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Structure and magnetic property of $Ce_xEu_{1-x}CoO_3$ prepared by means of the thermal decomposition of $Ce_xEu_{1-x}[Co(CN)_6]\cdot nH_2O$

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Abstract

$Eu[Co(CN)_6]\cdot 4H_2O$ and $Ce_xEu_{1-x}[Co(CN)_6]\cdot 4H_2O$ ($x = 0.1$, 0.15, 0.2, 0.3 and 0.4) were synthesized as the precursors to obtain the homogeneous perovskite-type oxides, $EuCoO_3$ and $Ce_xEu_{1-x}CoO_3$.

The oxides $EuCoO_3$ and $Ce_xEu_{1-x}CoO_3$ were obtained by the thermal decompositions of $Eu[Co(CN)_6]\cdot 4H_2O$ and $Ce_xEu_{1-x}[Co(CN)_6]\cdot 4H_2O$, respectively. In the ranges of $x \leq 0.5$, the lattice parameters of these perovskite-type oxides, a and b, linearly lengthen with the increase of the value of x, but those of c are nearly constant. These findings indicated that $Ce_xEu_{1-x}CoO_3$ was formed in the range of $x \leq 0.5$. The structures of $EuCoO_3$ and $Ce_xEu_{1-x}CoO_3$ were determined by means of the Rietveld method, and these oxides were orthorhombic and *Pnma*.

The magnetic susceptibility of $EuCoO_3$ showed the paramagnetic property, which includes Van Vleck's paramagnetism. The Co^{III} in $EuCoO_3$ were in the low ground spin state ($t_{2g}^6e_g^0$, $S = 0$), and the susceptibility of $EuCoO_3$ was dependent on the Eu^{III} in observed temperature ranges.

The valence combination of $Ce_{0.1}Eu_{0.9}CoO_3$ was considered to be $Ce_{0.1}^{III}Eu_{0.9}^{III}CoO_3$ from the temperature dependency of the magnetic susceptibility of $Ce_{0.1}Eu_{0.9}CoO_3$.

Keywords: Thermal decomposition of $Ce_xEu_{1-x}[Co(CN)_6]\cdot nH_2O$; Perovskite-type oxides of $Ce_xEu_{1-x}CoO_3$; Magnetic susceptibility

1. Introduction

A series of perovskite-type oxides, $LnCoO_3$ (Ln = La, Pr–Lu) have been investigated for their structures, electrical and magnetic properties for a long time [1,2]. For example, $LaCoO_3$ has two magnetic transitions at around 120 and 500 K [3–5]. Asai et al. [6] proposed that the first was the transition from the low spin ground state of Co^{III} ($t_{2g}^6e_g^0$, $S = 0$) to the intermediate spin state ($t_{2g}^5e_g^1$, $S = 1$), and the second was the transition from the intermediate spin state to the high spin state ($t_{2g}^4e_g^2$, $S = 2$).

In the series of oxides of $LnCoO_3$, only $CeCoO_3$ has not yet been obtained. The final products of the decomposition of $Ce[Co(CN)_6]\cdot 5H_2O$ were the mixture of CeO_2 and Co_3O_4. If the lanthanide ions of $LnCoO_3$ could be partly substituted by cerium ion, $Ln_xCe_{1-x}CoO_3$ should be obtained. However, the final product of the thermal decomposition of $La_xCe_{1-x}[Co(CN)_6]\cdot 5H_2O$ was a mixture of $LaCoO_3$, La_2O_3, CeO_2 and Co_3O_4, and $La_xCe_{1-x}CoO_3$ was not obtained.

Recently, authors succeeded to prepare $Ce_xEu_{1-x}CoO_3$ ($x = 0.1$ and 0.15) by the thermal decomposition of $Ce_xEu_{1-x}[Co(CN)_6]\cdot 4H_2O$. It is known that the normal valences of the lanthanide ions are +3, however, Ce^{3+} ion is more easily oxidized to Ce^{4+} ion than the other trivalent lanthanide ions. On the other hand, Eu^{2+} ion is more stable than the other divalent lanthanide ions. Therefore, the valence combinations of $Ce_x^{IV}Eu_x^{II}Eu_{1-2x}^{III}CoO_3$ and $Ce_x^{III}Eu_{1-x}^{III}CoO_3$ are expected for $Ce_xEu_{1-x}CoO_3$.

