = (E - 2\varepsilon n)\frac{dn}{dT}, \tag{20}$$

where

$$\frac{dn}{dT} = \frac{n(1-n)(E - 2\varepsilon n)}{T[k_B T - 2\varepsilon n(1-n)]}. \tag{21}$$

An applied magnetic field **B** affects the various d-electron states. For our purpose it is enough to take the Zeeman interaction as $H_Z=\beta_M g_e(\mathbf{SB})$. The free energy F is modified, and the magnetic moment $M=-(\partial F/\partial B)_T$ is obtained by direct calculations.[14] If one neglects the very weak dependence of n with **B**, one gets

$$M = n g_e \beta S B_S\left(\frac{g_e \beta \mathrm{SB}}{k_B T}\right), \tag{22}$$

where $B_S(x)$ is the Brillouin function of order S.

At low field, using the first-order expansion of the Brillouin function, the mean magnetic moment can be written as

$$M = n(g_e\beta)^2\frac{S(S+1)B}{3k_B T}, \tag{23}$$

and therefore, the magnetic susceptibility is

$$\chi = N_A n(g_e\beta)^2\frac{S(S+1)}{3k_B T}, \tag{24}$$

where N_A is the number of Co^{3+} ions per unit volume. The linear expansion coefficient is defined as

$$\beta = \frac{1}{R}\frac{d\Delta R}{dT}. \tag{25}$$

Inserting ΔR from Eq. (16) one obtains

$$\beta = \frac{\tau 20Dq}{kR^2}\frac{dn}{dT}. \tag{26}$$

V. PRESSURE DEPENDENCE OF T_C

Generally, the volume change ΔV of crystal is given as the derivative of the free energy over pressure P:

$$\Delta V = \left(\frac{\partial F}{\partial P}\right)_T = -k_B T\frac{\partial \ln Z}{\partial P} = n\left(\frac{\partial E}{\partial P} - n\frac{\partial \varepsilon}{\partial P}\right). \tag{27}$$

The total volume is $V=V_0+\Delta V$, where V_0 is the volume at $T=0$ K. The variation of volume with temperature is given as

$$\frac{dV}{dT} = \left(\frac{\partial E}{\partial P} - 2n\frac{\partial \varepsilon}{\partial P}\right)\frac{dn}{dT}. \tag{28}$$

The linear thermal expansion coefficient $\beta(T)$ can be expressed as

$$\beta(T) = \frac{1}{3V}\frac{dV}{dT} = \frac{1}{3V}\left(\frac{\partial E}{\partial P} - 2n\frac{\partial \varepsilon}{\partial P}\right)\frac{dn}{dT}. \tag{29}$$

Now, we find the relationship between the expansion coefficient β, the heat capacity C_V, and the pressure derivative of T_C. Combining Eqs. (20) and (29) one finds

$$\frac{3\beta(T)V(T)}{C_V(T)} = \frac{\frac{\partial tR}{\partial P} - 2n\frac{\partial \varepsilon}{\partial P}}{tR - 2\varepsilon n}. \tag{30}$$

The last relationship is valid for any temperature in particular for $T=T_C$. At the critical temperature $n=1/2$ and the last equation gives the relationship between values of the expansion coefficient $\beta(T_C)$ and the heat capacity $C_V(T_C)$. On the other hand, from Eq. (17) one obtains

$$\frac{\frac{dT_C}{dP}}{T_C} = \frac{d\ln T_C}{dP} = \frac{\frac{\partial E}{\partial P} - \frac{\partial \varepsilon}{\partial P}}{E - \varepsilon}. \tag{31}$$

The right-hand side of Eq. (30) at T_C (with $n=1/2$) is equal to the right-hand side of Eq. (31). Therefore, finally one gets

$$\frac{dT_C}{dP} = \frac{T_C}{C_V(T_C)} 3\beta(T_C)V(T_C). \tag{32}$$

The last equation expresses the pressure dependence of dT_C/dP in terms of the expansion coefficient and the specific heat. It is known as the Ehrenfest equation. The pressure dependence of T_C will be discussed and estimated in the next section.

