



Antiferromagnetism of $LnRhO_3$ ($Ln =$ rare earth)

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ABSTRACT

The crystallographic and magnetic properties of perovskite-type rhodite $LnRhO_3$ ($Ln =$ rare-earth ions except Ce and Pm) were studied. $LnRhO_3$ ($Ln =$ La, Eu, Lu) shows paramagnetism with very small susceptibility, suggesting that the Rh^{3+} ion has no magnetic moment. $LnRhO_3$ ($Ln =$ Nd, Sm, Gd, Tb, Dy, Ho, Er, Yb) shows antiferromagnetic transition at temperatures between 0.5 and 3.5 K; however, no transition was observed for $LnRhO_3$ ($Ln =$ Pr, Tm) down to 0.5 K. The effective moment μ_{eff} agrees with the theoretical moment of free rare-earth ions, indicating the dominant magnetic contribution of rare-earth ions. The Weiss temperature Θ has a strong correlation with the spin value of rare-earth ions, suggesting that the superexchange interaction is a dominant interaction in $LnRhO_3$. The magnetization of antiferromagnetic samples tends to be saturated above 20–30 kOe, but the moments at 70 kOe are far from the theoretical moments. Antiferromagnetic samples seem to have an intermediate state and require a more intense magnetic field to attain saturation.

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1. Introduction

Rare-earth oxides have long been a subject of studies on magnetism because of their interesting magnetic properties caused by the large spin and orbital angular momenta of rare-earth ions. However, the recent discovery of possible spin frustration phenomena in Nd_2BaZnO_5 [1] has attracted renewed attention to rare-earth oxides. In rare-earth oxides, the magnetic moment of 4f electrons is shielded by the outer shell electrons, and, therefore, magnetic dipole interaction between rare-earth ions is often comparable or superior to the superexchange interaction in rare-earth oxides [2,3]. However, understanding of the magnetic interaction between rare-earth ions in these materials seems insufficient. Among rare-earth oxides, perovskite-type oxides have suitable structural characteristics to study the magnetic interaction because they have a rather simple crystal structure and larger distance between the nearest rare-earth ions than other compounds, such as Nd_2BaZnO_5 , in which spin frustration is explained by the Shastry–Sutherland

model (S–S model) [4]. Although there have been many studies on perovskite-type rare-earth oxides, no clear understanding of the magnetic interaction in them has been obtained. This seems to be due to the fact that those studies were performed for materials in which another magnetic ion coexists with rare-earth ions. Perovskite-type rhodite $LnRhO_3$ ($Ln =$ rare-earth ions) is thought to be the most suitable system to elucidate the magnetic interaction between rare-earth ions because rhodium ions (Rh^{3+} ion) prefer the low spin state with no magnetic moment in a perovskite-type structure. Therefore, magnetic interaction between rare-earth ions can be evaluated without being obstructed by other magnetic ions.

Contrary to the case of other perovskite-type rare-earth oxides, such as rare-earth orthoaluminates [2], all the $LnRhO_3$ ($Ln =$ rare-earth ions except Ce and Pm) have been confirmed to have the same crystal structure [5]. In this paper, in order to reveal the magnetic interaction between rare-earth ions, the crystallographic properties and low temperature magnetic properties of $LnRhO_3$ are investigated, and the relative strength between the superexchange interaction and the magnetic dipole–dipole interaction in $LnRhO_3$ is discussed.

2. Experimental

Polycrystalline specimens of $LnRhO_3$ ($Ln =$ rare earth except Ce and Pm) were prepared by the solid-state reaction using high-purity raw materials of Rh_2O_3

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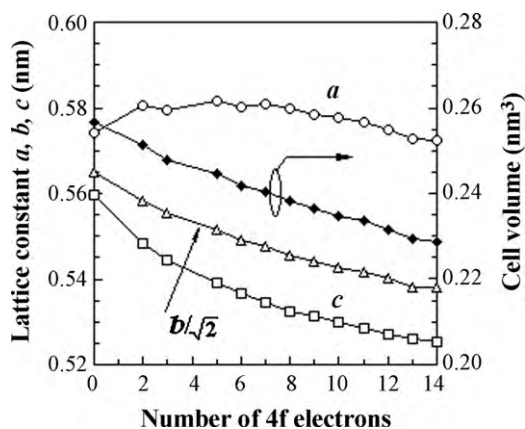


Fig. 1. Lattice parameters and cell volume of LnRhO_3 (Ln = rare earth except Ce and Pm) as a function of the number of 4f electrons.

