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THERMODYNAMIC APPROACH OF SPIN-STATE EXCITATIONS IN $LaCoO_3$

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Magnetic susceptibility and heat capacity due to spin-state excitations in $LaCoO_3$ were analyzed with an irregular solution model composed of Co^{3+} ions in the low-spin ground state and in the high-spin excited state. An energy-levels diagram proposed by Ropka and Radvanskii [1] was used for the high-spin excited state. This analysis showed that the entropy of mixing is less than that of ideal solutions and the enthalpy of mixing is negative, indicating that the high-spin Co ions are arranged as far apart as possible.

Keywords: *entropy of mixing, heat capacity, lanthanum cobalt oxide, magnetic susceptibility, regular solution, spin state*

Introduction

Spin-crossover complexes such as $[Fe(phen)_2(NCS)_2]$ show a temperature-induced phase transition from the low-spin state of Fe^{2+} to the high-spin state [2, 3]. Electron-lattice coupling plays an important role for the transition to occur, which is evidenced by a large change in bond distances between an iron ion and ligands and the transition entropy larger than the spin-only value. Other characteristic of spin-crossover phenomena is variety of strength in cooperative effects, e.g. the heat capacity anomaly is sharp in $[Fe(phen)_2(NCS)_2]$ [4] but broad in $[Fe(2\text{-}pic)_3]Cl_2\cdot CH_3OH$ [5]. Such a spin-crossover phenomenon also occurs in $LaCoO_3$ crystal [6–8]. The comparison of spin-crossover phenomena between complexes and oxides is interesting to understand cooperative effects in condensed matter.

The magnetic susceptibility of $LaCoO_3$ shows a broad maximum around 100 K as shown in Fig. 1a. This behavior has been understood as thermal excitation of Co^{3+} ions from the low-spin ground state with an electronic configuration t_{2g}^6 to the excited state. The excited state is unclear even at present. According to Tanabe–Sugano diagram, only a high-spin state with a configuration $t_{2g}^4 e_g^2$ is probable for the excited state [9]. In fact, ESR study of $LaCoO_3$ reported that the excited state is a triplet with g-factor 3.35 [10], indicating that 15 degenerate energy levels of a high-spin excited state split into the low-lying triplet state due to spin-orbit interaction. On the other hand, Potze *et al.* proposed that an intermediate-spin state with a configuration $t_{2g}^5 e_g^1$ is possible for the excited state when a contribution from ligand hole state to the electronic state is large [11]. Korotin *et al.* calculated that the energy of high-spin state of $LaCoO_3$ is much larger by 0.65 eV than that of low-spin state [12].

In our previous studies [13, 14], temperature dependences of magnetic susceptibility and heat capacity of $LaCoO_3$ were analyzed with a model in which $LaCoO_3$ is regarded as a regular solution composed of low-spin and high-spin Co^{3+} ions. The analyzed results indicate that negatively large enthalpy of mixing assists Co^{3+} ions to excite up to the high-spin state with high energy. This regular solution model quantitatively reproduced the experimental magnetic susceptibility. However, it was difficult to reproduce both magnetic susceptibilities and excess heat capacities simultaneously. In the present study, the heat capacity and magnetic susceptibility were re-analyzed with an irregular solution model.

Irregular solution model

A free energy of a solution composed of low-spin and high-spin Co^{3+} ions is written as

$$G=(1-f)G_{LS}+fG_{HS}+\Delta_{mix}G \tag{1}$$

where f is a fraction of high-spin Co^{3+} ions. G, H and S with a subscript LS (or HS) indicate a free energy, enthalpy, and entropy of a state in which all Co^{3+} ions are in the low-spin state (or high-spin state). $\Delta_{mix}G$ is a free energy of mixing and written as

$$\Delta_{mix}G=\Delta_{mix}H-T\Delta_{mix}S \tag{2}$$

with an enthalpy of mixing $\Delta_{mix}H$ and entropy of mixing $\Delta_{mix}S$.

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Only a contribution from 3d electrons of Co^{3+} ions to the free energy is considered in the present model. Because the low-spin state is a singlet, S_{LS} is zero. It is provided that H_{LS} is independent of temperature. When the value of H_{LS} is set at zero, G_{LS} is zero and then

$$G = fG_{HS} + \Delta_{mix} G \quad (3)$$

$$H = fH_{HS} + \Delta_{mix} H \quad (4)$$

$$S = fS_{HS} + \Delta_{mix} S \quad (5)$$

where H_{HS} and S_{HS} are calculated as follows from 15 energy levels of the high-spin state reported by Ropka and Radvanskii [1].