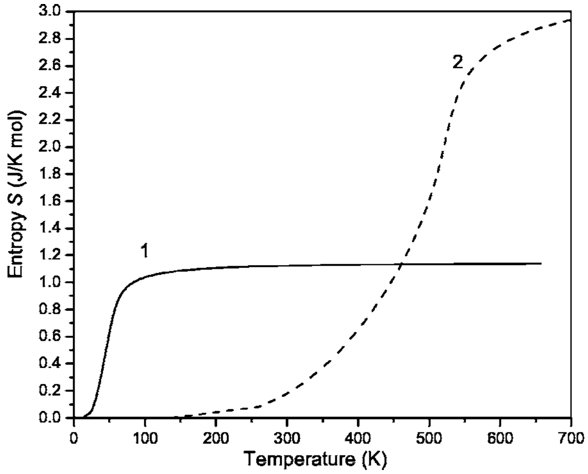

FIG. 1. Electron entropy vs temperature [drawn using Eqs. (14) and (18)]. 1: $E_1=106.9$ cm^{-1}, $\varepsilon_1=56.0$ cm^{-1}, and $g_1=3$. 2: $E_2=1254.2$ cm^{-1}, $\varepsilon_2=660.0$ cm^{-1}, and $g_2=5$. The same parameter set is used to draw Figs. 2–4.

VI. RESULTS AND DISCUSSION

The numerous experimental data show that in LaCoO$_3$ is observed electron conversion at two temperature T_1 and T_2. Hence, one should use a model with two set of levels within the term $^5T_{2g}$. The calculations of electron states with an account of the spin-orbit interaction performed in Ref. 5 clearly show three group of states with degeneracy 3, 5, and 7. The factor of spectroscopic splitting $g_{\|}=3.35$ and $g_{\perp}=3.55$ found for the lowest state with degeneracy 3 is in very good agreement with observation.[4] We assume that the electron conversion at the temperature range T_1 is associated with a transition to the lowest state and at temperature T_2 with a transition to the first excited state with degeneracy 5. Since the interval between the critical temperature in the T_1 and T_2 range is large, it is possible to make the model calculations for each interval separately. We expect that the transition to the highest state with degeneracy 7 is at higher temperature and is unobservable. This assumption is realistic because the Jahn-Teller coupling to the trigonal mode in the $^5T_{2g}$ term is weak. Neither e_g orbitals are split (when filled by two electrons with parallel spins) nor t_{2g} orbitals (when filled with three electrons with spin up and one electron with spin down). That means that the T_{2g} term is mainly split by the spin-orbit interaction. Then the observed electron conversion at T_1 and T_2 can be considered as the transition to the first and second levels. We interpret that on average some portion of two electrons is thermally promoted to the lowest level at T_1 and the other portion of two electrons is promoted at T_2. The ground state is $^1A_{1g}$ at $T=0$ K. With a temperature increase the excited state is a mixture of two electron configurations $t_{2g}^6e_g^0$ and $t_{2g}^4e_g^2$—i.e., $^1A_{1g}$ and $^5T_{2g}$. We note that in the $^5T_{2g}$ term (at $T=0$ K) two electrons stay at one-electron orbitals e which are much more strongly influenced by a covalent expansion than the lowest t_{2g} orbitals due to the high value Dq of the crystal field. The transition which involves two electrons is energetically favorable as compared with the transition where one electron is promoted to the e_g orbital while the other five stay on t_{2g}. The Tanabe-Sugano diagrams show that the term $^3T_1$ with configuration $t_{2g}^5e_g^1$ is higher in energy in a considered range of Dq/B than the term $^5T_{2g}$. The term $^3T_1$ will be shifted up even more if one takes into account a different expansion of t_{2g} and e_g orbitals, which is ignored in the Tanabe-Sugano diagrams. Even, if the transition to the IS state is supported by first principles calculations, one should take into account that these calculation ignore directly the gross aspect of two-electron Coulomb repulsion in the unfilled d electron shell. Further, we shall use the two-level model where each level is accounted for with a proper weight.