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In this paper, the oxides of $EuCoO_3$ and $Ce_xEu_{1-x}CoO_3$ were prepared by means of the thermal decomposition of $Eu[Co(CN)_6]\cdot 4H_2O$ and $Ce_xEu_{1-x}[Co(CN)_6]\cdot 4H_2O$ in air atmosphere, respectively. The structures of $EuCoO_3$ and $Ce_xEu_{1-x}CoO_3$ were studied by means of the Rietveld analysis [7,8] of their powder X-ray diffractions. The magnetic susceptibilities of these oxides also were measured to determine the valence combination of Ce and Eu ions.

2. Experimental

2.1. Chemicals and preparations

$Eu[Co(CN)_6]\cdot 4H_2O$ was prepared by mixing equimolar of $K_3[Co(CN)_6]$ and $Eu(NO_3)\cdot 6H_2O$ in an aqueous solution and heating at ca. 360 K. $Ce_xEu_{1-x}[Co(CN)_6]\cdot 4H_2O$ ($x = 0.1$, 0.15, 0.2, 0.3 and 0.4) were also prepared by mixing $0.2\,mol\,dm^{-3}$ $K_3[Co(CN)_6]$ aqueous solution, $0.2 \times x\,mol\,dm^{-3}$ $Ce(NO_3)\cdot 6H_2O$ aqueous solution and $0.2 \times (1 - x)\,mol\,dm^{-3}$ $Eu(NO_3)\cdot 6H_2O$ aqueous solution, and heating the mixture at ca. 360 K.

$Ce(NO_3)\cdot 6H_2O$ and $Eu(NO_3)\cdot 6H_2O$ were purchased from Shinetsu Chemical Co., both the purities were 99.9% and used without further purification. $K_3[Co(CN)_6]$ was obtained from Sigma Aldrich Co., and used after the purification by recrystallization from distilled water [9–11].

$EuCoO_3$ and $Ce_xEu_{1-x}CoO_3$ ($x = 0.1$ and 0.15) were prepared by heating $Eu[Co(CN)_6]\cdot 4H_2O$ and $Ce_xEu_{1-x}[Co(CN)_6]\cdot 4H_2O$ to 1473 K for 2 h under air atmosphere in ADVANTEC electric furnace KT-1533, respectively.

2.2. Measurements

Thermogravimetry (TG) and differential thermal analysis (DTA) curves were simultaneously recorded on a Rigaku Thermoflex TAS200. About 10 mg of sample was weighed into a platinum crucible and heated to 1273 K with the heating rate of $10\,K\,min^{-1}$ in the air atmosphere. An α-alumina was used as a reference [9–16].

X-ray powder diffraction (XRD) profiles were obtained by means of the method previously described [9–13]. The lattice parameters of $Eu[Co(CN)_6]\cdot 4H_2O$, $Ce_xEu_{1-x}[Co(CN)_6]\cdot 4H_2O$ ($x = 0.1$, 0.2, 0.3 and 0.4), $EuCoO_3$ and $Ce_xEu_{1-x}CoO_3$ ($x = 0.1$ and 0.15) were predicted by use of the CELL program [17], and the refinements of the structures of $EuCoO_3$ and $Ce_xEu_{1-x}CoO_3$ ($x = 0.1$ and 0.15) were performed by means of the Rietveld method by use of the RIETAN2000 [7,8].

The magnetic susceptibility of $EuCoO_3$ and $Ce_xEu_{1-x}CoO_3$ ($x = 0.1$ and 0.15) were measured in a SQUID magnetometer, Quantum Design MPMS-XL in the temperature range from 5 to 300 K with an applied magnetic field at 10,000 Oe.