(99.9%) and Ln_2O_3 (99.9%, Ln = La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu) or Tb_4O_7 (99.9%). An appropriate amount of oxide powder was thoroughly mixed using an agate mortar, and, after being pelletized under the pressure of 100 kg/cm², the mixture was calcined at 950 °C for 10 h in an oxygen atmosphere (1 atm). The calcination was repeated at 1000 °C. After being reground and pressed into a pellet, the mixture was sintered at 1100–1300 °C for 12 h in an oxygen atmosphere (1 atm), the temperature being dependent on the rare-earth ion contained in the oxides, according to the rare-earth ion which is contained in the oxides.

The crystal structure of the specimens was characterized by X-ray powder diffraction using $\text{CuK}\alpha$ radiation and Rietveld refinement for the diffraction data. The magnetic properties were characterized at temperatures from 2 to 100 K using a superconducting quantum interference device (SQUID) magnetometer under applied magnetic fields up to 70 kOe. The chemical composition and homogeneity of the specimens were characterized by electron-probe microanalysis (EPMA) using wavelength-dispersive spectrometers. Specific heat measurements were carried out at temperatures between 0.5 and 20 K using a ³He refrigerator.

3. Results and discussion

It was confirmed by EPMA that all samples were homogeneous and there was no precipitation of Rh metal. In the X-ray powder diffraction profiles for LnRhO_3 (Ln = rare earth except Ce and Pm), there was no trace of raw materials or a second phase, and all the data could be refined assuming the GdFeO_3 -type structure of the space group $Pnma$. The lattice parameters and cell volume are shown in Fig. 1 as a function of the number of 4f electrons. Parameters b and c decrease monotonically as the 4f electron increases; however, there is a very small composition dependence in parameter a . The cell volume shows a linear decrease, reflecting the lanthanide contraction. The crystal structure of LnRhO_3 is shown in Fig. 2. A rare-earth ion has 12 ligand oxygen ions ($z = 12$) and six neighbor rare-earth ions, and each rare-earth ion is linked with six neighbor rare-earth ions via oxygen ions, as shown in Fig. 2a. It is also seen that rare-earth ions also form a triangular lattice. Furthermore, nearest-neighbor rare-earth ions also form a simple cubic lattice (Fig. 2b) without the mediation of oxygen ions. Therefore, it is likely that there are two kinds of magnetic interactions in LnRhO_3 , i.e., superexchange interaction and magnetic dipole interaction, between rare-earth ions.

Fig. 3 shows the temperature dependence of the magnetic susceptibility χ measured for specimens LnRhO_3 (Ln = rare earth except Ce and Pm). LnRhO_3 (Ln = La, Lu, Eu) shows paramagnetism with very small susceptibility and weak temperature dependence. It is well known that Rh^{3+} with six 4d electrons prefers a low spin state with no magnetic moment. Since La^{3+} , Eu^{3+} , and Lu^{3+} are non-magnetic, the very small susceptibility observed for LnRhO_3 (Ln = La, Lu, Eu) indicates that the Rh^{3+} ion is in the low spin state in LnRhO_3 . On the contrary, LnRhO_3 (Ln = Sm, Gd, Tb, Dy, Ho, Yb) shows antiferromagnetic transition at a temperature between 2 and 4 K and Curie–Weiss-type paramagnetic behavior above the transi-

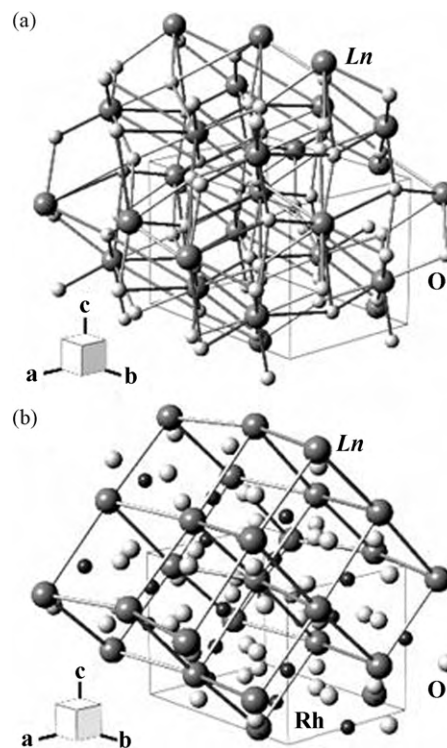


Fig. 2. (a) Rare-earth network drawn by focusing on the link via oxygen ions and (b) rare-earth lattice drawn by focusing on the path without oxygen ions.

