Ga^{3+} substitution effects in the weak ferromagnetic oxide $LaCo_{0.8}Rh_{0.2}O_3$

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Magnetization and x-ray diffraction have been measured on polycrystalline samples of $LaCo_{0.8-y}Rh_{0.2}Ga_yO_3$ for $0 \leqslant y \leqslant 0.15$ in order to understand the spin state of Co^{3+} through the Ga^{3+} substitution effect. The ferromagnetic order in $LaCo_{0.8}Rh_{0.2}O_3$ below 15 K is dramatically suppressed by the Ga^{3+} substitution as the ferromagnetic volume fraction is linearly decreased. The normal state susceptibility also systematically decreases with the Ga content from which we find that one Ga^{3+} ion reduces 4.6 μ_B per formula unit. We have evaluated how the concentration of the high-spin-state Co^{3+} changes with temperature by using an extended Curie-Weiss law and have found that the substituted Rh^{3+} ion stabilizes the high-spin-state Co^{3+} ion down to low temperatures. We find that Ga^{3+} preferentially replaces the high-spin-state Co^{3+}, making a remarkable contrast to our previous finding that Rh^{3+} preferentially replaces the low-spin-state Co^{3+}. These results strongly suggest that the magnetically excited state of $LaCoO_3$ at room temperature is a mixed state of the high-spin-state Co^{3+} and the low-spin-state Co^{3+}.

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I. INTRODUCTION

The perovskite cobalt oxide $LaCoO_3$ has been investigated for its various physical properties. The fivefold degenerate $3d$ orbitals in Co^{3+} ions are split into the doubly degenerate e_g orbitals in the upper energy level and the triply degenerate t_{2g} orbitals in the lower energy level due to the Coulomb interaction between the Co^{3+} ions and the O^{2-} ions coordinated octahedrally. The six d electrons in the $3d$ orbitals of a Co^{3+} ion are fully occupied in t_{2g} orbitals in the low-spin state (t_{2g}^6, $S = 0$) when the crystal-field splitting is larger than the Hund coupling. The Co^{3+} ions take the high-spin state ($e_g^2 t_{2g}^4$, $S = 2$) for the opposite condition. $LaCoO_3$ is a fascinating material with respect to the spin state because the Co^{3+} ion in $LaCoO_3$ can show spin-state crossover with temperature,[1] magnetic field,[2] or pressure.[3] It is theoretically suggested that the Co^{3+} ion in $LaCoO_3$ can take the intermediate-spin state ($e_g^1 t_{2g}^5$, $S = 1$) when the hybridization between the e_g orbitals and O $2p$ orbitals is taken into account.[4]

The magnetic susceptibility of $LaCoO_3$ decreases with decreasing temperature below 90 K except for a low-temperature upturn due to the oxygen vacancies,[5] takes a maximum at around 90 K, and has Curie-Weiss-like behavior around room temperature.[1] This indicates that the Co^{3+} ion is nonmagnetic in the ground state and that its magnetic state is thermally activated. The change from the nonmagnetic ground state to the magnetically excited state is also observed via NMR[6] and neutron scattering.[7] The excited state of $LaCoO_3$ at room temperature has been theoretically and experimentally studied[1–4,6–17] but is still controversial. In 1966, Raccah and Goodenough proposed an NaCl-type spin-state order consisting of the high-spin and low-spin states of Co^{3+} as the excited state of $LaCoO_3$.[8] They suggested that the displacement of O^{2-} ions toward the low-spin-state Co^{3+} stabilizes the excited state due to the different crystal fields. No evidence for the spin-state order has been observed until now. Aside from such a static order, a dynamically mixed state of the high-spin and low-spin states (HS-LS model) is suggested from soft x-ray-absorption spectroscopy,[9] heat capacity combined with the magnetic susceptibility,[10,11] ESR,[12] and the unrestricted Hartree-Fock calculation.[13] In 1996, Korotin *et al.*proposed another model in which the excited state of $LaCoO_3$ is the intermediate-spin state (IS model),[4] which is qualitatively different from the HS-LS model. This model is supported by the pressure dependence of the structure,[2] x-ray-photoemission spectroscopy,[14] neutron diffraction,[15] synchrotron x-ray powder diffraction,[16] and infrared spectroscopy.[17]