Our model includes two free parameters E and ε. We shall apply the corresponding formula twice at temperature T_1 and T_2. Therefore we need two sets of values E_1, ε_1 and E_2, ε_2. We note that the critical temperature (17) is directly related to our parameters. To model the transition at $T_1 \approx 50$ K we take $E_1=106.9$ cm^{-1}, $\varepsilon_1=56.0$ cm^{-1} and degeneracy $g_1=3$. For the transition at $T_2 \approx 500$ K we take $E_2=1254.2$ cm^{-1}, $\varepsilon_2=660.0$ cm^{-1}, and $g_2=5$. The E_1 and E_2 correspond to different energies of excited levels with respect to the ground LS state. According to Eq. (8), E_1 and E_2 are function of B, C, and Dq. ε_1 and ε_2 depend mainly on the strength of the breathing-mode distortion within an assumed “partial” electron configuration of two e_g electrons. The energy E_2 is shifted from the energy E_1 by the value following from the spin-orbit interaction.[5]

Figure 1 shows the variation of entropy for each temperature range. The entropy for the transition around T_1 was multiplied by the weighting factor 4/16 while that around T_2 by the factor 6/16 (the same weighting factors are used to draw the other figures). The entropy at T_2 is larger than at T_1 due

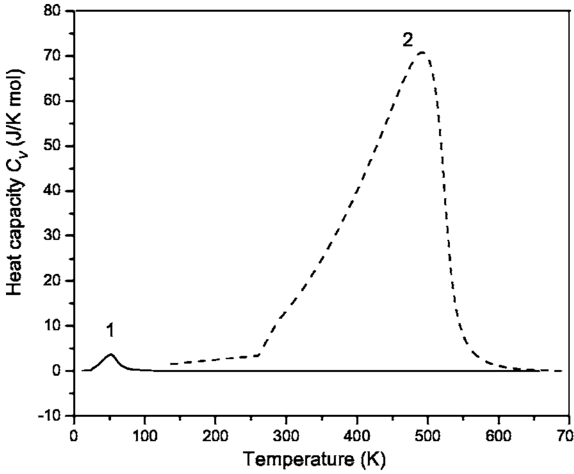

FIG. 2. Molar electron specific heat vs temperature [according to Eq. (20)]. 1: low-temperature range electron transition. 2: high-temperature transition.

to the larger orbital degeneracy. We note that this is only the electronic entropy and a comparable contribution can give the vibrational entropy. The electronic heat is shown in Fig. 2. Experimentally it is observed together with the lattice specific heat. The peak around T_2 is large, and in Fig. 1 of Ref. 11 it is shown as a broad heat capacity hump. The peak around T_1 is discussed there only using model considerations. The peak at T_2 is higher than that of T_1 not only due to the large orbital degeneracy at T_2 but also due to the larger lattice vibration heat capacity in this temperature range. This means that at T_2 the vibrational entropy is much larger than at T_1. The magnetic susceptibility is given in Fig. 3. It is in full agreement with the observation presented in Fig. 1 of Ref. 9. The peak at T_2 is much smaller than at T_1 (opposite situation to that for the specific heat). The reason for this is that spin substates at higher temperature are occupied more homogenously than spin substates of the lowest level at temperature T_1. Finally, in Fig. 4 the electronic expansion coefficient is presented (the parameters used are given below, when estimating ΔR). The calculation reproduces the observation around temperature T_1 shown in Fig. 2 of Ref. 9 which includes also the expansion due to lattice vibrations. The reason why the peak at T_2 is larger than that at T_1 is the same as in the case of the heat capacity. The increase ΔR of the interatomic distance Co–O is obtained from Eq. (16). Assuming the classical case of the crystal field with $\tau=5$, we take $R=2$ Å, $Dq=1000\ \text{cm}^{-1}$, and $n\approx 0.8$. One needs to know the force constant k of the metal-ligand bond in the octahedron surrounding the Co^{3+} ion. The metal ion participates only in the vibrational mode of symmetry T_{2g}. The ligands participate in the T_{2g} as well as in the breathing-mode distortion and some others. The force constant of the T_{2g} mode is comparable to that of the A_{1g} mode. For its estimation, the force constant of the T_{2g} mode is taken as $k=\omega^2 M$ where $\omega\approx 300\ \text{cm}^{-1}$ is the average vibrational frequency of the mode and M its reduced mass; we approximate this reduced mass by the Co ion mass. Taking the corresponding weighting coefficients one finds $\Delta R=0.04$ Å for temperature T_1 and $\Delta R=0.08$ Å for T_2. These values can be compared with the increase of the ionic radius of the Co^{3+} in HS state (0.61 Å) as compared with the LS state (0.545 Å).[10,16]

