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# Thermodynamical analysis of spin-state transitions in $LaCoO_3$: Negative energy of mixing to assist thermal excitation to the high-spin excited state

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Magnetic susceptibility and heat capacity due to the spin-state transition in $LaCoO_3$ were calculated by a molecular-field model in which the energy-level diagram of high-spin state reported by Ropka and Radwanski [Phys. Rev. B **67**, 172401 (2003)] is assumed for the excited state, and the energy and entropy of mixing of high-spin Co ions and low-spin Co ions are introduced phenomenologically. The experimental data below 300 K were well reproduced by this model, which proposes that the high-spin excited state can be populated even if the energy of high-spin state is much larger than that of low-spin state, because the negatively large energy of mixing reduces the net excitation energy. The stability of each spin state including the intermediate-spin state is discussed based on the present results and other reports.

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## I. INTRODUCTION

Perovskite-type cobalt oxides, such as $LnCoO_3$ (Ln denotes a rare-earth element),[1–5] $LnBaCo_2O_{5.5}$,[6–12] and $Pr_{0.5}Ca_{0.5}CoO_3$,[13–15] attract many researchers because of the peculiar temperature-induced spin-state transitions. The spin-state transitions are closely connected with electrical conductivity and often appeared as a metal-insulator transition. This connection implies that stability of a certain spin state is determined by not only crystal field and Hund's coupling but also by transfer energy and electron correlation. Because the competition of four (or more) energies is absent for either spin-crossover phenomena in complexes or metal-insulator transitions in transition-metal oxides, the spin-state transitions in perovskite-type cobalt oxides are interesting to advance the physics of 3*d*-electron systems in solids. However, it is still unclear what kinds of spin state are realized even in the most simple perovskite-type cobalt oxide, $LaCoO_3$.

The magnetic susceptibility of $LaCoO_3$ shows a broad maximum around 100 K.[1–5] This behavior has been understood as a spin-state transition of $Co^{3+}$ ions from the low-spin ground state with configuration $t_{2g}^6$ to the excited state. The excited state is unclear even at present. According to Tanabe-Sugano diagram,[16] only a high-spin state with configuration $t_{2g}^4e_g^2$ is probable for the excited state with the small excitation energy ~180 K. However, Potze *et al.* proposed that intermediate-spin state with configuration $t_{2g}^5e_g^1$ is possible for the excited state when the ligand hole state is important.[17] In addition, Korotin *et al.* reported that the energy of high-spin state of $LaCoO_3$ is much larger by 0.65 eV than that of low-spin state.[18] Since their reports, many experimental and theoretical results have been reported and discussed in connection with the excited state.[19–26]

