PHYSICAL REVIEW B **67**, 144424 (2003)

Negative cooperative effect on the spin-state excitation in $LaCoO_3$

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(Received 3 March 2003; published 28 April 2003)

The experimental magnetic susceptibility and heat capacity of $LaCoO_3$ due to spin-state excitation in the range 2–300 K were well reproduced by a one-lattice molecular-field model with negative cooperative effect; an energy separation between the low-spin ground state and the excited state increases when increasing the fraction of excited Co ions. It was suggested that the negative effect originates from the difference in covalency of the Co-O bond between low-spin and excited spin states, which is supported by Al, Ga, and Rh substitution effects.

DOI: 10.1103/PhysRevB.67.144424 PACS number(s): 75.20.−g, 75.30.Wx, 75.40.Cx

I. INTRODUCTION

Spin-crossover complexes, such as $[\mathrm{Fe(phen)_2(NCS)_2}]$, show a temperature-induced phase transition from low-spin to high-spin ground states.[1] It is well known that an electron-lattice coupling is important to induce the cooperative phenomenon. This coupling is reflected by a large volume change at the phase transition. In addition, the transition entropy is much larger than the spin-only value, which originates from the intramolecular degrees of freedom in ligands. Such a spin-crossover phenomenon also occurs in $LaCoO_3$.[2–13] The crystal structure of $LaCoO_3$ is much different from complexes, which should induce a different cooperative effect on the spin-crossover phenomenon. In fact, it occurs by two steps accompanying the small and large entropy changes around 100 and 500 K,[2] but anomalous volume changes occur around both temperatures.[3]

The spin-crossover phenomenon around 100 K in $LaCoO_3$ is not a phase transition but a thermal excitation. However, the mechanism and even the spin state of the excited state are controversial at the present. One important result to make them controversial is that the experimental magnetic susceptibility below ~ 300 K is much smaller than the theoretical value calculated from Boltzmann distribution assuming the low-spin ground state $(S=0)$ and the high-spin excited state $(S=2)$. It has been attempted to explain the smallness by a temperature-dependent activation energy,[4] by 1:1 long-range or short-range ordering of the low-spin and the high-spin Co ions,[5] by an intermediate-spin excited state $(S=1)$,[3,6,7] and by an antiferromagnetic interaction between excited Co ions.[8] Another important result is that the heat capacity anomaly around 50 K is small and that the excess entropy obtained by subtracting the lattice contribution is at most $R\ln 2$ up to 300 K.[2] Even taking account of the difficulty to estimate the lattice contribution, the peak intensity of the heat capacity anomaly is much smaller than 1:3, 1:5, 1:9, and 1:15 Schottky anomalies. Stolen *et al.*[2] suggested that the excited intermediate-spin state without orbital degeneracy splits into singlet and doublet states by spin-orbit interaction, because the two levels composed of the low-spin ground state and the singlet excited state are consistent with the excess entropy of $R\ln 2$. However, this suggestion is inconsistent with the temperature dependence of the magnetic susceptibility, because the singlet excited state should be nonmagnetic.[9] In addition, a recent ESR experiment clarified that the excited state is a triplet with a large g factor (3.35).[10] However, even by using an accurate energy level structure, the magnetic susceptibility is ~ 3 times larger than the experimental one, as pointed out by the authors.[10]