Kyomen *et al.*[10] have found that the substitution effects of two nonmagnetic ions, Ga^{3+} ($3d^{10}$, $S = 0$) and Rh^{3+} (t_{2g}^6, $S = 0$), for Co^{3+} differ from each other. The magnetic susceptibility of $LaCo_{1-x}Ga_xO_3$ decreases with increasing Ga content, indicating that the Ga^{3+} substitution for Co^{3+} does not change the nonmagnetic ground state. On the other hand, a Curie-Weiss-like susceptibility develops at low temperatures for $x > 0.04$ in $LaCo_{1-x}Rh_xO_3$. In contrast to the difference of the substitution effects for the magnetization between two species of nonmagnetic ions, the electrical resistivity and Seebeck coefficients of $LaCo_{1-x}Ga_xO_3$ (Ref. 18) and $LaCo_{1-x}Rh_xO_3$ (Ref. 19) at high temperatures show similar behavior. Generalized gradient approximation (GGA) + U calculations indicate that the Rh^{3+} substitution stabilizes the high-spin-state Co^{3+} due to elastic interactions between the cations with different ionic radii and electronic interactions associated with the unfilled $4d$ shell of Rh^{3+}.[20] In our previous study, we measured the x-ray diffraction and magnetization of the polycrystalline samples of $LaCo_{1-x}Rh_xO_3$ in the range of $0 \leqslant x \leqslant 0.9$ in order to investigate the magnetism induced in the solid solution of the two nonmagnetic end phases of $LaCoO_3$ and $LaRhO_3$ (Ref. 21) and found a ferromagnetic ordering below 15 K in the range of $0.1 \leqslant x \leqslant 0.4$. This ferromagnetic ordering is driven only by Co^{3+} ions and is distinguished from that observed in $La_{1-x}Sr_xCoO_3$ wherein the coexistence of Co^{3+} and Co^{4+} ions is essential.[22,23] We further found that the effective magnetic moment of $LaCo_{1-x}Rh_xO_3$ evaluated at room temperature is independent of the Rh content x for $0 \leqslant x \leqslant 0.5$. It is also found that the lattice volume for $LaCo_{1-x}Rh_xO_3$ is larger than that expected from Vegard's law. These results suggest that a Rh^{3+} ion is

preferentially substituted for a low-spin-state Co^{3+} ion and that the excited state of $LaCoO_3$ is described with the HS-LS model.

In this paper, we have measured the x-ray diffraction and the magnetization of $LaCo_{0.8-y}Rh_{0.2}Ga_yO_3$ ($0 \leqslant y \leqslant 0.15$) in order to clarify the Ga^{3+} substitution effect on the ferromagnetism as well as the spin state of Co^{3+}. The reason why $LaCo_{0.8}Rh_{0.2}O_3$ is chosen as the initial phase for the Ga^{3+} substitution is that this composition gives the largest magnetization at low temperatures with the highest Curie temperature.

II. EXPERIMENTS

Polycrystalline samples of $LaCo_{0.8-y}Rh_{0.2}Ga_yO_3$ ($0 \leqslant y \leqslant 0.15$) were prepared by a conventional solid-state reaction. A mixture of La_2O_3 ($3N$), Co_3O_4 ($3N$), Rh_2O_3 ($3N$), and Ga_2O_3 ($4N$) with stoichiometric molar ratios was ground and calcined for 24 hours at 1000 °C in air. The calcined powder was ground, pressed into a pellet, and sintered for 48 hours at 1200 °C in air. These pellets were cooled slowly to room temperature in the furnace by switching off the power after sintering. We expect that the oxygen content stayed around a thermal-equilibrium value and was close to the value for $La_{0.8}Sr_{0.2}Co_{1-x}Rh_xO_{3-\delta}$ ($\delta \leqslant 0.03$).[24]

X-ray diffraction was measured with a Rigaku RAD-IIC (Cu $K\alpha$ radiation), and no impurity phases were detected for the prepared samples. Magnetization in field-cooling (FC) and zero-field-cooling (ZFC) processes were measured using a superconducting-quantum-interference-device (SQUID) magnetometer (Quantum Design MPMS) from 5 to 300 K in an applied field of 1 T for $LaCo_{0.8-y}Rh_{0.2}Ga_yO_3$ ($0 \leqslant y \leqslant 0.15$). Magnetization-field ($M$-$H$) curves at $T = 2$ K for $LaCo_{0.8-y}Rh_{0.2}Ga_yO_3$ ($0 \leqslant y \leqslant 0.15$) were measured in sweeping $\mu_0 H$ from 0 to 7 T and from 7 to 0 T.