Many research groups reported that the experimental magnetic susceptibility is well reproduced by a model assuming temperature-independent excitation energy and the intermediate-spin excited state, with spin quantum number 1, *g* factor 2, and orbital degeneracy 1 or 3.[20–22] However, this model is inconsistent with the heat capacity data[19,24] and the results of an electron spin resonance (ESR) experiment[23] as mentioned below. The solid circles in Fig. 1 represent the heat capacity of $LaCoO_3$.[24] The dashed and dotted lines in the figure are heat capacity curves of 1:9 and 1:3 Schottky anomalies, respectively, with a temperature-independent excitation energy 180 K, where numerals surrounding the colon are degeneracies of the ground state and excited state, respectively. It is found that the 1:9 Schottky anomaly exceeds the experimental heat capacity. This model is clearly improper, because the experimental heat capacity includes not the only the electronic contribution but also lattice contribution. Even the 1:3 Schottky anomaly would be improper for the following reason. The open squares and triangles in Fig. 1 represent the heat capacities of $LaAlO_3$ and $LaGaO_3$, respectively.[24] It is found from the figure that if the 1:3 Schottky anomaly were present, the lattice heat capacity of $LaCoO_3$ should be comparable to or smaller than the heat capacity of $LaAlO_3$ at least around 60 K. Taking account of the fact that either the formula weight or unit cell volume of $LaCoO_3$ is close to that of $LaGaO_3$ rather than that of $LaAlO_3$, the lattice heat capacity of $LaCoO_3$ should be close to that of $LaGaO_3$ rather than that of $LaAlO_3$. Therefore, it is natural to consider that the actual heat capacity anomaly in $LaCoO_3$ is smaller than the 1:3 Schottky anomaly, as firstly pointed out by Stolen *et al.*[19] In 2002, Noguchi *et al.* reported the results of an ESR experiment of $LaCoO_3$.[23] They showed that the excited state is a triplet and the *g* factor is 3.35. According to these authors, the magnitude of the *g* factor is close to the value of high-spin $Fe^{2+}$ ions doped in MgO. In addition, Ropka and Radwanski succeeded in describing the ESR results by the atomiclike term $^5D$.[25] These reports imply that the excited state is a high-spin state. However, Noguchi *et al.* pointed out that the magnetic susceptibility calculated using the triplet state and assuming a temperature-independent excitation energy is 2–3 times larger than the experimental one.[23] But this is consistent with what was mentioned above, namely, the 1:3 Schottky anomaly is larger than the experimental heat capacity anomaly. Thus, the results of heat capacity and ESR studies imply that the population of the excited state is much smaller than that expected from the calculation assuming the

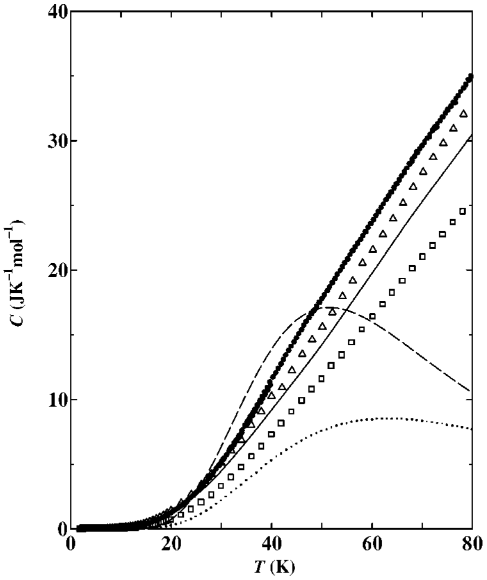

FIG. 1. Heat capacities: Solid circles, $LaCoO_3$; open squares, $LaAlO_3$; open triangles, $LaGaO_3$; dashed line, 1:9 Schottky anomaly; dotted line, 1:3 Schottky anomaly; solid line, lattice contribution supposed for $LaCoO_3$.

temperature-independent excitation energy. (It should be noted that the calculated magnetic susceptibility is reduced by introducing the antiferromagnetic interaction as reported in some papers,[4,5] but on the other hand, the heat capacity is not reduced appreciably by introducing a magnetic interaction because the number of energy levels does not change.) Based on this consideration, we proposed in our previous paper[24] that the excitation energy increases with increasing population of Co ions in the excited state and thus with increasing temperature. This model, assuming the triplet excited state reported by Noguchi *et al.*,[23] well reproduced both the experimental magnetic susceptibility and small heat capacity anomaly around 50 K. However, the reproducibility was poor for the heat capacity above 100 K.

The high-spin excited state looks inconsistent with the energy difference, 0.65 eV, between low-spin and high-spin states calculated by the local spin density approximation $(\mathrm{LDA})+U$ approach,[18] because the actual excitation energy is about 180 K at least at low temperatures. However, it should be noted that their calculations[18] were carried out only for three pure states such that all Co ions are in the low-spin, intermediate-spin, or high-spin state. Therefore, their calculations never predict the effect of mixing two or three kinds of Co ions in different spin states. In general, the energy of a mixture is not equal to the sum of energies of pure components. For example, when water and sulfuric acid are mixed, a large heat evolution occurs, which indicates that the enthalpy of the mixture is smaller by the evoluted heat than the sum of the enthalpies of pure water and pure sulfuric acid. The evoluted heat is referred to as enthalpy of mixing. In fact, Zhuang *et al.*[26] reported the importance of mixing effects by theoretical calculations using the unrestricted Hartree-Fock approximation of the multiband *d-p* model. The results are tabulated in Table I in addition to the results of Korotin *et al.* The results of Zhuang *et al.* indicate that the energy of state in which 50% high-spin Co and 50% low-spin Co ions are ordered in a rock-salt type is much smaller than the average of energies of two pure states in which all Co ions are in the low-spin state and in which all Co ions are in the high-spin state, and furthermore smaller than the energy of pure state in which all Co ions are in the intermediate-spin state.