In order to understand the smallness of the magnetic susceptibility and the heat capacity, the suggestion by Goodenough and co-workers is important.[5] They suggested that a thermally excited high-spin Co ion (Co^{3+}) stabilizes the low-spin state $(\mathrm{Co}^{\mathrm{III}})$ of the nearest neighbor Co ions, because six O^{2-} ions surrounding the Co^{3+} displace toward the $\mathrm{Co}^{\mathrm{III}}$ due to the weak covalency of the Co^{3+}-O^{2-} bond as compared to the $\mathrm{Co}^{\mathrm{III}}$-$\mathrm{O}^{2-}$ bond. This model reduces the number of Co ions contributing to the spin-state excitation. Such an effect would occur when the excited state is an intermediate-spin state, because the population of the e_g orbital would decrease the covalency. A similar covalency effect has been investigated as a substitution effect of Co ions in $LaSrCoO_4$ by Al or Ga ions.[14] Either 50% Al or Ga substitution stabilizes the low-spin state of Co ions in spite of the fact that the ion radius of Ga^{3+} is larger than Co^{3+} and that of Al^{3+} is smaller than $\mathrm{Co}^{\mathrm{III}}$ (see Table I). Their interpretation is that the low-spin state of Co ions is stabilized by Al or Ga substitution because the covalency of the Co-O bond is stronger than the covalency of the Al-O or Ga-O bond. Madhusudan *et al.* have reported that Al or Cr substitution of Co in $LaCoO_3$ stabilizes the low-spin state of Co ions,[11] which is consistent with this interpretation.

The effect of interaction between the excited high- and low-spin ions on the spin-state excitation has been analyzed by a molecular-field model based on the following idea.[17–20]

TABLE I. Pauling electronegativities (Ref. 15) and Shannon ion radius (Ref. 16).

Atom	Electronegativity	Ion	Radius
Co	1.8	$\mathrm{Co}^{\mathrm{III}\ a}$	0.545
		$\mathrm{Co}^{3+\ b}$	0.61
Al	1.5	Al^{3+}	0.535
Ga	1.6	Ga^{3+}	0.62
Rh	2.2	Rh^{3+}	0.665

[a] Low-spin Co.
[b] High-spin Co.

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In complexes, the energy separation between low- and high-spin states decreases with an increase in the fraction of high-spin ions (one-lattice model).[17–19] In LaCoO$_3$, the lattice was divided into two sublattices according to Goodenough's model[5] and the energy separation in one lattice increases as the fraction of high-spin ions in the other lattice (two-sublattice model) is increased.[19,20] Unfortunately, there was no quantitative comparison with the experimental data of LaCoO$_3$.

In the present study, it is shown that the two-sublattice model has difficulty is reproducing the experimental magnetic susceptibility and the heat capacity of LaCoO$_3$ simultaneously, and that the one-lattice model reproduced both the experimental data well, while the cooperative effect on the energy separation is negative. In addition, we confirmed that the substitution effect in LaCoO$_3$ is consistent with the interpretation of Demazeau *et al.*,[14] which supports that the negative cooperative effect in pure LaCoO$_3$ is connected with the difference in covalency of Co-O bond between the low-spin ground state and the excited spin state. This implies that the interaction is electronic in origin, in contrast with the main importance of electron-lattice coupling in spin-crossover complexes.

II. EXPERIMENT

A LaCoO$_3$ single crystal was grown by a floating-zone method. LaGaO$_3$ and LaCo$_{1-x}$Rh$_x$O$_3$ polycrystals were prepared by a solid-state reaction method. LaAlO$_3$, LaCo$_{1-x}$Al$_x$O$_3$, and LaCo$_{1-x}$Ga$_x$O$_3$ polycrystals were prepared by a precursor method using citric acid. La$_2$O$_3$, CoC$_2$O$_4 \cdot 2$H$_2$O, Al(NO$_3$)$\cdot 7$H$_2$O, Ga$_2$O$_3$, and Rh$_2$O$_3$ were used for the starting materials. Powder x-ray diffraction measurements using Cu $K\alpha$ radiation (MAC Science, MXP18HF) confirmed each sample to be a single phase. The crystal system of the samples was rhombohedral except for orthorhombic for LaCo$_{0.5}$Rh$_{0.5}$O$_3$, LaRhO$_3$, and LaGaO$_3$. Lattice parameters were determined by using Si as an internal standard. dc magnetizations were measured in the range 5-300 K and under 50 kOe using a superconducting quantum interference device magnetometer (Quantum Design, MPMS5S). Heat capacities were measured in the range 2-300 K by a relaxation method using PPMS (Quantum Design). The heat capacities of LaAlO$_3$ and LaGaO$_3$ were used for the base line.