tion temperature. No antiferromagnetic transition was observed for LnRhO_3 (Ln = Pr, Nd, Er, Tm) in the magnetization measurement down to 1.9 K. However, as shown in Fig. 4, in the preliminary specific heat measurement, a peak was observed in the temperature dependence of the specific heat for LnRhO_3 (Ln = Nd, Sm, Gd, Tb, Er, Yb). Since the peak temperature of LnRhO_3 (Ln = Sm, Gd, Tb, Yb) agrees well with their Néel temperature T_N , the peak is considered to be the antiferromagnetic transition. Therefore, the T_N 's of NdRhO_3 and ErRhO_3 were determined from the specific heat measurement to be 1.61 and 0.91 K, respectively. No transition was observed in the magnetization and specific heat measurements for LnRhO_3 (Ln = La, Pr, Eu, Tm, Lu). It is well recognized that La^{3+} , Eu^{3+} , and Lu^{3+} are non-magnetic ions, and, therefore, the formation of magnetic order is not expected for these specimens. On the other hand, the Tm^{3+} ion is known to have a non-magnetic singlet ground state (Γ_2) in the crystal field [6–8]; therefore, no magnetic order is formed even at very low temperatures. In the case of Pr, non-Kramers and virtually singlet (or quasidoublet, in which two singlets are separated by small crystal field energy) characters have been reported for PrMnO_3 and $\text{PrFe}_3(\text{BO}_3)_4$, respectively [9–12]. When the ground state of Pr is singlet in PrRhO_3 , no magnetic order is formed similarly to the case of Tm, and Van Vleck paramagnetism is observed at low temperature.

The temperature dependence of the reciprocal magnetic susceptibility χ^{-1} is shown in Fig. 5. The Curie constant C and Weiss temperature Θ were determined by fitting the higher-temperature linear portion of $\chi^{-1}(T)$ data to the Curie–Weiss law. The Néel temperature T_N , Θ , and the effective magnetic moment μ_{eff} deduced from the C are listed in Table 1, and the μ_{eff} is shown in Fig. 6 as a function of the number of 4f electrons. The experimental μ_{eff} almost agrees with the theoretical effective moment $g_J \sqrt{J(J+1)}$, suggesting that the magnetism of LnRhO_3 is attributed to the magnetism of rare-earth ions. Although the reason that experimental μ_{eff} of Yb deviates considerably from the theoretical moment is not clear at present, the difference observed for Pr and Nd ions is consid-

Table 1

Spin value $S(S+1)$, total angular momentum $J(J+1)$, theoretical moment $g\sqrt{J(J+1)}$, Weiss temperature Θ , Néel temperature T_N , and effective moment μ_{eff} evaluated from the results of susceptibility and specific heat measurements.

Ln	4f electrons	$S(S+1)$	$J(J+1)$	$g\sqrt{J(J+1)}$ (μ_B)	Θ (K)	$T_{N,\text{mag}}^a$ (K)	$T_{N,\text{heat}}^a$ (K)	μ_{eff} (μ_B)
La	0	0	0	0	-0.43	×	†	0.24
Pr	2	2	20	3.58	-7.05	×	†	2.85
Nd	3	3.75	24.75	3.62	-0.99	×	1.61	2.71
Sm	5	8.79	8.75	0.84	-1.60	2.5	2.53	0.47
Eu	6	12	0	0	-	×	†	-
Gd	7	15.75	15.75	7.94	-2.5	2.2	1.93	8.16
Tb	8	12	42	9.78	-4.51	2.2	1.81	9.05
Dy	9	8.75	63.75	10.65	-2.87	3.2	*	10.2
Ho	10	6	72	10.60	-2.23	2.4	*	10.1
Er	11	3.75	63.75	9.58	-6.46	×	0.91	9.07
Tm	12	2	42	7.56	-9.36	×	†	7.45
Yb	13	0.75	15.75	4.53	-0.37	2.3	2.24	2.73
Lu	14	0	0	0	-0.10	×	†	0.22

×, no transition down to 1.9 K; †, no transition down to 0.5 K; -, could not be evaluated; *, not measured.