TABLE I. Energies of states in which Co ions are of low-spin (LS), intermediate-spin (IS), or high-spin (HS) state reported by Korotin *et al.* (Ref. 18) and Zhuang *et al.* (Ref. 26).

| State | Energy (eV)[18] | Energy (eV)[26] |
|---|---|---|
| 100% LS | 0 | 0 |
| 100% IS | 0.24 | 0.19 |
| 100% HS | 0.65 | 0.66 |
| 50% LS/50% IS[a] | - | ~0.20 |
| 50% LS/50% HS[b] | - | ~0.05 |

[a] LS Co and IS Co ions are ordered in a rocksalt type.

[b] LS Co and HS Co ions are ordered in a rocksalt type.

In the present paper, magnetic susceptibility and heat capacity due to the spin-state transition in $LaCoO_3$ are recalculated by a molecular-field model using the full energy level diagram reported by Ropka and Radwanski.[25] This calculation reproduced the experimental magnetic susceptibility and heat capacity up to 300 K well. This result suggests that the enthalpy of the mixing of high-spin Co ions and low-spin Co ions is negatively large and thus the high-spin state can be populated even around 50 K, even if the energy of pure state in which all Co ions are in the high-spin state is much larger than the energy of another pure state in which all Co ions are in the low-spin state. The stability of each spin state is discussed based on the present results and theoretical results reported by Korotin *et al.*[18] and Zhuang *et al.*[26] It is found that the present results are consistent with their results.

## II. CALCULATION METHOD

In the following, energy is used instead of enthalpy for simplification. The total Helmholtz free energy is expressed by

$$F = E - TS \tag{1}$$

$$= (1-f)F_{\mathrm{LS}} + fF_{\mathrm{HS}} + E_{\mathrm{mix}} - TS_{\mathrm{mix}}, \tag{2}$$

$$S_{\mathrm{mix}} = -R\{(1-f)\ln(1-f) + f\ln f\}, \tag{3}$$

where $F_{\mathrm{LS}}$ and $F_{\mathrm{HS}}$ are the Helmholtz free energy of pure states in which all Co ions are in the low-spin (LS) and high-spin (HS) state, respectively, $f$ is a fraction of Co ions in the high-spin state, and $E_{\mathrm{mix}}$ and $S_{\mathrm{mix}}$ are the energy and entropy of mixing, respectively. Assuming that only 3*d* electrons contribute to the free energy,

$$F_{\mathrm{LS}} = E_{\mathrm{LS}} = E^0_{\mathrm{LS}}, \tag{4}$$

$$F_{\mathrm{HS}} = E_{\mathrm{HS}} - TS_{\mathrm{HS}}, \tag{5}$$

TABLE II. Energy level $\varepsilon_i$, degeneracy $d_i$, and magnetic moment $m_i$ reported by Ropka and Radwanski (Ref. 25).