III. RESULTS AND DISCUSSION

A. Substitution effect on the stability of the low-spin state

Figures 1(a), 1(b), and 1(c) show the experimental magnetic susceptibilities per Co 1 mol of LaCo$_{1-x}M_x$O$_3$ for M = Al, Ga, and Rh, respectively. The temperature showing a magnetic susceptibility peak in LaCoO$_3$ around 100 K increased as increasing x when M = Al and Ga. These substitution effects are same as those reported in LaSrCoO$_4$.[14] On the other hand, the peak disappeared even for the $x = 0.04$ sample when M = Rh. These results indicate that the low-spin state of Co ions is stabilized by Al or Ga substitution, but unstabilized by Rh substitution.

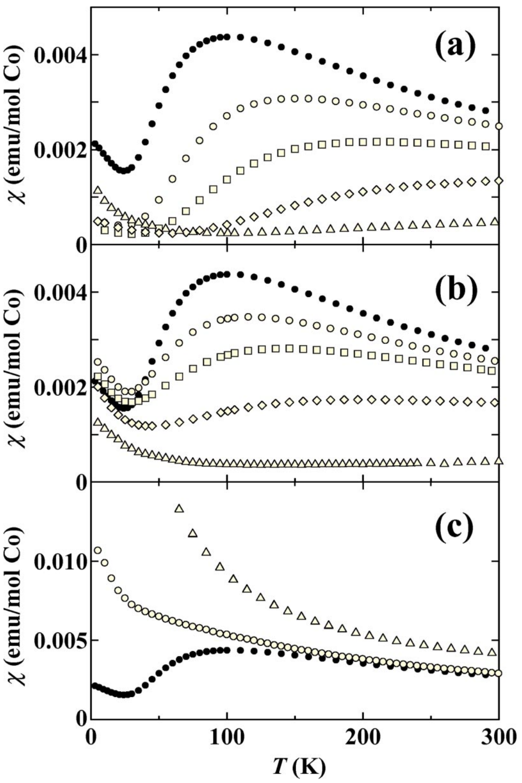

FIG. 1. Experimental magnetic susceptibility of LaCo$_{1-x}M_x$O$_3$. (a) M = Al, (b) M = Ga, (c) M = Rh: ●, $x = 0$; ○, $x = 0.04$; □, $x = 0.08$; ◇, $x = 0.19$; △, $x = 0.50$.

Figure 2(a) shows the composition dependence of the unit cell volume per formula unit at room temperature, and Figs. 2(b) and 2(c) show the lattice parameters of a rhombohedral unit cell. It is found that the composition dependences of M = Al and Ga samples deviate downward from those expected from Vegard's law, as represented by solid lines in Fig. 2(a). This indicates that the fraction of low-spin Co ions at room temperature was increased by Al or Ga substitution. On the other hand, the unit cell volume of M = Rh sample seems to deviate slightly upward from Vegard's law, indicating the decrease of the fraction of low-spin Co ions at room temperature. These results are consistent with the results of magnetic susceptibility measurements.

The Pauling electronegativity is a useful indicator to estimate the covalency. Pauling electronegativities of Co, Al, Ga, and Rh atoms are tabulated in Table I.[15] Because the electronegativity of an O atom is 3.5, the cation with larger electronegativity has a stronger covalency with an O atom. It is thus found that the covalencies of Al-O and Ga-O bonds are weaker than that of the Co-O bond, and that the covalency of the Rh-O bond is stronger than that of the Co-O bond. The order of the covalencies is intuitively right, because it is well known that the Co-O bond includes a large $d^7\underline{L}$ contribution,[6] where $\underline{L}$ is a hole in oxygen, and that Rh^{3+} ions in LaRhO$_3$ are in the low-spin state up to high temperatures.[21] Therefore, according to Demazeau *et al.*,[14] Al or Ga substitution stabilizes the low-spin state of Co ions, but Rh substitution unstabilizes the low-spin state. This is