III. RESULTS AND DISCUSSION

From the x-ray-diffraction measurements, we find that the crystal system of the samples at room temperature is orthorhombic, meaning that the Ga^{3+} substitution does not change the orthorhombic structure of $LaCo_{0.8}Rh_{0.2}O_3$. Figures 1(a) and 1(b) show the lattice volume per formula unit and the lattice constants for $LaCo_{0.8-y}Rh_{0.2}Ga_yO_3$ ($0 \leqslant y \leqslant 0.15$), respectively. The two quantities are essentially independent of the Ga content, remarkably differing from the Rh^{3+} substitution effect, wherein the lattice volume increases by 1 Å^3 from $LaCo_{0.8}Rh_{0.2}O_3$ to $LaCo_{0.65}Rh_{0.35}O_3$.[21]

Figure 2(a) shows the temperature dependence of the magnetization for $LaCo_{0.8-y}Rh_{0.2}Ga_yO_3$ per formula unit in the range of $0 \leqslant y \leqslant 0.15$ at 1 T. Magnetization over all the temperature range decreases with increasing Ga content whereas the Curie-Weiss-like temperature dependence remains intact. Figure 2(b) shows the applied-field dependence of the magnetization (M-H curve) at $T = 2$ K for $LaCo_{0.8-y}Rh_{0.2}Ga_yO_3$ ($0 \leqslant y \leqslant 0.15$). The spontaneous magnetization observed for $y = 0$ is strongly suppressed by Ga^{3+} substitution and is not visible for $y = 0.15$. It indicates that the weak ferromagnetism is severely suppressed by Ga^{3+} substitution.

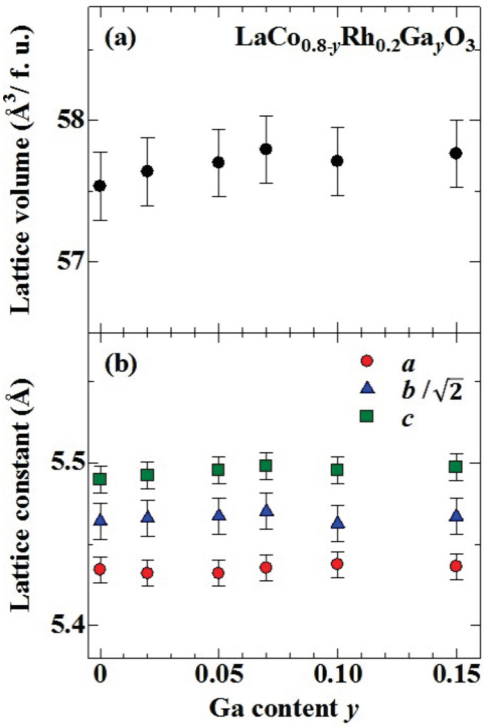

FIG. 1. (Color online) The Ga-content dependence of (a) the lattice volume and (b) the lattice constants for $LaCo_{0.8-y}Rh_{0.2}Ga_yO_3$ ($0 \leqslant y \leqslant 0.15$).

Here, we compare the effects of the Ga^{3+} substitution on the magnetization with those of the Rh^{3+} substitution. Figures 3(a) and 3(b) show the temperature dependence of the reciprocal magnetization for $LaCo_{0.8-y}Rh_{0.2}Ga_yO_3$ ($0 \leqslant y \leqslant 0.1$) and $LaCo_{1-x}Rh_xO_3$ ($x = 0.2$ and 0.3), respectively. The inverse magnetization increases by the Ga^{3+} substitution much more drastically than by the Rh^{3+} substitution. Considering that $y = 0.1$ and $x = 0.3$ correspond to a 10% substitution for $LaCo_{0.8}Rh_{0.2}O_3$, we should emphasize that at least two kinds of Co^{3+} ions exist in $LaCo_{0.8}Rh_{0.2}O_3$; one is nonmagnetic, and the other is magnetic. This favors the HS-LS model rather than the uniform IS model.