| $\varepsilon_i$ (K) | $d_i$ | $m_i$ (units of $\mu_B$) |
|---|---|---|
| 0 | 1 | 0 |
| 7 | 2 | ±3.35 |
| 346 | 2 | ±3.10 |
| 378 | 2 | ±1.84 |
| 395 | 1 | 0 |
| 895 | 1 | 0 |
| 910 | 2 | ±0.64 |
| 920 | 2 | ±1.70 |
| 930 | 1 | 0 |
| 945 | 1 | 0 |

$$E_{\mathrm{HS}} = E_{\mathrm{HS}}^0 + \sum_i d_i \varepsilon_i \exp(-\varepsilon_i/T)/Z, \tag{6}$$

$$S_{\mathrm{HS}} = R \ln Z + RT\frac{\partial \ln Z}{\partial T}, \tag{7}$$

where $E_{\mathrm{HS}}^0$ is energy of the lowest level of high-spin state. Because the low-spin state is a singlet, the entropy is zero. The free energy, energy, and entropy of high-spin state are calculated from the partition function $Z$ by using the energy level diagram shown in Table II. The equilibrium condition, $\partial F/\partial f = 0$, gives

$$f = \frac{\exp(S_{\mathrm{HS}}/R)}{\exp(S_{\mathrm{HS}}/R) + \exp(\Delta/RT)}, \tag{8}$$

$$\Delta = E_{\mathrm{HS}} - E_{\mathrm{LS}} + \frac{\partial E_{\mathrm{mix}}}{\partial f} \tag{9}$$

$$= \Delta_0 + \sum_i d_i \varepsilon_i \exp(-\varepsilon_i/T)/Z, \tag{10}$$

$$\Delta_0 = E_{\mathrm{HS}}^0 - E_{\mathrm{LS}}^0 + \frac{\partial E_{\mathrm{mix}}}{\partial f}. \tag{11}$$

Here, $\Delta$ is the partial molar energy, in other words, the net excitation energy as a function of $f$. It is assumed that $E_{\mathrm{HS}}^0 - E_{\mathrm{LS}}^0$ is independent of temperature. This assumption would be consistent with the theoretical results by Korotin *et al.*,[18] which indicate that $E_{\mathrm{HS}}^0 - E_{\mathrm{LS}}^0$ is not sensitive to temperature though either $E_{\mathrm{LS}}^0$ or $E_{\mathrm{HS}}^0$ decrease with increasing temperature. In the present calculation, $\Delta_0$ is expanded up to the three orders, namely,

$$\Delta_0 = \Delta_1 + \Delta_2 f + \Delta_3 f^2 + \Delta_4 f^3. \tag{12}$$

When $\Delta_i$'s are determined, $f$ can be estimated from Eq. (8) by a self-consistent method.

$\Delta_i$'s are determined by fitting the experimental magnetic susceptibility data to the following equation:

$$\chi = f N_A \frac{\langle m\mu_B \rangle}{H_{\mathrm{ext}}} + \frac{C_{\mathrm{CW}}}{T-\theta}, \tag{13}$$

$$\langle m\mu_B \rangle = \sum_i m_i \mu_B \exp\{-(\varepsilon_i - m_i \mu_B H_{\mathrm{ext}})/T\}/Z, \tag{14}$$

where $N_A$, $H_{\mathrm{ext}}$, and $\mu_B$ are Avogadro's number, external magnetic field, and Bohr magneton, respectively. The second term in Eq. (13) corresponds to the upturn observed in the experimental data below about 30 K. By using the obtained best fit parameters, the heat capacity is calculated by the following equation:

$$C = T\frac{\partial}{\partial T}\{S_{\mathrm{mix}} + f S_{\mathrm{HS}}\}. \tag{15}$$

Here, the contribution from the second term in Eq. (13) is ignored.