$$H_{HS} = \varepsilon_{HS} + \sum_{i=1}^{15} \varepsilon_i \exp(-\varepsilon_i / k_B T)/Z \quad (6)$$

$$S_{HS} = R\ln Z + RT\frac{\partial \ln Z}{\partial T} \quad (7)$$

where ε_{HS} is the energy of the lowest level of high-spin state, ε_i's ($1 \le i \le 15$) are the energy difference between the lowest level and i^{th} level, and Z is the partition function. It is provided that ε_{HS} and ε_i's are independent of temperature. The mixing entropy is divided into two terms as follows.

$$\Delta_{mix} S = \Delta_{mix}^{ideal} S + \Delta_{mix}^{excess} S \quad (8)$$

$$\Delta_{mix}^{ideal} S = -R[(1-f)\ln(1-f) + f\ln f] \quad (9)$$

where $\Delta_{mix}^{excess} S$ is a deviation of entropy of mixing from those of ideal solutions or regular solutions. It is provided that $\Delta_{mix}H$ and $\Delta_{mix}^{excess} S$ do not depend on temperature but only on f. Under equilibrium, $\partial G/\partial f = 0$ and then

$$f = \frac{1}{1+\exp\left(\dfrac{G_{HS} + \partial\Delta_{mix} H/\partial f - T\partial\Delta_{mix}^{excess} S/\partial f}{RT}\right)} \quad (10)$$

Results and discussion

Open circles in Figs 1a and b show experimental magnetic susceptibilities and excess heat capacities of $LaCoO_3$ [13]. The excess heat capacities were estimated by subtracting a baseline,

$$C_{base} = 0.67C_{LaGaO_3} + 0.33C_{LaAlO_3} \quad (11)$$

from the experimental heat capacities, where C_{LaGaO_3} and C_{LaAlO_3} are experimental heat capacities of $LaGaO_3$ and $LaAlO_3$, respectively. The coefficient 0.67 was chosen for C_{base} to coincide with the heat capacities of $LaCoO_3$ below 10 K. The total enthalpy and entropy are obtained from the excess heat capacities, as indicated by solid circles in Figs 1c and d. The excess heat capacity and magnetic susceptibility are expressed by

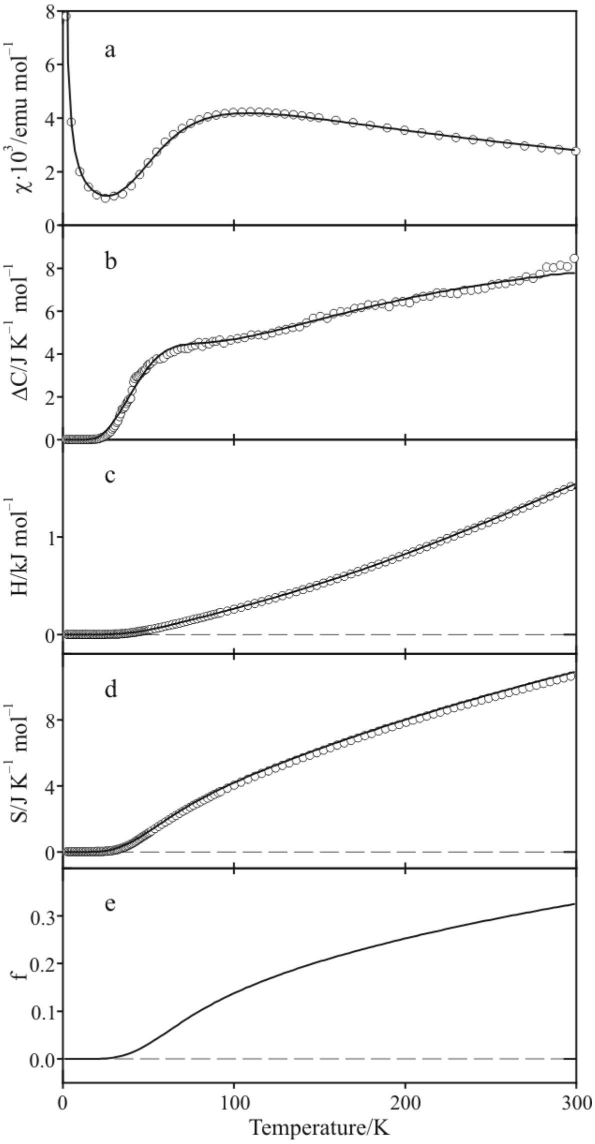

Fig. 1 a – Experimental magnetic susceptibility and b – excess heat capacity of $LaCoO_3$. c – enthalpy and d – entropy obtained by integrating the data in b. e – Fraction of high-spin Co^{3+} ions. Solid lines are calculation curves obtained with an irregular solution model