^a $T_{N,\text{mag}}$ and $T_{N,\text{heat}}$ are the Néel temperature determined by magnetic measurement and specific heat measurement, respectively.

ered to be due to their ground state. As mentioned above, the Pr^{3+} ion often has a singlet ground state (Γ_1 $^3\text{H}_4$ ground state) in various compounds [9–12]. It is also well accepted that the magnetic moment of materials with a singlet ground state approaches zero

as the temperature decreases, and, therefore, the effective moment μ_{eff} deduced from the temperature dependence of the susceptibility may be affected by the temperature variation of the moment. On the other hand, it is also well known that the 10-fold degenerate state of Nd^{3+} ion splits in the crystal field to two Γ_8 quartets (Γ_{8-1} and Γ_{8-2}) and one Γ_6 doublet. The ground state of Nd^{3+} is considered to be Γ_{8-1} quartet, and the Γ_{8-1} quartet often splits into four singlets [9]. When Nd^{3+} has a singlet ground state, the same phenomenon that appears in Pr^{3+} would occur, and experimental moments obtained by the Curie–Weiss law may deviate from the theoretical moments. In addition, it is well known that the large angular momentum of rare-earth ions affects the susceptibility measurement even at temperatures above T_N . The deviation observed for heavy rare-earth ions must be caused by the angular momentum of rare-earth ions. The large anisotropy due to the angular momentum will obstruct rare-earth moments to align along the direction of the applied field. Therefore, considerable error would be caused when the Curie constant is determined from the results of susceptibility measurements. This must be the reason for the slight difference between the theoretical and experimental μ_{eff} .

As shown in Table 1, Θ of LnRhO_3 appears to be irrelevant to the number of 4f electrons. The value of Θ indicates the strength

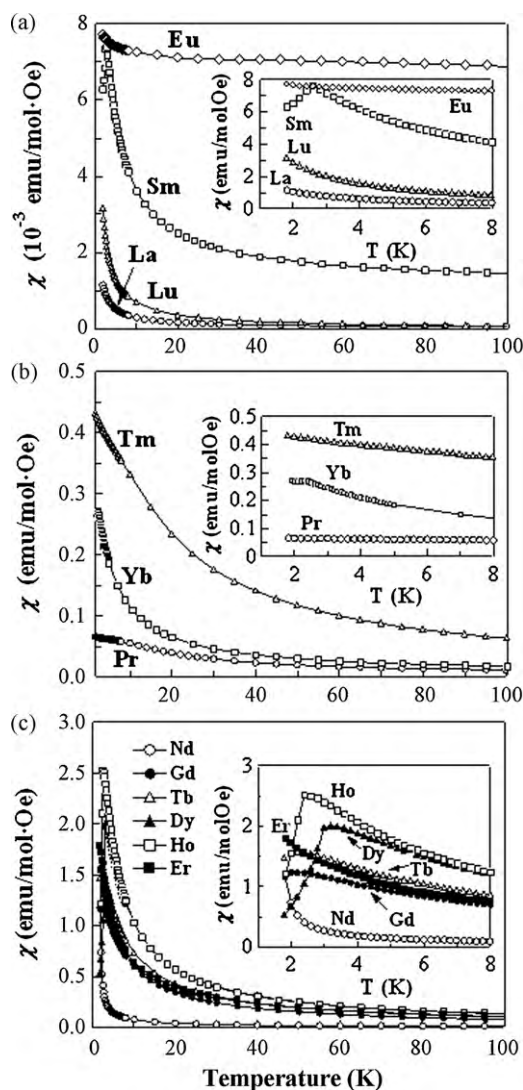


Fig. 3. Temperature dependence of the magnetic susceptibility χ measured for specimens of LnRhO_3 (Ln = rare earth except Ce and Pm) under an applied field of 1 kOe.

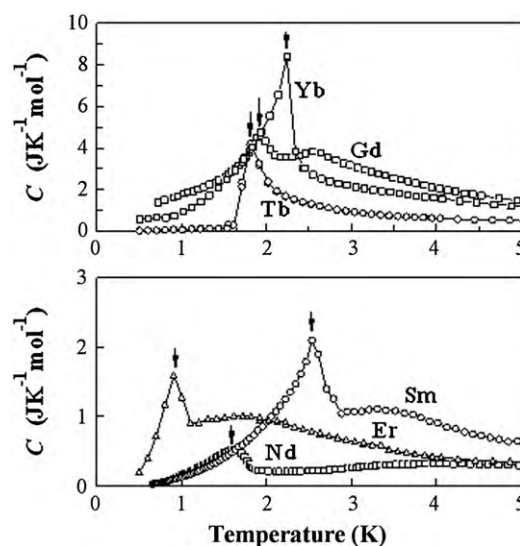


Fig. 4. Temperature dependence of the specific heat for specimens of LnRhO_3 (Ln = Nd, Sm, Gd, Tb, Er, Yb).