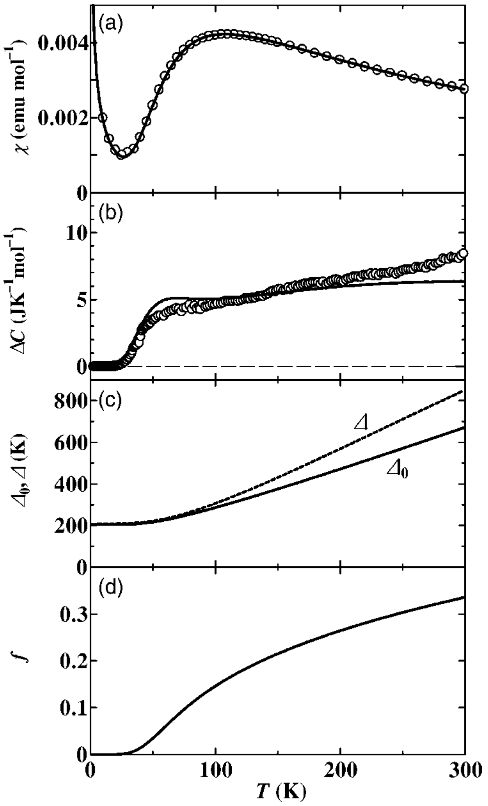

FIG. 2. (a) Magnetic susceptibility, (b) heat capacity, (c) net excitation energy, and (d) fraction of Co ions in the high-spin excited state: Circles and lines represent the experimental data and the calculated curves, respectively.

## III. RESULTS

The open circles in Fig. 2(a) represent the real part of ac magnetic susceptibility of $LaCoO_3$ measured with amplitude 10 Oe and frequency 1 kHz. The best fit parameters obtained by fitting are tabulated in Table III and the fitted curve is indicated by the solid line in the figure. It is found that this model reproduced the experimental data well. The open circles in Fig. 2(b) represent the experimental excess heat capacity obtained by subtracting the lattice contribution from the experimental data shown in Fig. 1. The lattice contribution indicated by the solid line in Fig. 1 was estimated by the

TABLE III. Best fit parameters.

| Parameter | Best fit value |
|---|---|
| $\Delta_1$ | 205 K |
| $\Delta_2$ | 305 K |
| $\Delta_3$ | 556 K |
| $\Delta_4$ | 7980 K |
| $C_{\mathrm{CW}}$ | 0.025 emu $\mathrm{mol}^{-1}$ K |
| $\theta$ | −3 K |

same method as reported in our previous paper,[24] namely,

$$C_{\mathrm{base}} = 0.67 C_{\mathrm{LaGaO_3}} + 0.33 C_{\mathrm{LaAlO_3}}, \tag{16}$$

where $C_{\mathrm{LaGaO_3}}$ and $C_{\mathrm{LaAlO_3}}$ are the heat capacity of $\mathrm{LaGaO_3}$ and $\mathrm{LaAlO_3}$, respectively. We believe that the experimental data are well reproduced by the calculation, taking account of the difficulty in estimating the lattice contribution. Therefore, the assumptions for the present calculation would be reasonable. The excitation energy and the fraction of Co ions in the high-spin excited state are shown in Figs. 2(c) and 2(d), respectively. It is found that the excitation energy increases with increasing temperature. The population of high-spin Co ions at 300 K is only 33%. The small population might be consistent with the result that Co 2*p* x-ray absorption spectroscopy line shape at room temperature looks like the low-spin state.[27] Figure 3 shows the *f* dependence of the excitation energy calculated from Eqs. (10) and (12). It is found that the temperature-dependent excitation energy originates from the excitation energy increasing with increasing *f*. We called this negative cooperative effect in our previous paper.[24] Therefore, the present result is qualitatively same as our previous one. Though the excess heat capacity above 100 K was not well reproduced by our previous calculation,[24] the reproducibility was improved by the present calculation possibly because the full energy level diagram was used for the excited state. The *f* dependence of total energy *E* in Eq. (1) is indicated by the thick solid line in Fig. 4. [$E^0_{\mathrm{LS}}$ was set to be zero and the second term in Eq. (6) was ignored.] The total energies at $f=0$ and 1 calculated by Korotin *et al.* are indicated by solid circles. The total energies at $f=0$, 0.5, and 1.0 calculated by Zhuang *et al.* are indicated by solid squares. The present result seems to be connected smoothly with their values, particularly the value at $f=0.5$, as indicated by the thin solid line.