The HS-LS model is also supported by the Ga-content dependence of the lattice volume and the lattice constants for $LaCo_{0.8-y}Rh_{0.2}Ga_yO_3$ shown in Fig. 1. The experimental results naturally indicate that the Ga^{3+} ion is substituted for the Co^{3+} ion with the same ionic radius. According to the literature,[25] the ionic radius of the Ga^{3+} ion (0.62 Å) is larger than that of the low-spin-state Co^{3+} (0.54 Å) but is close to that of the high-spin-state Co^{3+} (0.61 Å). It seems that Ga^{3+} is preferentially substituted for the high-spin-state Co^{3+}.

Let us further discuss the Ga^{3+} substitution effects on the spin system. We fit the H/M-T curves from 40 to 70 K shown in Fig. 3(a) using the Curie-Weiss law given by

$$\frac{M}{\mu_0 H} = \frac{N\mu_B^2 \mu_{\text{eff}}^2}{3k_B(T-\theta)} \tag{1}$$

and have evaluated the effective magnetic moment μ_{eff} and the Curie temperature θ. Figure 4(a) shows the Ga-content dependence of μ_{eff}. The evaluated μ_{eff} is 2.1 μ_B for $y = 0$, which linearly decreases with increasing Ga content. We

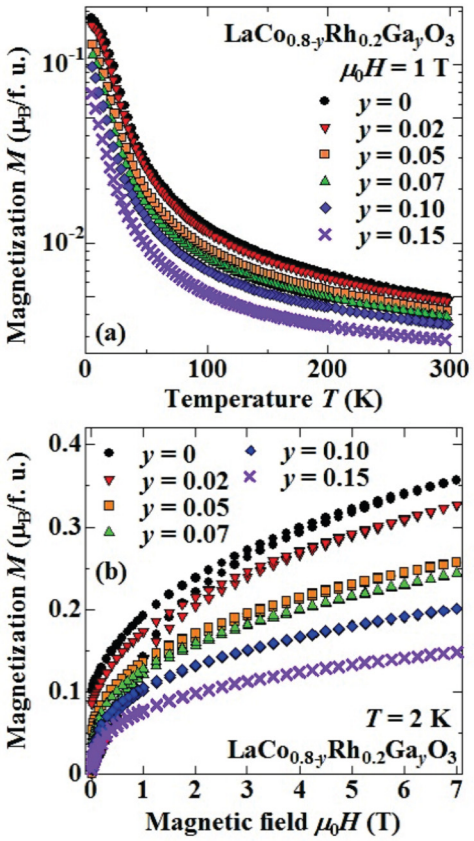

FIG. 2. (Color online) (a) Temperature dependence of the magnetization for $LaCo_{0.8-y}Rh_{0.2}Ga_yO_3$ ($0 \leqslant y \leqslant 0.15$) taken at 1 T. (b) Magnetization-field curves for $LaCo_{0.8-y}Rh_{0.2}Ga_yO_3$ ($0 \leqslant y \leqslant 0.15$) at 2 K.

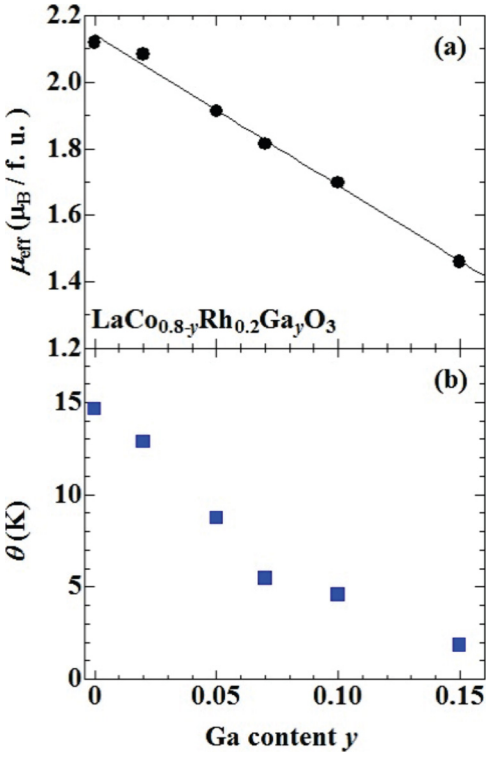

FIG. 4. (Color online) Ga-content dependence of (a) the effective magnetic moment and (b) the Curie temperature for $LaCo_{0.8-y}Rh_{0.2}Ga_yO_3$ ($0 \leqslant y \leqslant 0.15$) which are evaluated from fitting the *H*/*M*-*T* curves for $LaCo_{0.8-y}Rh_{0.2}Ga_yO_3$ ($0 \leqslant y \leqslant 0.15$) from 40 to 70 K using the Curie-Weiss law. The solid line in (a) represents the linear fit of the data.