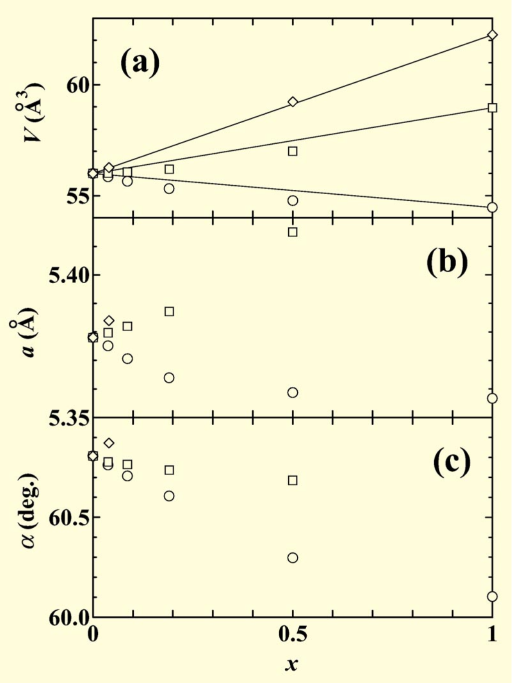

FIG. 2. (a) Unit cell volume per formula unit, (b) and (c) lattice parameters of rhombohedral unit cell for $LaCo_{1-x}M_xO_3$ at room temperature: ○, $M=Al$; □, $M=Ga$; ◇, $M=Rh$. Solid lines in (a) represent values expected from Vegard's law.

consistent with the present results. This excellent correlation implies that the factor to stabilize each spin state of Co ions in $LaCoO_3$ is much different from that of Fe ions in a spin-crossover complex, because Ganguli *et al.* mentioned that the substitution effect of Fe in $[Fe(phen)_2(NCS)_2]$ by Mn, Co, Ni, and Zn is correlated with the size of the substitution ion.[22]

B. Molecular-field calculation

The results of Sec. III A naturally suggest that an excited high- or intermediate-spin Co ion stabilizes the low-spin state of other Co ions, as mentioned in Sec. I. However, the two-sublattice model did not reproduce the experimental magnetic susceptibility and heat capacity of $LaCoO_3$, the details of which are described in Sec. III B 2. On the other hand, the one-lattice model well reproduced the experimental data, as described in Sec. III B 1. In these calculations, we ignored magnetic interaction between the excited Co ions, because only a small ferromagnetic correlation has been reported to exist in $LaCoO_3$ even at room temperature.[12] The weak magnetic interaction can be understood by considering that the excited Co ions are apart from each other because of the repulsive interaction between the excited Co ions.

1. One-lattice model

According to one-lattice model,[17,19,18] the total Gibbs free energy including the interaction enthalpy term $H_{\rm int}$, is expressed by

$$G=(1-f)G_{\rm LS}+fG_{\rm ES}-TS_{\rm mix}+H_{\rm int}, \tag{1}$$

TABLE II. Excited states used for calculations and the reproducibilities of calculation

Excited state	S	g	ν	1 [a]	2 [b]
I	1	2	3	C	C
II	1	2	3×3	C	C
III	1	3.35	3	A	D
IV	1	3.35	3×3	B	D
V	2	2	5	A	D
VI	2	2	5×3	B	D

[a] Reproducibility of one-lattice model.