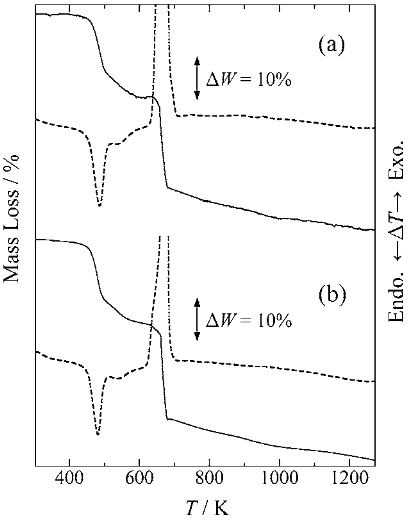

Fig. 1. TG–DTA curves of $Eu[Co(CN)_6]\cdot 4H_2O$ and $Ce_{0.1}Eu_{0.9}[Co(CN)_6]\cdot 4H_2O$: (a) $Eu[Co(CN)_6]\cdot 4H_2O$; (b) $Ce_{0.1}Eu_{0.9}[Co(CN)_6]\cdot 4H_2O$. (—) TG; (- - -) DTA.

3. Results and discussion

3.1. The structure of $Ce_xEu_{1-x}[Co(CN)_6]\cdot 4H_2O$

The TG–DTA curves for $Eu[Co(CN)_6]\cdot 4H_2O$ and $Ce_{0.1}Eu_{0.9}[Co(CN)_6]\cdot nH_2O$ are shown in Fig. 1. The dehydration took place at least two stages, and these complexes were tetrahydrates from the thermal gravimetries [14,15]. Fig. 2 shows the XRD profiles of $Eu[Co(CN)_6]\cdot 4H_2O$ and $Ce_xEu_{1-x}[Co(CN)_6]\cdot 4H_2O$ ($x = 0.1$, 0.2, 0.3 and 0.4).

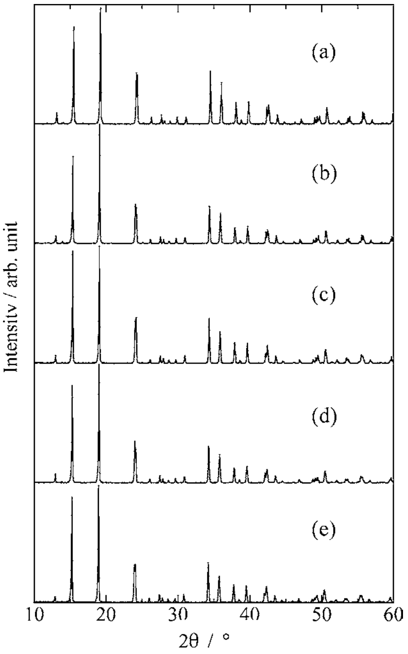

Fig. 2. XRD profiles of $Eu[Co(CN)_6]\cdot 4H_2O$ and $Ce_xEu_{1-x}[Co(CN)_6]\cdot 4H_2O$: (a) $Eu[Co(CN)_6]\cdot 4H_2O$; (b) $x = 0.1$; (c) $x = 0.2$; (d) $x = 0.3$; (e) $x = 0.4$.

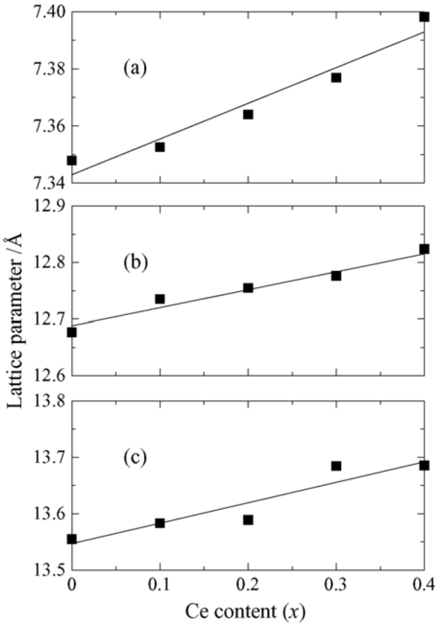

Fig. 3. Lattice parameters of $Eu[Co(CN)_6]\cdot 4H_2O$ and $Ce_xEu_{1-x}[Co(CN)_6]\cdot 4H_2O$: (a) *a*-axis; (b) *b*-axis; (c) *c*-axis.