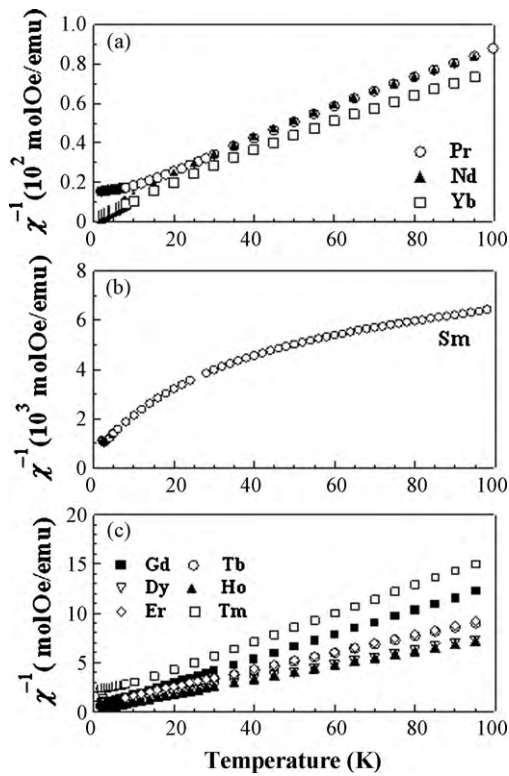


Fig. 5. Temperature dependence of the reciprocal magnetic susceptibility χ^{-1} measured for specimens of LnRhO_3 (Ln = rare earth except Ce and Pm).

of magnetic interactions that contribute to the formation of a magnetic order. The Θ is plotted in Fig. 7a as a function of the spin value $S(S+1)$. In general, the Weiss temperature Θ is proportional to $S(S+1)$ following the molecular field theory. It is evident that the Θ is almost proportional to $S(S+1)$ except for the cases of Pr, Er, and Tm. It is well known that the magnetic moment of some rare-earth ions, such as Pr^{3+} and Tm^{3+} , depends on the temperature and the $\chi^{-1}(T)$ of these ions deviates from a straight line [6,13,8]. Therefore, the Θ obtained from the $\chi^{-1}(T)$ data does not necessarily reflect the strength of dominant magnetic interactions in the system. From this point of view, we disregard the data of PrRhO_3 and TmRhO_3 for the present time in discussing the magnetism of LnRhO_3 . The relation between Θ and $S(S+1)$ suggests that the magnetic interaction between rare-earth ions depends strongly on the spin values of such ions. On the contrary, as shown in Fig. 7(b), no correlation was observed between Θ and the total angular momentum

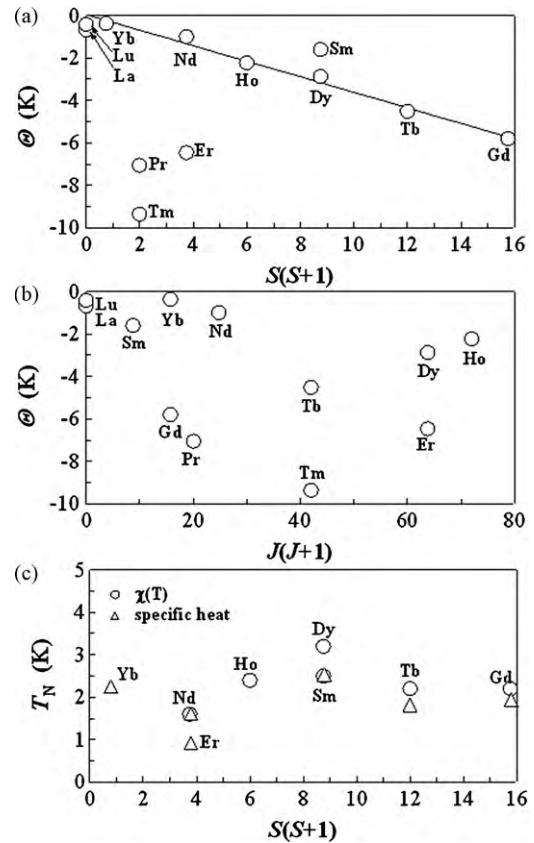


Fig. 7. (a) Weiss temperature Θ of LnRhO_3 as a function of $S(S+1)$, (b) Θ of the same specimens as a function of $J(J+1)$, and (c) T_N of the same specimens as a function of $S(S+1)$.