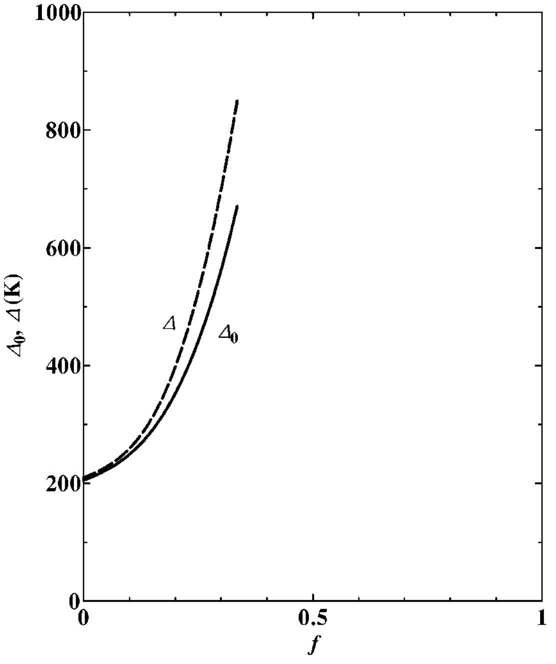

FIG. 3. *f* dependence of net excitation energy.

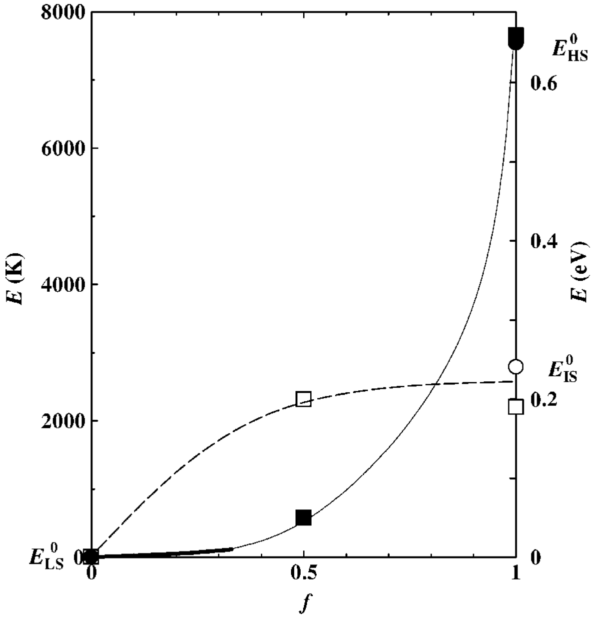

FIG. 4. *f* dependence of total energy. $E^0_{\mathrm{LS}}$ was set to be zero. The thick solid line is the present result. The thin solid line [dashed line] is the proposed total energy of state in which *f* high-spin (HS) [intermediate-spin (IS)] Co ions and $1-f$ low-spin (LS) Co ions are mixed. The circles and squares are results of Korotin *et al.* (Ref. 18) and Zhuang *et al.*, respectively, tabulated in Table I. Open and solid symbols indicate LS-IS and LS-HS mixtures, respectively.