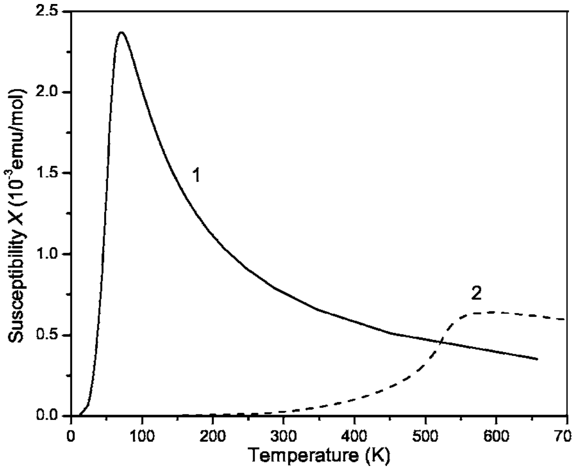

FIG. 3. Molar susceptibility χ vs temperature [according to Eq. (24)]. 1: low-temperature range electron transition. 2: high-temperature transition.

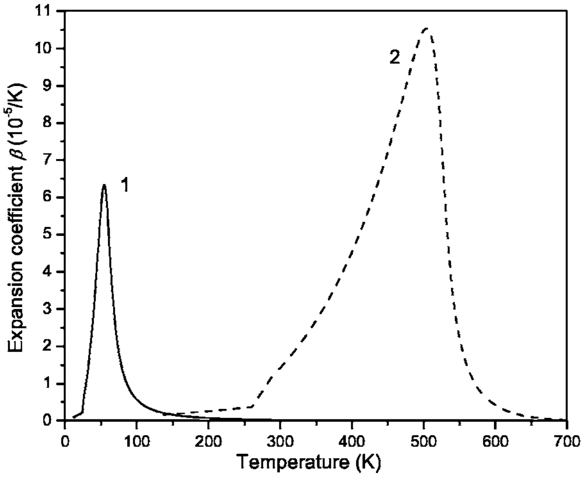

FIG. 4. Electronic expansion coefficient β vs temperature [according to Eq. (26)]. 1: low-temperature range electron transition. 2: high-temperature transition.

In LaCoO_3 the low-spin phase of cobalt coexists with the high-spin phase. The adiabatic approximation breaks around the temperatures T_1 and T_2 because the electrons are strongly coupled to the vibrations of atoms. This results in a shift of the equilibrium displacement coordinates. Therefore the low-spin state to high-spin state ratio depends on temperature as well as on pressure. Using the calculated values of $\beta(T_C)$ and $C_V(T_C)$ it follows from Eq. (32) that dT_C/dP is positive and slightly larger at T_2 than at T_1. Because the crystal volume in the low-spin state is smaller than in the high-spin state of cobalt, the pressure increase will favor the low-spin phase. This means that at elevated hydrostatic pressure the phase transition will occur at higher temperatures than at ambient pressure. At this point we mention a possible isotope shift of the critical temperature. The substitution of ^{16}O by ^{18}O decreases the Co–O bond length by 0.0005 Å. This directly

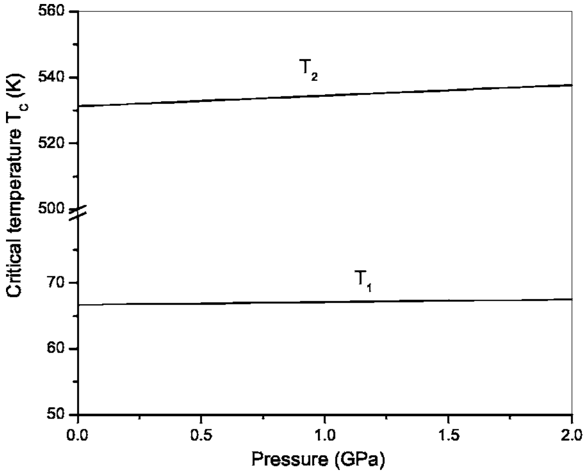

FIG. 5. The critical temperature T_C vs pressure.

influences the strength of the crystal field, and it causes an isotope dependence of T_C. However, the pressure of 0.1 GPa causes this order bond length change and, hence, the isotope substitution effect may be undetectable. It is very difficult to calculate the pressure dependence of T_C. Formula (17) contains the energy ε which changes with the bond length as $1/R^6$ and the energy E which contains the contribution Dq which varies as $1/R^5$ and B and C which varies more slowly due to the covalent effect. In our estimation we assumed that the energy varies as $1/R^5$ and we used the scaling factor $R_0/R=(PB_0'/B_0+1)^{(1/3B_0')}$ following from the Murnaghan equation of state. Taking the bulk modulus $B_0=150$ GPa and the default value of its pressure derivative, $B_0'=4.0$, and the previous values of E_1, ε_1, E_2, and ε_2 we obtained the graph shown in Fig. 5. Asai *et al.*[10] investigated the pressure dependence of the 100-K spin-state transition through magnetization measurements. Our rough estimation is in accordance with their measurements. However, above 0.5 GPa they observed a nonlinear dependence of E_1 on pressure (in their notation the energy gap between LS and IS states).