$J(J+1)$. Therefore, we consider that the dominant magnetic interaction between rare-earth ions is the superexchange interaction via oxygen ions in the LnRhO_3 system. The linear relation between Θ and $S(S+1)$ suggests that the exchange energy is almost constant regardless of the type of rare-earth ion.

In the LnRhO_3 system, as shown in Fig. 2b, each rare-earth ion has six nearest-neighbor rare-earth ions at almost symmetrical positions, and thus the magnetic dipole-dipole interaction between rare-earth ions should be zero or very small. Therefore, in conclusion, rare-earth ions make a major contribution to the superexchange interaction between rare-earth ions and the formation of a magnetic order in LnRhO_3 . In the LnRhO_3 system, SmRhO_3 is considered to be a typical material to confirm the above consideration. SmRhO_3 has a relatively large Néel temperature ($T_N = 2.5$ K) that is comparable with those of other antiferromagnetic LnRhO_3 . It is well known that the ground state of free Sm^{3+} ions with an odd number of 4f electrons ($4f^5$) splits in the crystal field, establishing the Kramer's doublet ground state, which has a finite magnetic moment even at 0 K in spite of the zero moment of the free ion. However, the value of the magnetic moment reported for this ground state is $0.14 \mu_B/\text{Sm}$ [14]. This value is considerably smaller than those of other magnetic rare-earth ions. The theoretical moment of the Sm ion was calculated by applying the formula

$$\text{magnetic moment} = \langle \text{gs} | \mathbf{L}_z + 2\mathbf{S}_z | \text{gs} \rangle = g_J \langle \text{gs} | J_z | \text{gs} \rangle$$

to the ground state (gs) wave functions [15]

$$|\alpha\rangle = \frac{1}{\sqrt{6}} \{ |5/2\rangle - \sqrt{5} | -3/2\rangle \}$$

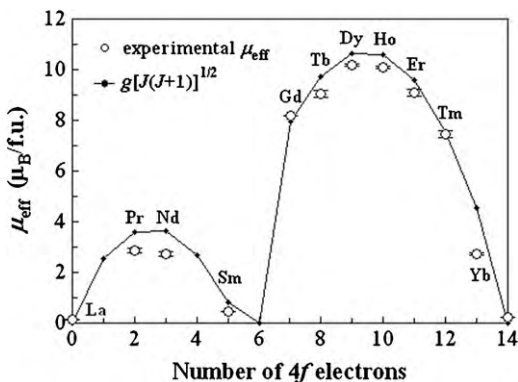


Fig. 6. Effective magnetic moment μ_{eff} for LnRhO_3 , theoretical effective moment $g_J \sqrt{J(J+1)}$ as a function of the number of 4f electrons.

and

$$|\beta\rangle = \frac{1}{\sqrt{6}}\{|-5/2\rangle - \sqrt{5}|3/2\rangle\}$$

for $J=5/2$, where J and M are the quantum numbers for the total angular momentum operator $\mathbf{J}=\mathbf{L}+\mathbf{S}$ and the z component of \mathbf{J} , respectively. $0.24\mu_B/\text{Sm}$ was obtained using $g_J=2/7$. This value seems consistent with that reported by Geller et al.; however, these values are extremely small in comparison with those of other rare-earth ions. Therefore, the relatively large T_N (2.5 K) and $|\Theta|$ (2.6 K) of SmRhO_3 cannot be attributed to the magnetic dipole interaction, which strongly depends on the magnetic moment of the total angular momentum \mathbf{J} . Since the values of T_N and $|\Theta|$ of SmRhO_3 agree well and the Θ lies almost on the linear relation between Θ and the $S(S+1)$, it is clear that the superexchange interaction plays a key role in the formation of a magnetic order in SmRhO_3 as it does in LnRhO_3 ($\text{Ln}=\text{Nd}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Yb}$).

Since the superexchange interaction is dominant in this system, spin frustration would not occur in the LnRhO_3 system. The strength of the superexchange interaction can be estimated from the value of $|\Theta|$. The strength of the superexchange interaction is estimated from the $|\Theta|$ ($=5\text{ K}$) of GdRhO_3 as $5/12\text{ K}$ using the number ($=12$) of Gd–O–Gd paths around a Gd ion. According to the molecular field approximation, the Néel temperature T_N of LnRhO_3 must depend on $S(S+1)$. The T_N of LnRhO_3 is shown in Fig. 7c as a function of $S(S+1)$. There is no correlation between the T_N and the spin value. Although the exact reason for this result is presently unclear, some possible causes can be considered; (1) the difference in the spin value of the ground state between a free ion and an ion in crystal and (2) the effect of the triangular lattice of rare-earth ions. However, further detailed studies using a novel experimental technique must be performed to gain a deeper understanding of this issue.