$$\Delta C = T\left(\frac{\partial S}{\partial T}\right) \quad (12)$$

and

$$\chi = \frac{C}{T} + (1-f)\chi_0^{LS} + f\chi_0^{HS} + fN_A \frac{\sum_{i=1}^{15} m_i \mu_B \exp[-(\varepsilon_i - m_i \mu_B H)/k_B T]}{ZH} \quad (13)$$

where m_i's are magnetic moments of i^{th} level [1]. The first term of Eq. (13) is a contribution from paramagnetic impurities present in the sample as found from an upturn in the experimental curve below 30 K. The second and third terms are contributions from Van Vleck [15] and/or diamagnetic contributions of low-spin and high-spin Co^{3+} ions, respectively. The experimental magnetic susceptibilities and excess heat capacities were fitted by Eqs (10), (12) and (13). Then, $\Delta_{mix}H$ and $\Delta_{mix}^{excess}S$ were expanded by power functions of f. C=0.0174 emu mol^{-1} K, χ_0^{LS}=3.17·10^{-4} emu mol^{-1} and χ_0^{HS}= –1.68·10^{-4} emu mol^{-1} were obtained by the fitting. Solid lines in Figs 1a–d indicate the obtained temperature dependence of χ, ΔC, H and S. It is found that both the excess heat capacity and magnetic susceptibility were well reproduced by the fitting. A solid line in Fig. 1e indicates the temperature dependence of f obtained by the fitting.

A thick solid line in Fig. 2a indicates f dependence of $f\varepsilon_{HS}+\Delta_{mix}H$. It is impossible to extract $\Delta_{mix}H$ from the data, because ε_{HS} is unknown. Korotin *et al.* reported that ε_{HS} is 63 kJ mol^{-1} [12]. A thin solid line in Fig. 2a indicates $f\varepsilon_{HS}$ with ε_{HS}=63 kJ mol^{-1}. This large ε_{HS} results in negatively large $\Delta_{mix}H$ at any f, which indicates that strong repulsive interaction acts between high-spin Co^{3+} ions. This is the same conclusion as our previous papers in which a regular solution model was used for analysis [13, 14]. A thick solid line in Fig. 2b indicates f dependence of $\Delta_{mix}S$. A thin solid line and a dotted line indicate $\Delta_{mix}^{ideal}S$ and $\Delta_{mix}^{excess}S$, respectively. It is found that $\Delta_{mix}^{excess}S$ is not zero but negative. This is consistent with the strong repulsive interaction acting between high-spin Co^{3+} ions, because the interaction decreases probability to realize states in which high-spin Co ions locate near each other.

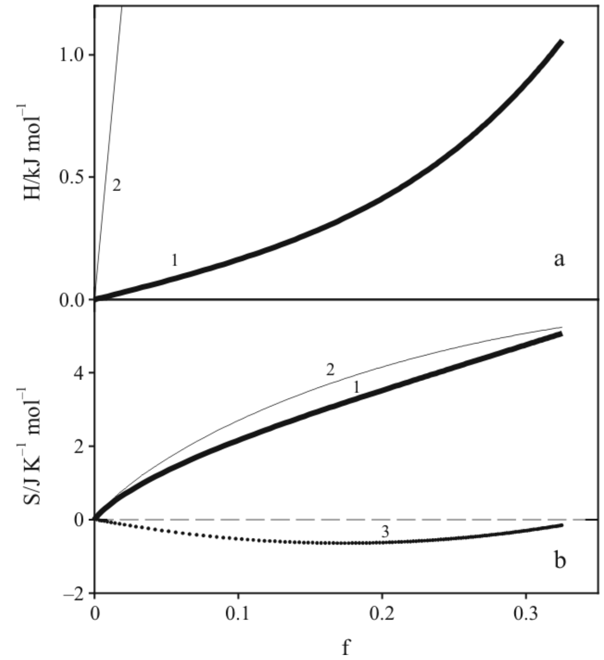

Fig. 2 a – 1 – $f\varepsilon_{HS}+\Delta_{mix}H$; 2 – $f\varepsilon_{HS}$. b – 1 – $\Delta_{mix}S$; 2 – $\Delta_{mix}^{ideal}S$; 3 – $\Delta_{mix}^{excess}S$. See text for details

Conclusions

The entropy of mixing of Co^{3+} ions in the low-spin ground state and high-spin excited state was less than that of ideal solutions or regular solutions. The finite $\Delta_{mix}^{excess}S$ would be just the reason why the regular solution model did not reproduce the experimental heat capacity and magnetic susceptibility simultaneously [14]. The present result is reasonable because the enthalpy of mixing is large. This supports validity of the simple solution model for $LaCoO_3$.

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