evaluate from the slope of the solid line shown in Fig. 4(a) that one Ga^{3+} ion decreases 4.6 μ_B, which is consistent with our claim that Ga^{3+} replaces the high-spin-state Co^{3+} of 4.9 μ_B. The Ga-content dependence of θ is shown in Fig. 4(b) where θ linearly decreases with increasing Ga content. This indicates that the magnetic interaction between the high-spin-state Co^{3+} ions is suppressed by Ga^{3+} substitution, further consolidating our claim that the high-spin-state Co^{3+} ions are substituted by Ga^{3+} ions.

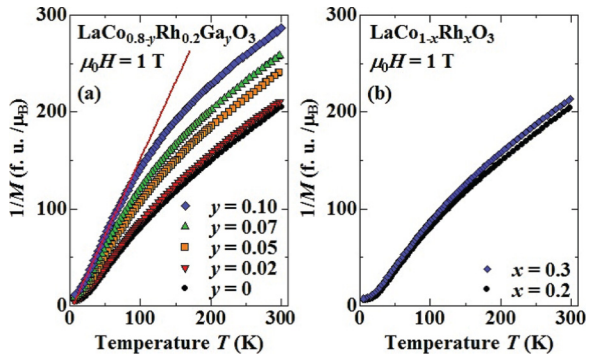

FIG. 3. (Color online) Temperature dependence of the reciprocal magnetization for (a) $LaCo_{0.8-y}Rh_{0.2}Ga_yO_3$ ($0 \leqslant y \leqslant 0.1$) and (b) $LaCo_{1-x}Rh_xO_3$ ($x = 0.2$ and 0.3). The solid line in (a) represents the linear fit of the data for $y = 0.10$ from 40 to 70 K.

Next, we discuss the *M*-*H* curves of $LaCo_{0.8-y}Rh_{0.2}Ga_yO_3$ ($0 \leqslant y \leqslant 0.15$) shown in Fig. 2(b). Figure 5(a) shows *M*-*H* curves normalized by the value of magnetization at $\mu_0 H = 7$ T for $LaCo_{0.8-y}Rh_{0.2}Ga_yO_3$ ($0 \leqslant y \leqslant 0.15$) where all the curves fall onto a single curve above 3 T. This indicates that the Ga^{3+} substitution dilutes the magnetization of $LaCo_{0.8}Rh_{0.2}O_3$. The normalization factor is shown in Fig. 5(b), representing the volume fraction of the magnetic phase in a simplest approximation. The volume fraction linearly decreases with increasing Ga content, indicating that the high-spin-state Co^{3+} ions are reduced by Ga^{3+} substitution. We evaluate from the solid line shown in Fig. 5(b) the critical concentration to be $y = 0.25$ at which the magnetic volume fraction disappears. This suggests that the content of the high-spin-state Co^{3+} ion is about 0.25 per formula unit in $LaCo_{0.8}Rh_{0.2}O_3$.

Let us evaluate the temperature dependence of the concentration of the high-spin-state Co^{3+} from the temperature dependence of the magnetization shown in Fig. 2(a). When the number of the magnetic ions N in Eq. (1) depends on temperature [$N = N(T)$], Eq. (1) is rewritten as

$$\frac{\mu_0 H}{M} = \frac{3k_B}{N(T)\mu_B^2\mu_{\rm eff}^2}T - \frac{3k_B}{N(T)\mu_B^2\mu_{\rm eff}^2}\theta. \qquad (2)$$

The Curie temperature θ is proportional to the number of the nearest-neighbor sites of the magnetic ions z within the mean-field approximation. When the content of the high-spin-state Co^{3+} is changed with temperature, we can simply assume that