Fig. 8 shows the magnetic-field dependence of the magnetization measured for specimens of LnRhO_3 ($\text{Ln}=\text{rare earth except Ce and Pm}$) at 1.9 K. The $M(H)$ curves of antiferromagnetic LnRhO_3 ($\text{Ln}=\text{Nd}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Yb}$) tend to be saturated at higher applied fields above 20–30 kOe. The magnetization of LnRhO_3 ($\text{Ln}=\text{Dy}, \text{Ho}$), in particular, increases linearly at lower magnetic fields; however, it increases rapidly at an applied field between 2 and 4 kOe. The $M(H)$ curves of LnRhO_3 ($\text{Ln}=\text{Dy}, \text{Ho}$) are reversible for increasing and decreasing magnetic fields. It is well accepted that spin flopping occurs when the exchange field H_m or the anisotropy field H_a is comparable to the applied field. In the case of $H_m > H_a$, the applied field rotates rare-earth moments against H_a , keeping the antiferromagnetic spin arrangement, which is perpendicular to the easy axis. After the rotation, the $M(H)$ curve reflects the perpendicular susceptibility, which is much larger than that of the parallel susceptibility in the antiferromagnetic state. This must be the reason that the $M(H)$ curves of LnRhO_3 ($\text{Ln}=\text{Dy}, \text{Ho}$) change their curvature at an applied field in the range of 2–4 kOe. On the other hand, no rapid increase was observed in the $M(H)$ curves of other antiferromagnetic LnRhO_3 samples. This seems to be due to the measurement temperature (1.9 K). When the measurement is performed at sufficiently low temperature below T_N , these antiferromagnetic samples may show similar magnetic transition. The $M(H)$ curves of LnRhO_3 ($\text{Ln}=\text{La}, \text{Eu}, \text{Lu}$) show paramagnetic behavior; the magnetization shows a linear increase up to 70 kOe. Fig. 9 shows the magnetization n_B at 70 kOe together with the theoretical ground state moment $g_J\mu_B$. Although the $M(H)$ curves of LnRhO_3 ($\text{Ln}=\text{Nd}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Yb}$) tend to be saturated above 20–30 kOe, the experimental values of n_B are far from the theoretical values and almost 1/2 of theoretical moment for samples with heavy rare-earth ions. Similar behavior was observed for oxides and intermetallic compounds such as $\text{Dy}_3\text{Al}_5\text{O}_{12}$ and DyCo_2Si_2 [16–19]. For example, $\text{Dy}_3\text{Al}_5\text{O}_{12}$ is saturated at 1.06 K with a magnetic moment of $\sim 6.6\mu_B$, however, this value is consid-