The crystal structure of $Eu[Co(CN)_6]\cdot 4H_2O$ was orthorhombic and *Cmcm* [18]. The crystal structures of $Ce_xEu_{1-x}[Co(CN)_6]\cdot 4H_2O$ ($x = 0.1$, 0.2, 0.3 and 0.4) were assumed to be orthorhombic and *Cmcm* because their profiles were similar to those of $Eu[Co(CN)_6]\cdot 4H_2O$. The X-ray diffraction peaks of $Ce_xEu_{1-x}[Co(CN)_6]\cdot 4H_2O$ shifted into lower angles with increase of the value of x. The lattice parameters predicted by use of the CELL program, were linearly expanded with the increase of the value of x (Fig. 3).

3.2. The structure of $Ce_xEu_{1-x}CoO_3$

Fig. 4 shows the XRD profiles of the residues obtained by heating $Eu[Co(CN)_6]\cdot 4H_2O$ and $Ce_xEu_{1-x}[Co(CN)_6]\cdot 4H_2O$ ($x = 0.1$, 0.15, 0.2, 0.3 and 0.4) to 1473 K in air atmosphere. The final product of $Eu[Co(CN)_6]\cdot 4H_2O$ was $EuCoO_3$ [19]. The profiles for $x = 0.1$ and 0.15 were similar to that of $EuCoO_3$. However, the peaks of CeO_2 [20], Eu_2O_3 [21] and Co_3O_4 [22] appeared on the profiles for $x \geq 0.2$. In the ranges of $x \leq 0.5$, the lattice parameters of a and b linearly lengthen with the increase of the value of x, but those of c are nearly constant. In the ranges of $x \geq 0.2$, the lattice parameters of a, b and c are almost constant values (Fig. 5). These results indicate that Eu atoms in $EuCoO_3$ can be replaced with Ce atoms in the range of $x \leq 0.5$ leading to formation of $Ce_xEu_{1-x}CoO_3$.

The XRD profiles for $EuCoO_3$, $Ce_{0.1}Eu_{0.9}CoO_3$ and $Ce_{0.15}Eu_{0.85}CoO_3$ were refined by means of the Rietveld method [7,8]. The observed profiles of these oxides showed good agreement with the calculated ones (Fig. 6). The reliability factors and the goodness of fit indicator S are shown in Table 1. These oxides were orthorhombic and *Pnma*.

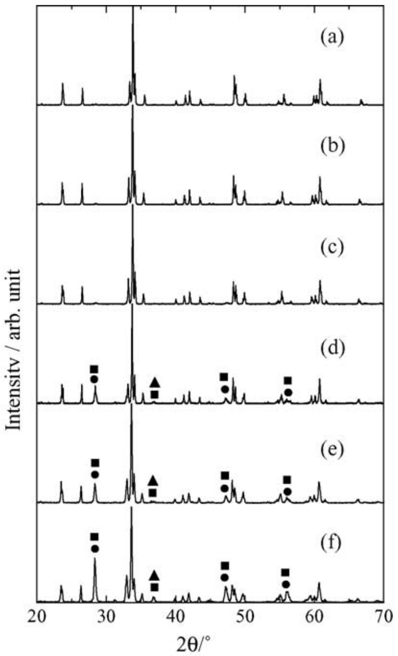

Fig. 4. XRD profiles of the residues of $Eu[Co(CN)_6]\cdot 4H_2O$ and $Ce_xEu_{1-x}[Co(CN)_6]\cdot 4H_2O$ heated at 1473 K: (a) $Eu[Co(CN)_6]\cdot 4H_2O$; (b) $x = 0.1$; (c) $x = 0.15$; (d) $x = 0.2$; (e) $x = 0.3$; (f) $x = 0.4$. (●) CeO_2; (■) Eu_2O_3; (▲) Co_3O_4.