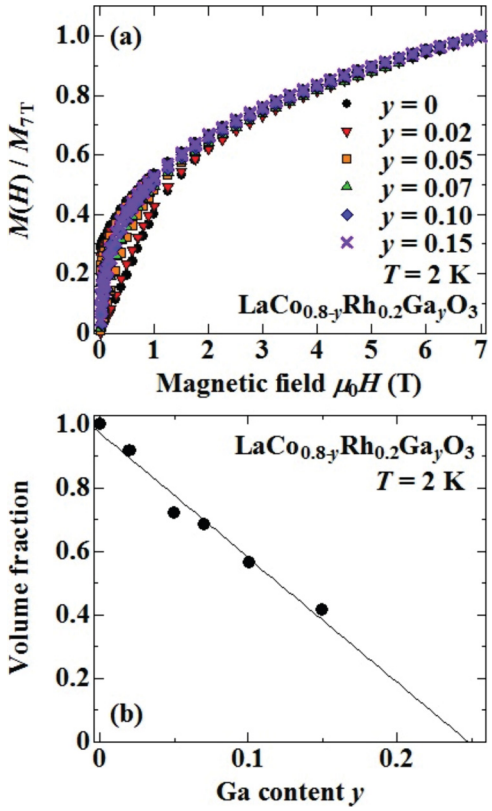

FIG. 5. (Color online) (a) Magnetization-field curves normalized by the value of the magnetization taken at 7 T for $LaCo_{0.8-y}Rh_{0.2}Ga_yO_3$ ($0 \leqslant y \leqslant 0.15$) at 2 K. (b) Ga-content dependence of the volume fraction (see text) for $LaCo_{0.8-y}Rh_{0.2}Ga_yO_3$ ($0 \leqslant y \leqslant 0.15$) at 2 K. The solid line represents the linear fit of the data.

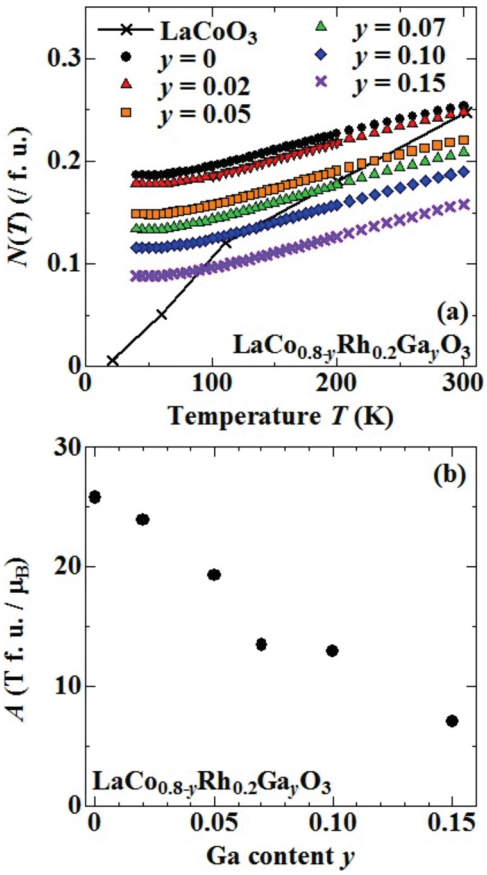

FIG. 6. (Color online) (a) The content of the high-spin-state Co^{3+} [$N(T)$] in $LaCo_{0.8-y}Rh_{0.2}Ga_yO_3$ ($0 \leqslant y \leqslant 0.15$) plotted as a function of temperature. For comparison, $N(T)$ in $LaCoO_3$ is also plotted (taken from Ref. 8). The detailed calculation method is described in the text. (b) Ga-content dependence of the parameter A for $LaCo_{0.8-y}Rh_{0.2}Ga_yO_3$ ($0 \leqslant y \leqslant 0.15$) (see text).