[b] Reproducibility of two-lattice model.

$$S_{\rm mix}=-R\{(1-f)\ln(1-f)+f\ln f\}, \tag{2}$$

where $G_{\rm LS}$ and $G_{\rm ES}$ are Gibbs free energies when all Co ions are in low-spin and excited spin states, respectively, f is a fraction of excited spin Co ions, and $S_{\rm mix}$ is a mixing entropy. The equilibrium condition $\partial G/\partial f=0$ gives

$$f=\frac{\nu}{\nu+\exp(\Delta/RT)}, \tag{3}$$

$$\Delta=H_{\rm ES}-H_{\rm LS}+\frac{\partial H_{\rm int}}{\partial f} \tag{4}$$

$$=\Delta_0+\Delta_1 f+\Delta_2 f^2+\Delta_3 f^3+\cdots, \tag{5}$$

where $H_{\rm LS}$ and $H_{\rm ES}$ are enthalpies when all Co ions are in the low-spin and excited spin states, respectively, and ν is a degeneracy of an excited Co ion. The magnetic susceptibility and heat capacity are expressed by

$$\chi=fN_{\rm A}\frac{g\mu_{\rm B}^2S(S+1)}{3k_{\rm B}T}, \tag{6}$$

$$C=T\frac{\partial}{\partial T}\{S_{\rm mix}+fR\ln\nu\}. \tag{7}$$

f was determined by a self-consistent method at each temperature, and the Δ_i's in Eq. (5) were determined by a nonlinear least-square fitting of the magnetic susceptibility data using the sum of Eq. (6) and a Curie-Weiss term, $C_{\rm CW}/(T-T_{\rm C})$. The heat capacity was calculated by using Δ_i's obtained by the fitting. Δ was expanded up to three orders of f, because at least four terms were necessary in order to reproduce the experimental magnetic susceptibility. Six excited states labeled by I–VI were assumed for the calculations as tabulated in Table II. The quality for the calculation to reproduce the experimental magnetic susceptibility and heat capacity was ranked by A–D in the order of goodness, which were described in the fifth and sixth columns of Table II.

The open circles in Fig. 3(a) represent the experimental magnetic susceptibility of $LaCoO_3$. The solid lines in the figure are the calculated curves for six excited states. All the curves reproduced the experimental data, though a small deviation exists at high temperature region. The open circles

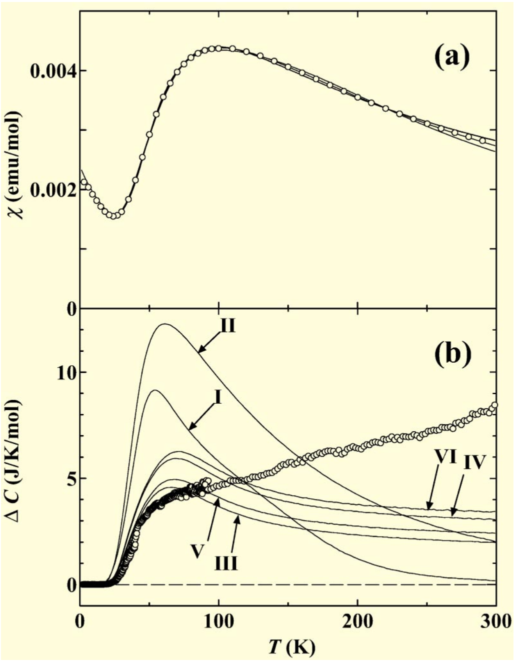

FIG. 3. (a) Magnetic susceptibility and (b) excess heat capacities of $LaCoO_3$: Solid circles and solid lines represent the experimental and the calculated values for one-lattice models with the excited states of I–VI, respectively.