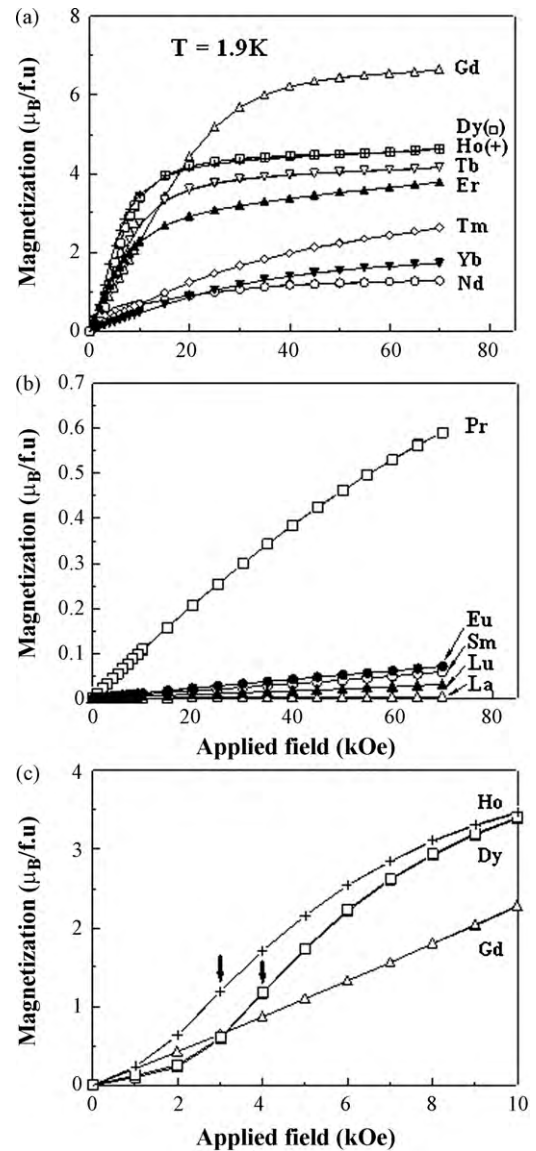


Fig. 8. Magnetic-field dependence of the magnetization measured for specimens of LnRhO_3 ($\text{Ln}=\text{rare earth except Ce and Pm}$) at 1.9 K.

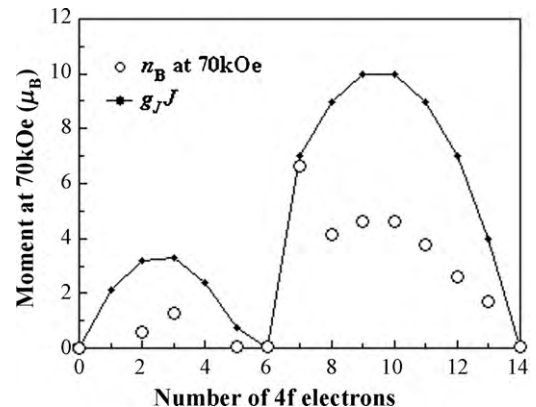


Fig. 9. Experimental magnetization n_B at 1.9 K under an applied field of 70 kOe and theoretical ground state moment $g_J\mu_B$ as a function of the number of 4f electrons.

erably smaller than the theoretical moment ($10 \mu_B$) of free Dy^{3+} ion. On the other hand, $DyCo_2Si_2$ shows two step metamagnetic transitions at around 20 and 40 kOe at 4.2 K, and the magnetization n_B ($\sim 5 \mu_B$) observed at intermediate state between first and second transition is one half of the saturation moment ($\sim 10 \mu_B$). Therefore, there is quite a possibility that antiferromagnetic $LnRhO_3$ (Ln = heavy rare earth) has an intermediate state above low field metamagnetic transition like $DyCo_2Si_2$ and intense magnetic field more than 70 kOe is required to realize actual magnetic saturation.

Tm has a singlet ground state as mentioned above, and $TmRhO_3$ should thus have no magnetic moment; however, considerable moment is observed actually. Presumably, the excited state of the Tm ion is modulated by the intense magnetic field and mixed with the singlet ground state, inducing a moment on the Tm ion. Contrary to the n_B of heavy rare-earth ions, the n_B values of Pr and Nd are considerably smaller than the theoretical value. This seems to be due to the singlet ground state. The possible singlet ground state of the Pr ion was mentioned above. When the singlet ground state is also realized in the Nd ion, the n_B of $NdRhO_3$ must be zero. However, as in the case of Tm, when the excited state of Pr and Nd is mixed into the ground state under an intense magnetic field, a small magnetic moment would appear on these ions.

4. Conclusion

Polycrystals of $LnRhO_3$ (Ln = rare earth except Ce and Pm) were prepared by the solid-state reaction, and their magnetic properties were investigated. An antiferromagnetic transition was observed for $LnRhO_3$ (Ln = Nd, Sm, Gd, Tb, Dy, Ho, Er, Yb) at a temperature below 4 K; however, antiferromagnetic behavior was not observed for $LnRhO_3$ (Ln = La, Pr, Eu, Tm, Lu) at temperatures down to 0.5 K. The effective moments obtained from the susceptibility measurements indicate that rare-earth ions make a major contribution to the magnetism of $LnRhO_3$ and the Rh^{3+} ion prefers the low spin state with no magnetic moment. The asymptotic Curie temperature of antiferromagnetic samples has a correlation with the spin value of rare-earth ions, suggesting that the superexchange interaction between rare-earth ions is a dominant interaction for the formation of antiferromagnetic order in the $LnRhO_3$ system. The magnetizations of $LnRhO_3$ (Ln = Nd, Gd, Tb, Dy, Ho, Er, Yb) saturate almost at 70 kOe; however, the magnetizations are considerably smaller than the theoretical moments. This suggests that another mag-

netic transition at more intense magnetic fields is required to attain saturation magnetization. It is quite possible that a metamagnetic-like transition occurs in antiferromagnetic samples of the $LnRhO_3$ system at very low temperature under very intense magnetic fields.

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