In conclusion, in this paper, we have shown that a model involving the coupling of the electronic states to totally symmetric distortions describes the main features of the low-spin to high-spin transition. In this model the energy of the upper electronic state depends indirectly on temperature by means of the term εn. Therefore the derived electron distribution function n can describe the first-order and second-order phase transitions depending on the parameters used, i.e., the distribution is a very steep or gradual function of temperature. This function possesses larger flexibility than the Boltzmann distribution function with excitation energy independent of temperature. Within one model we approximately reproduced the observed susceptibility, electronic specific heat, and expansion coefficient as well as the bond length increase for temperature T_1 and T_2. The pressure dependence of the critical temperature is also accounted for qualitatively. We explain it within the scenario of a LS to HS transition. There is no need to use the IS state to explain the experimental data.

ACKNOWLEDGMENTS

We would like to thank B. Clerjaud and A. Suchocki for fruitful discussions. This work is partially supported by a grant from the Polish Ministry of Education and Science for the years 2006–2009.

---

[1] H. Watanabe, *Operator Methods in Ligand Field Theory* (Prentice-Hall, Englewood Cliffs, NJ, 1966).

[2] G. Vankó, J.-P. Rueff, A. Manttila, Z. Nemth, and A. Shukla, Phys. Rev. B **73**, 024424 (2006).

[3] M. Medarde, C. Dallera, M. Grioni, J. Voigt, A. Podlesnyak, E. Pomjakushina, K. Conder, Th. Neisius, O. Tjernberg, and S. N. Barilo, Phys. Rev. B **73**, 054424 (2006).

[4] S. Noguchi, S. Kawamata, K. Okuda, H. Nojiri, and M. Motokawa, Phys. Rev. B **66**, 094404 (2002).

[5] Z. Ropka and R. J. Radwanski, Phys. Rev. B **67**, 172401 (2003).

[6] J. Baier, S. Jodlauk, M. Kriener, A. Reichl, C. Zobel, H. Kierspel, A. Freimuth, and T. Lorenz, Phys. Rev. B **71**, 014443 (2005).

[7] J. Q. Yan, J. S. Zhou, and J. B. Goodenough, Phys. Rev. B **70**, 014402 (2004).

[8] T. Vogt, J. A. Hriljac, N. C. Hyatt, and P. Woodward, Phys. Rev. B **67**, 140401(R) (2003).

[9] C. Zobel, M. Kriener, D. Bruns, J. Baier, M. Grüninger, T. Lorenz, P. Reutler, and A. Revcolevschi, Phys. Rev. B **66**, 020402(R) (2002).

[10] A. Asai, O. Yokokura, M. Suzuki, T. Naka, T. Matsumoto, H. Takahashi, N. Mri, and K. Kohn, J. Phys. Soc. Jpn. **66**, 967 (1997).

[11] S. Stølen, F. Grønvold, H. Brinks, T. Atake, and H. Mori, Phys. Rev. B **55**, 14103 (1997).

[12] D. J. Newman and B. Ng, in *Crystal Field Handbook*, edited by D. J. Newman and B. Ng (Cambridge University Press, Cambridge, England, 2000), Chap. 5, p. 85.

[13] J. H. Van Vleck, J. Chem. Phys. **7**, 72 (1939).

[14] S. W. Biernacki and B. Clerjaud, Phys. Rev. B **72**, 024406 (2005).

[15] S. W. Biernacki and H.-J. Schulz, Phys. Status Solidi B **200**, 173 (1997).

[16] R. Lengsdorf, M. Ait-Tahar, S. S. Saxena, M. Ellerby, D. I. Khomskii, H. Micklitz, T. Lorenz, and M. M. Abd-Elmeguid, Phys. Rev. B **69**, 140403(R) (2004).