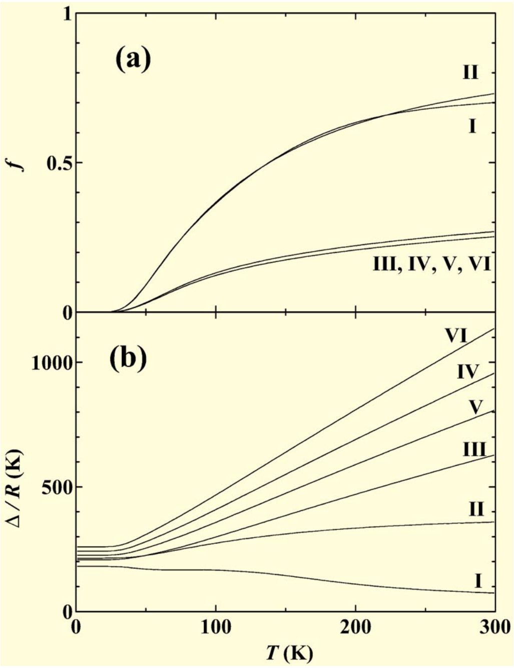

FIG. 4. (a) Calculated fraction of excited spin Co ions and (b) calculated enthalpy separation between the low-spin and the excited spin states of $LaCoO_3$ for one-lattice models with the excited states of I–VI.

in Fig. 3(b) represent the experimental excess heat capacities of $LaCoO_3$. The excess heat capacities were estimated by subtracting a base line,

$$C_{\mathrm{base}}=(1-x)C_{\mathrm{LaGaO_3}}+xC_{\mathrm{LaAlO_3}}, \tag{8}$$

where $C_{\mathrm{LaGaO_3}}$ and $C_{\mathrm{LaAlO_3}}$ are experimental heat capacities of $LaGaO_3$ and $LaAlO_3$, respectively. $x=0.33$ was chosen for C_{base} to coincide with the heat capacities of $LaCoO_3$ below 10 K. The excess heat capacity of $LaCoO_3$ increases exponentially as increasing temperature and showed a shoulder around 50 K instead of a peak. The magnitude of the shoulder is $\sim 1/2$ or $\sim 1/3$ as large as the peak of the 1:3 or 1:5 Schottky anomaly, as pointed out by Stolen *et al.*[2] The solid lines in Fig. 3(b) represent the calculated curves for six excited states. The excited states III and V well reproduced the magnitude of the shoulder. The reproducibility is indicated by A in the fifth column of Table II. The larger experimental data at high temperatures are possibly due to the underestimation of the base line, because the expanded volume due to the excitation of the excited spin state would decrease the atomic force constant and thus increase the excitation of lattice vibration. In fact, an anomalous lattice softening has been observed with increasing temperature.[13] The excited states I and II are not appropriate for the actual excited state, because the peaks around 60 K are about 2–3 times larger than the experimental shoulder. The reproducibility in this case is indicated by C. Taking account of the difficulty in estimating the lattice contribution, the calculated curves of IV and VI might have well reproduced the shoulder intensity. The reproducibility is indicated by B.

Figures 4(a) and 4(b) show the calculated f and Δ/R, respectively. The temperature dependences of f are similar for III to VI, and f is less than 30% even at 300 K. The small f is consistent with the assumption of ignoring the magnetic interaction between the excited Co ions. Except for I, Δ increases with increasing temperature. Such a temperature dependence is the same as reported by Naiman *et al.*[4] Naiman *et al.* considered the following. The $^5T_2$ level in a cubic crystal field splits into sublevels due to the rhombohedral distortion of $LaCoO_3$. Because the rhombohedral distortion decreases with increasing temperature, the splitting of the $^5T_2$ level decreases and thus the energy separation between the low-spin ground state and the lowest sublevel of $^5T_2$ increases with increasing temperature. This consideration is interesting because the rhombohedral distortion was actually decreased by Al or Ga substitution, as shown in Fig. 2(c). However, the unit cell volume increases with increasing temperature. This volume effect unstabilizes the low-spin state and decreases the energy separation between the low-spin state and the center of gravity of $^5T_2$ sublevels, as mentioned by Naiman *et al.* themselves.[4] Thus, the temperature dependence of the energy separation between the low-spin ground state and the lowest $^5T_2$ sublevel should be determined by the relative strength of the volume effect and the rhombohedral distortion effect if only the structural effects are taken into account. However, it is difficult to consider that the rhombohedral distortion effect is larger than the volume effect. Therefore, it is natural to interpret that Δ increases with increasing f (not temperature). This phenomenon is similar to the negative cooperative effect reported in binuclear iron (II) helicates in propylene carbonate.[23] This effect is opposite to that in the crystalline spin-crossover complex, in which Δ decreases with increasing f (positive cooperative effect), namely, the excitation of a high-spin ion accelerates the excitation of the other ions and thus induces a cooperative spin-state phase transition. The negative cooperative effect never induces a phase transition. This is also different from Goodenough's model,[5] because he considered that the excitation of a high-spin Co ion stabilizes the low-spin state of Co ions in the nearest neighbor sites and the high-spin state in the next nearest neighbor sites, which also induces a phase transition to a rock-salt-type ordering of Co^{3+} and $\mathrm{Co}^{\mathrm{III}}$ when the interaction is large.[19]