z is proportional to $N(T)$. Since θ is proportional to $N(T)$ in this approximation, the second term of Eq. (2) is independent of temperature. Then we can evaluate the second term of Eq. (2) expressed as

$$A = \frac{3k_B}{N(T)\mu_B^2\mu_{\text{eff}}^2}\theta(T) \tag{3}$$

by extrapolating the reciprocal magnetic susceptibility towards 0 K. After determining the value of A, we obtain $N(T)$ from Eq. (2) as

$$N(T) = \frac{3k_BT}{\mu_B^2\mu_{\text{eff}}^2\left(\frac{\mu_0 H}{M} + A\right)}, \tag{4}$$

where we set $\mu_{\text{eff}}^2 = 24$ as the high-spin-state value. Figure 6(a) shows the thus obtained $N(T)$ in $LaCo_{0.8-y}Rh_{0.2}Ga_yO_3$ ($0 \leqslant y \leqslant 0.15$) together with $N(T)$ in $LaCoO_3$ reported by Haverkort *et al.*[9] Note that N(300 K) are almost the same values between $LaCo_{0.8}Rh_{0.2}O_3$ and $LaCoO_3$, indicating that the Rh^{3+} substitution does not change the content of the high-spin-state Co^{3+}.[26] With decreasing temperature, $N(T)$ of $LaCoO_3$ decreases to zero at low temperatures. On the contrary, $N(T)$ of $LaCo_{0.8}Rh_{0.2}O_3$ is 0.2 per formula unit at 40 K, indicating that the Rh^{3+} substitution stabilizes the high-spin-state Co^{3+} down to low temperatures. We further emphasize that N(40 K) of $LaCo_{0.8}Rh_{0.2}O_3$ is close to the critical concentration of 0.25 evaluated in Fig. 5(b). $N(T)$ of $LaCo_{0.8-y}Rh_{0.2}Ga_yO_3$ ($0 \leqslant y \leqslant 0.15$) exhibits a downward parallel shift, suggesting that the Ga^{3+} substitution effect is static and local. Figure 5(b) shows the Ga-content dependence of the constant A, which linearly decreases with increasing Ga content.

Finally, we discuss an origin of the Rh^{3+} and Ga^{3+} substitution effects for Co^{3+} in $LaCoO_3$. Our experimental results indicate that Rh^{3+} and Ga^{3+} seem to replace the low-spin- and high-spin-state Co^{3+}, respectively. In the HS-LS model, it is proposed that the high-spin-state Co^{3+} stabilizes the nearest-neighbor low-spin-state Co^{3+} and that the low-spin-state Co^{3+} has the opposite interaction.[8] We extend the idea and propose that Rh^{3+} and Ga^{3+} stabilize the neighboring high-spin-state and low-spin-state Co^{3+}, respectively. A similar behavior is observed in $La_{1-x}Sr_xCoO_3$ ($x < 0.01$) where one low-spin-state Co^{4+} ion and six intermediate-spin-state Co^{3+} ions form a heptamer polaron (spin-state polaron) at low temperatures.[27,28] We expect that Rh^{3+} and Ga^{3+} substitutions also induce another type of short-range ordering for the spin state of Co^{3+}. Further microscopic measurements, which are in progress, are needed in order to clarify this phenomenon.

IV. SUMMARY

We have measured the magnetization and the lattice volume for $LaCo_{0.8-y}Rh_{0.2}Ga_yO_3$ ($0 \leqslant y \leqslant 0.15$). The magnetization is reduced by Ga^{3+} substitution more strongly than by Rh^{3+} substitution, and the lattice volume is almost independent of the Ga^{3+} substitution. These results suggest that a Ga^{3+} ion is selectively substituted for a high-spin-state Co^{3+}. We find that one Ga^{3+} ion removes an effective magnetic moment of 4.6 μ_B, which is close to the effective magnetic moment (4.9 μ_B) of the high-spin-state Co^{3+}. We further find that 25% of the Co^{3+} ions survives as the high-spin state for $LaCo_{0.8}Rh_{0.2}O_3$ at 2 K. We evaluate the temperature dependence of the concentration of the high-spin-state Co^{3+} in $LaCo_{0.8-y}Rh_{0.2}Ga_yO_3$ ($0 \leqslant y \leqslant 0.15$) and find that the Rh^{3+} substitution partially stabilizes the high-spin state of Co^{3+} to the lowest temperature. We conclude that Ga^{3+} and Rh^{3+} act as if they were substituted for the high-spin-state Co^{3+} and low-spin-state Co^{3+}, respectively. These results strongly suggest that the magnetically excited state of $LaCoO_3$ is a mixed state of the high-spin- and the low-spin-states Co^{3+}.

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