3.3. The magnetic property of $EuCoO_3$

The magnetic susceptibility of $EuCoO_3$, χ_m ($EuCoO_3$) was measured in the temperature ranges from 5 to 300 K (Fig. 7). The χ_m ($EuCoO_3$) remained almost constant at

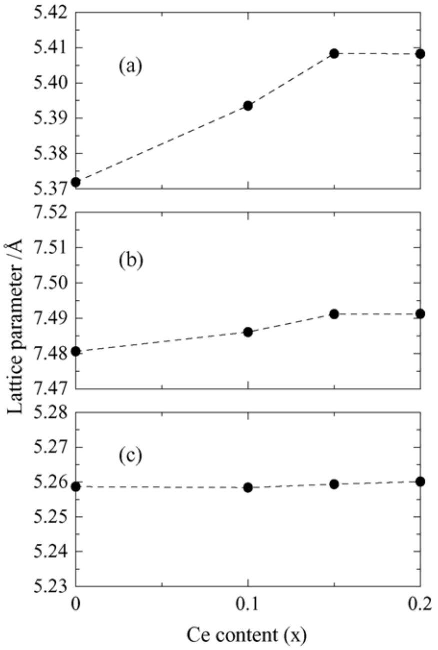

Fig. 5. Lattice parameters of $EuCoO_3$ and $Ce_xEu_{1-x}CoO_3$: (a) *a*-axis; (b) *b*-axis; (c) *c*-axis.

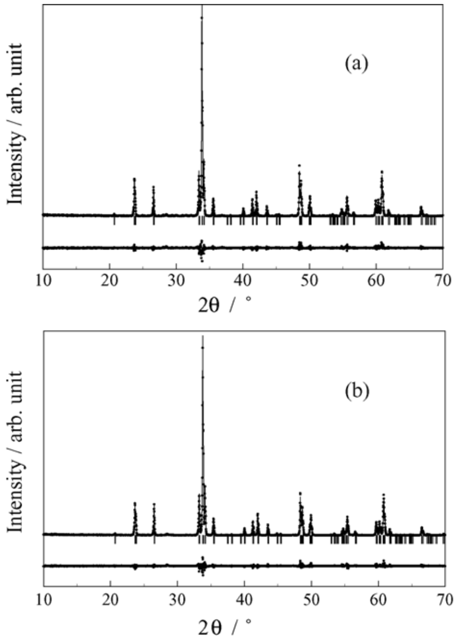

Fig. 6. Rietveld refinement profile of $EuCoO_3$ and $Ce_{0.1}Eu_{0.9}CoO_3$: (a) $EuCoO_3$; (b) $Ce_{0.1}Eu_{0.9}CoO_3$.The dotted line is the observed X-ray diffraction profile, and the solid line is the calculated one. The bottom curve shows the difference of observed and calculated ones, and the small bars indicate the angular positions of the allowed Bragg reflections.

lower temperature than 100 K and then decreased with the increase of the temperature. The temperature dependency of χ_m ($EuCoO_3$) shows that $EuCoO_3$ has the paramagnetic property, which includes Van Vleck's paramagnetism. The deviation from the paramagnetism observed below 20 K is ascribable to the contribution of impurities [6].

Table 1
Crystallographic data of $EuCoO_3$ and $Ce_{0.1}Eu_{0.9}CoO_3$

	$EuCoO_3$	$Ce_{0.1}Eu_{0.9}CoO_3$
2θ range (°)	10–70	10–70
Step scan increment (°)	0.02	0.02
Count time (s)	3	3
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pnma*	*Pnma*
a (Å)	5.3719(2)	5.3935(2)
b (Å)	7.4808(3)	7.4861(2)
c (Å)	5.2589(2)	5.2584(2)
Reliability factor		
R_{wp} (%)[a]	19.85	17.89
R_p (%)[b]	12.17	12.24
R_e (%)[c]	15.34	14.75
R_I (%)[d]	4.57	3.14
R_F (%)[e]	3.89	3.16
S[f]	1.29	1.21

[a] *R*-weighed pattern.
[b] *R*-pattern.
[c] *R*-expected.
[d] *R*-integrated intensity.
[e] *R*-structure factor.
[f] The 'goodness-of-fit' indicator.