The negative cooperative effect would be connected mainly not with the elastic property but the electronic state, because the substitution effect is correlated not with the ion size but the electronegativity. In addition, the band nature of Co $3d$ electron system might be connected with the long-range character, in that the excitation of a Co ion has an influence on the electronic state of Co ions far from the excited Co ion.

2. Two-sublattice model

The same calculation as in Sec. III B 1 was carried out by using two-sublattice model according to Bari *et al.*[19] In this model, energy separations of sublattices A and B are represented by

$$\Delta_{\mathrm{A}}=\Delta_0+\Delta_1 f_{\mathrm{A}}+\Delta_2 f_{\mathrm{B}}, \tag{9}$$

$$\Delta_{\mathrm{B}}=\Delta_0+\Delta_1 f_{\mathrm{B}}+\Delta_2 f_{\mathrm{A}}, \tag{10}$$

where $\Delta_1 \leqslant 0$ and $\Delta_2 \geqslant 0$. The experimental magnetic susceptibility can not be reproduced by two-sublattice model with excited states of III, IV, V, and VI. The reproducibility in this case is indicated by D in Table II. It is easily found from the following fact. The two-lattice model gives a minimum of magnetic susceptibility peak around 100 K when only half of Co ions excite thermally with a constant activation energy, namely, $\Delta_1=0$ and $\Delta_2=\infty$. Even in this case, the calculated magnetic susceptibility exceeds the experimental value when the excited states of III, IV, V, and VI are assumed. The experimental magnetic susceptibility were reproduced by two-sublattice model with excited states of I and II. However, the heat capacities calculated by using Δ_i's obtained by a least-square fitting of the magnetic susceptibility data are about 2–3 times larger than the experimental one. The calculated heat capacity curves are similar to those of one-lattice model with excited states of I and II. These results conclude that two-sublattice model is not appropriate for the mechanism of spin-state excitation in $\mathrm{LaCoO_3}$.

IV. CONCLUSION

In conclusion, experimental magnetic susceptibility and heat capacity of $\mathrm{LaCoO_3}$ due to spin-state excitation in the range 2–300 K were well reproduced by a one-lattice molecular-field model with negative cooperative effect. The calculation suggests that III or V in Table II are most probably excited states, and that I and II are unsuitable. It is important that even in either III or V (and IV or VI), the negative cooperative effect is necessary to reproduce the small heat capacity anomaly. The low-spin state of Co ions in $\mathrm{LaCoO_3}$ was stabilized by Al or Ga substitution. This suggested that the negative cooperative effect occurring in pure $\mathrm{LaCoO_3}$ is connected with the covalency of a Co-O bond weaker in the excited state than in the ground low-spin state, which was originally suggested by Goodenough and co-workers.[5]

The negative cooperative effect would be the reason why the spin-state excitation below ~ 300 K in $\mathrm{LaCoO_3}$ does not occur as a phase transition. The difference in the cooperative effect between $\mathrm{LaCoO_3}$ and the spin-crossover complex originates from the difference in not only the elastic property but also the electronic state of the $3d$ electron system originating from the entirely different crystal structure.

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