## IV. DISCUSSION

Because the present calculation cannot determine $E^0_{\mathrm{HS}}$ and $E^0_{\mathrm{LS}}$ in Eq. (11), the values in Table I are used for discussion. According to them, $E^0_{\mathrm{HS}} - E^0_{\mathrm{LS}}$ is ~0.65 eV. This value results in a negatively large energy of mixing, namely, $\partial E_{\mathrm{mix}}/\partial f \approx -0.63$ eV at the limit $f \rightarrow 0$, because $\Delta_0 \approx 200$ K there. This negatively large energy of mixing is consistent with the results of Zhuang *et al.*[26] as found from Fig. 4. This indicates that large energy reduction ~0.63 eV occurs in addition to the energy gain ~0.65 eV when a Co ion is excited to the high-spin state. The effect of mixing was firstly discussed by Goodenough.[1] He considered that when a Co ion is excited to the high-spin state, the low-spin states of the nearest-neighbor Co ions are stabilized because the oxygen ions between them approach toward the nearest-neighbor Co ions due to the covalency of the Co(LS)—O bond being larger than that of Co(HS)—O bond. This is a candidate for large energy reduction, because the energy of electronic contribution is usually on the order of 1 eV. On the other hand, it is difficult to consider that the lattice contribution is the origin for the large energy reduction, because stretched Co(HS)—O bond and compressed Co(LS)—O bond should increase the elastic energy. Goodenough further considered that the high-spin states of next-nearest neighbor sites of the excited Co ion are stabilized.[1] This effect should accelerate the excitation to the high-spin state and thus make the temperature dependence of a physical quantity sharp. However, such a sharp temperature dependence has not been observed in the magnetic susceptibility, heat capacity, and volume expansion.[21] Therefore, we cannot accept this consideration. Instead, the present results suggest that the low-spin state is stabilized at any site. Of course, the stabilized energy would decrease with increasing distance between the excited high-spin Co ion and the other Co site. (This effect is not introduced in the present calculation because of the character of the mean-field approximation.) This indicates that repulsive interaction acts between high-spin Co ions and thus rocksalt type ordering of high-spin Co ions and low-spin Co ions would occur when the population of high-spin Co ions is 0.5. However, such an ordering would not appear below room temperature because the population is $\sim 0.33$ even around room temperature below which the high-spin Co ions would be located as far apart as possible in the low-spin matrix as shown in Fig. 5(a). In fact, such a rocksalt-type domain or short-range order has not been observed so far. This suggestion is an important point different from the consideration by Goodenough and Zhuang *et al.* and will be verified by calculating the energy of other states such as at $f=1/4$.

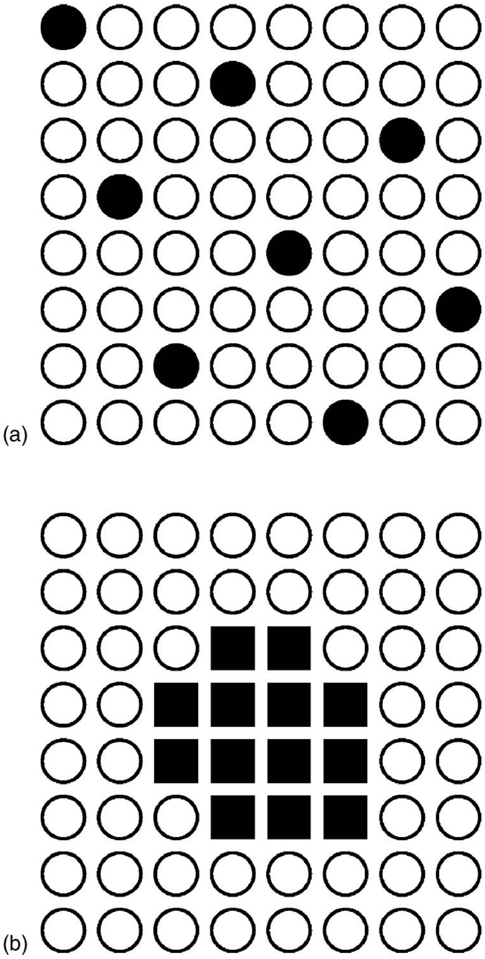

FIG. 5. Proposed arrangement of excited Co ions in the low-spin matrix of LaCoO$_3$. (a) High-spin Co ions are located as far apart as possible. (b) Intermediate-spin Co ions are collected to form domains. Open circles, solid circles, and solid squares indicate low-spin, high-spin, and intermediate-spin Co ions, respectively.