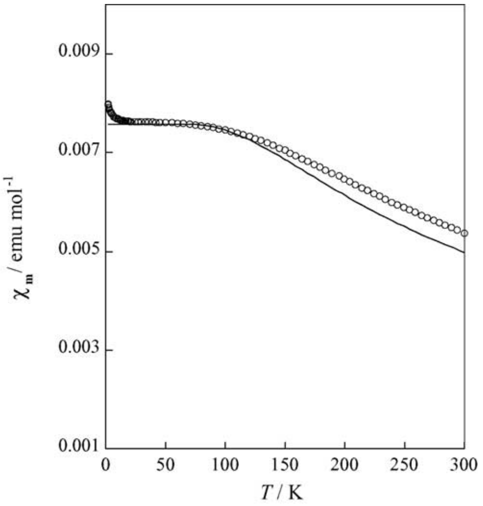

Fig. 7. The magnetic susceptibilities: (○) observed χ_m ($EuCoO_3$); (—) estimated χ_m (Eu^{III}) by use of Eq. (1).

In 1932, Van Vleck proposed the method to evaluate the magnetic susceptibility of any ion as follows [23]:

$$\chi_m = \frac{\sum_{|L-S|}^{|L+S|}\{\chi_{Curie} + \chi_{Van\ Vleck}\}(2J+1)\,e^{-E_J/k_BT}}{\sum_{|L-S|}^{|L+S|}(2J+1)\,e^{-E_J/k_BT}} \qquad (1)$$

where

$$\chi_{Curie} = \frac{N_A\mu_B^2 g_J^2 J(J+1)}{3k_BT} \qquad (2)$$

$$\chi_{Van\ Vleck} = \frac{N_A\mu_B^2}{6(2J+1)}\left\{\frac{F(J+1)}{E_{J+1}-E_J} - \frac{F(J)}{E_J - E_{J-1}}\right\} \qquad (3)$$

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)} \qquad (4)$$

and

$$F(J) = \frac{\{(S+L+1)^2 - J^2\}\{J^2 - (S-L)^2\}}{J} \qquad (5)$$

where, N_A, k_B and μ_B are the Avogadro's constant, Boltzmann's constant and Bohr's magnetron, respectively. In Eq. (1), the diamagnetic term was omitted, since it was negligibly small.

In 2001, Sudheendra et al. [24] reported that the transition temperature from the low spin ground state ($t_{2g}^6e_g^0$, $S=0$) of Co^{III} of $LnCoO_3$ to the intermediate spin state ($t_{2g}^5e_g^1$, $S=1$) increased with the decrease in the size of the lanthanide ion. The transition temperatures reported for $LaCoO_3$, $PrCoO_3$ and $NdCoO_3$ were 120, 220 and 275 K, respectively. Also and Miyahara [25] also reported that all Co^{III} of $GdCoO_3$ are in the low spin state at lower temperature than 300 K. These facts suggest that Co^{III} does not contribute to the χ_m ($EuCoO_3$). The relationship between the magnetic susceptibility and temperature of Eu^{III} ion estimated by use of Eq. (1), resembled to that of $EuCoO_3$ (Fig. 7).

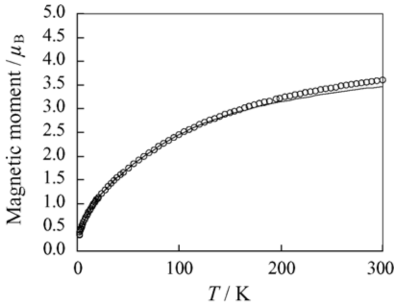

Fig. 8. The magnetic moment: (○) μ_{exp} of $EuCoO_3$ determined from the susceptibilities; (—) estimated μ_{eff} of Eu^{III} ion by use of Eq. (1).

The effective magnetic moment can be described as follows:

$$\mu_{eff} = \sqrt{\frac{3\chi k_B T}{N_A}} \tag{6}$$

Fig. 8 shows the experimental magnetic moment μ_{exp} ($EuCoO_3$) determined from the magnetic susceptibilities of Fig. 7 and the effective magnetic moment μ_{eff} (Eu^{III}) estimated from Eq. (1). The difference between the μ_{exp} of $EuCoO_3$ and μ_{eff} of Eu^{III} ion was very small. These findings indicate that almost all Co^{III} of $EuCoO_3$ are in the low spin ground state in observed temperature ranges, and the χ_m ($EuCoO_3$) must be depended on the Eu^{III}.

3.4. The magnetic property of $Ce_{0.1}Eu_{0.9}CoO_3$

Fig. 9 shows the relationships between the magnetic susceptibilities and temperatures for $Ce_{0.1}Eu_{0.9}CoO_3$ and $EuCoO_3$. The temperature dependency of the susceptibility of $Ce_{0.1}Eu_{0.9}CoO_3$ was different from that of $EuCoO_3$, and increased rapidly at lower temperatures than 120 K. Because Co^{III} is diamagnetic in these low temperature ranges, the susceptibility of $Ce_{0.1}Eu_{0.9}CoO_3$, χ_m ($Ce_{0.1}Eu_{0.9}CoO_3$) is dependent on the lanthanide ions.

To evaluate the magnetic property of $Ce_{0.1}Eu_{0.9}CoO_3$, two valence combinations, $Ce^{III}_{0.1}Eu^{III}_{0.9}CoO_3$ and $Ce^{IV}_{0.1}Eu^{II}_{0.1}Eu^{III}_{0.8}CoO_3$ were presumed. Considering the valence combinations, Ce^{IV} is diamagnetic, and Ce^{III} ($\mu_{eff} = 2.54\,\mu_B$) and Eu^{II} ($\mu_{eff} = 7.94\,\mu_B$) are paramagnetic. Assuming the additivity of the magnetic susceptibility, the χ_m ($Ce^{III}_{0.1}Eu^{III}_{0.9}CoO_3$) and χ_m ($Ce^{IV}_{0.1}Eu^{II}_{0.1}Eu^{III}_{0.8}CoO_3$) could be estimated by use of Eq. (1). Comparing the temperature dependency of the χ_m ($Ce_{0.1}Eu_{0.9}CoO_3$) to those of χ_m ($Ce^{III}_{0.1}Eu^{III}_{0.9}CoO_3$) and χ_m ($Ce^{IV}_{0.1}Eu^{II}_{0.1}Eu^{III}_{0.8}CoO_3$), the profile of χ_m ($Ce_{0.1}Eu_{0.9}CoO_3$) was similar to that of χ_m ($Ce^{III}_{0.1}Eu^{III}_{0.9}CoO_3$) (Fig. 10). This finding indicates that valence combination of $Ce_{0.1}Eu_{0.9}CoO_3$ was $Ce^{III}_{0.1}Eu^{III}_{0.9}CoO_3$.

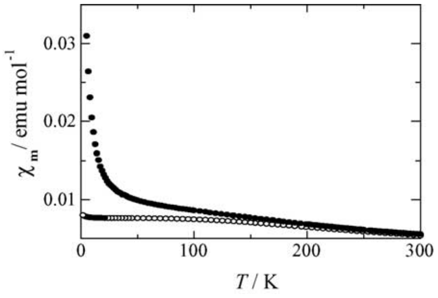

Fig. 9. The magnetic susceptibilities: (○) $EuCoO_3$; (●) $Ce_{0.1}Eu_{0.9}CoO_3$.

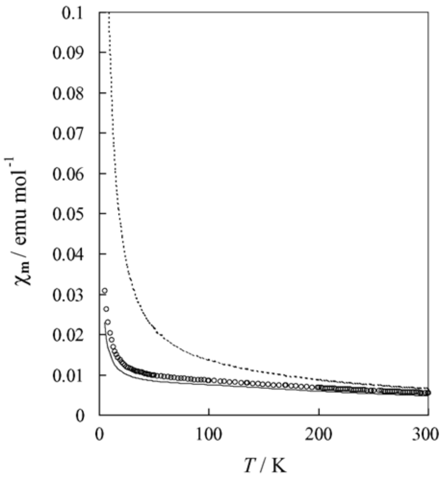

Fig. 10. The magnetic susceptibilities: (○) observed χ_m ($Ce_{0.1}Eu_{0.9}CoO_3$); (—) estimated χ_m ($Ce^{IV}_{0.1}Eu^{II}_{0.9}CoO_3$) by use of Eq. (1). (- - -): Estimated χ_m ($Ce^{III}_{0.1}Eu^{III}_{0.1}Eu^{III}_{0.8}CoO_3$) by use of Eq. (1).

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