Next, we discuss intermediate-spin state. Korotin *et al.* suggested that the intermediate-spin state becomes the ground state above about 150 K.[18] However, this is inconsistent with experimental data, because a large and sharp anomaly should be observed around 150 K in the magnetic susceptibility and heat capacity if such a sudden change occurred in the spin quantum number. The results of Zhuang *et al.* imply that the intermediate-spin state is not populated at low temperatures for the following reason. The open squares in Fig. 4 show the results of Zhuang *et al.* in connection with intermediate-spin state (see Table I). It is found that the energy of mixing is positively large at least at $f=0.5$. Assuming that the $f$ dependence of total energy of mixture composed of $1-f$ low-spin Co ions and $f$ intermediate-spin Co ions is like the dashed line in the figure, the intermediate-spin state cannot be populated at least at low temperatures because of the large $\partial E/\partial f$ at the limit $f\to 0$. This assumption indicates that the homogeneous mixture composed of low-spin Co ions and intermediate-spin Co ions is unstable thermodynamically when the contribution from the entropy term to the free energy is small, and thus the attractive interaction acts between intermediate-spin Co ions as shown in Fig. 5(b) when the intermediate-spin state is excited. The positive energy of mixing indicates that the excitation to the intermediate-spin state occurs cooperatively, which may be also consistent with experimental results mentioned below. LaCoO$_3$ shows another spin-state transition in connection with the metal-insulator transition around 500–600 K. Though the spin state above 600 K is unclear at present, Korotin *et al.* proposed that it is the intermediate-spin state above 600 K. In addition, the theoretical calculations[18,26] predict that the intermediate-spin state is metallic. Asai *et al.* reported that positive cooperative effect occurs for the spin-state transition around 500–600 K.[21] This is consistent with the heat capacity data, because a relatively sharp heat capacity anomaly has been observed around 530 K.[19] (It should be noted that it is unclear whether the spin-state transition around 500–600 K is a phase transition or not, because the heat capacity anomaly is sharp as compared to Schottky anomaly but broad as compared to a phase transition.) The origin of attractive interaction between intermediate-spin Co ions is supposed as follows. The metallic state is stabilized because of kinetic energy of conductive electrons reduced by the itinerant nature, which should be realized only when intermediate-spin Co ions are collected as shown in Fig. 5(b).

We suggest that the spin-state transition around 500–600 K is from a mixture of low-spin Co ions and high-spin Co ions to a pure state in which all Co ions are in the intermediate-spin state. The entropies at 600 K are at most $R\ln 2+0.5R\ln 15$ and $R\ln 9$ for the mixture and the pure state, respectively, because the fraction of high-spin state becomes ~0.5 at 600 K by extrapolating the present result in Fig. 2(d). The entropy change around 500–600 K is thus only ~1 J $K^{-1}$ $mol^{-1}$. Because this is much smaller than the experimental observation, at least 10 J $K^{-1}$ $mol^{-1}$,[19] it is supposed that other contributions such as the charge (or lattice) contribution play important roles in the spin-state transition around 500–600 K.

## V. CONCLUSION

In conclusion, the experimental magnetic susceptibility and heat capacity below 300 K due to the spin-state transition of $LaCoO_3$ are well reproduced by introducing the energy and entropy of the mixing of Co ions in the low-spin ground state and Co ions in the high-spin excited state with the energy level structure reported by Ropka and Radwanski.[25] The results indicate that the energy of mixing is negatively large which reduces the total energy and thus the net excitation energy. The reduction of covalent energy of Co—O bonds around the excited high-spin Co ion is proposed for the origin of negative energy of mixing according to Goodenough's suggestion.[1] The negative energy of mixing also indicates that repulsive interaction acts between Co ions in the high-spin excited state and thus predicts that there is no domain or short-range order composed of high-spin Co ions such as those reported in spin-crossover complexes.[28] In addition, we proposed that the excitation to the intermediate-spin state occurs cooperatively around 500–600 K possibly due to the reduction of kinetic energy of conductive electrons in the metallic state. We believe that the present results and suggestions are consistent with many experimental and theoretical results. These suggestions will be verified by theoretical calculations using the enlarged cell as carried out by Zhuang *et al.*[26]

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