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Van Vleck paramagnetism of the trivalent Eu ions

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Van Vleck paramagnetism of the trivalent Eu ions

Yusuke Takikawa, Shuji Ebisu, and Shoichi Nagata*

Department of Materials Science and Engineering, Muroran Institute of Technology
27-1 Mizumoto-cho, Muroran, Hokkaido, 050-8585 Japan

Magnetic susceptibilities of Eu$_2$O$_3$, EuF$_3$, and EuBO$_3$ have been measured over the wide temperature range 5 to 650 K. The Van Vleck paramagnetism, with the ground state of $^7F_0$ ($S = 3, L = 3$), has been investigated comprehensively. The temperature independent paramagnetism emerges manifestly below approximately 100 K. The variation of the susceptibility with temperature for EuBO$_3$ is in satisfactory agreement with the coupling constant $\lambda = 471$ K, where the spin-orbit interaction is $\lambda L S$ for the Russell-Saunders coupling on the basis of Van Vleck theory with one parameter $\lambda$. The value of $\lambda = 490$ K can fit the susceptibility data of EuF$_3$. The deviation from the theory arises in Eu$_2$O$_3$. This discrepancy originates mainly from the influence of the crystalline field. Susceptibility of Gd$_2$O$_3$, having the ground state of $^7S_{7/2}$ ($S = 7/2, L = 0$), is also presented as a magnetic standard compound in comparison with these results.

FAC numbers:

I. INTRODUCTION

The rare earth Eu$^{3+}$ ion has $4f^6$ electrons ($S = 3, L = 3$) which gives rise to seven energy levels, $^7F_0$, $^7F_1$, $^7F_2$, $^7F_3$, $^7F_4$, $^7F_5$, and $^7F_6$. The lowest ground state is $^7F_0$, which is not degenerate. Since the interval of the energy levels between the ground state $^7F_0$ and the successive first excited state $^7F_1$ is not large, but comparable with the thermal energy at the room temperatures, the levels of the multiplets are split by the spin-orbit interaction. The magnetic susceptibility of the majority for the rare earth ions satisfies the Curie's law, however europium and samarium ions are the exceptions because of the narrow energy separation. The most striking feature is that the temperature independent susceptibility arises in the low temperature region for Eu$^{3+}$. This type of the susceptibility is known as Van Vleck paramagnetism.

The crystal structure of EuBO$_3$ has been extensively examined by Levin et al. In this present study, the result of magnetic susceptibility of EuBO$_3$ will be clearly reported as a function of temperature over the wide range 5-650 K. Although the susceptibility of EuBO$_3$ was measured in the previous study, the temperature range was up to 300 K and the data were less accurate. In order to compare the result of EuBO$_3$ with other trivalent europium compounds, the susceptibilities of Eu$_2$O$_3$, EuF$_3$, and EuF$_4$ have been re-investigated because the temperature range was not wide enough in the previous works and the analytical calculations were not sufficient to understand these results. The characteristic feature of the Van Vleck paramagnetism is that the temperature variation of the susceptibility can be analyzed by means of one-parameter.

We present the paramagnetic susceptibility of Gd$_2$O$_3$ as a magnetic standard compound with the ground state of $^8S_{7/2}$, $L = 0$. The susceptibility of Gd$_2$O$_3$ has been reported by previous researchers.

The diamagnetic contribution to the susceptibility has been listed by Landolt-Börnstein. We take the Pascal's additive law of these diamagnetic susceptibilities.

The estimated values are as follows: -3.8x10$^{-5}$ emu per mole-f.u. for 1/2Gd$_2$O$_3$, -3.8x10$^{-5}$ emu per mole-f.u. for 1/2Eu$_2$O$_3$, -5.3x10$^{-5}$ emu per mole-f.u. for EuF$_3$, and -5.5x10$^{-5}$ emu per mole-f.u. for EuBO$_3$. All the data will be presented below after these diamagnetic corrections, which are extremely small in comparison with the observed susceptibilities. We have performed a comprehensive investigation for the Van Vleck paramagnetism of the trivalent Eu ions.

II. THE VAN VLECK PARAMAGNETIC SUSCEPTIBILITY

Fig. 1 shows the lowest multiplet $^7F_J$ which consists of seven energy levels, where $^7F_0$ is the ground state. The number of $f$-electron of Eu$^{3+}$ ion is 6 and the Hund rules give the spin quantum number $S = 3$ and the angular momentum $L = 3$. The spin-orbit interaction $\lambda L S$ with the coupling constant $\lambda$ forms the energy levels in Russell-Saunders coupling. The energy $E_J$ and the energy difference $E_J - E_{J-1}$ are given as

$$E_J = \frac{\lambda}{2} \{ J(J + 1) - L(L + 1) - S(S + 1) \}, \quad (1')$$

$$E_J - E_{J-1} = \lambda J. \quad (2)$$

When the separation of the multiplet components is sufficiently large compared to $k_B T$, only the lowest energy is taken into consideration of the temperature variations of the physical properties. Nevertheless, for the comparable case with $k_B T$, the contribution of the different components should be included. The Zeeman Hamiltonian has the form

$$\mathcal{H}_{\text{Zeeman}} = -\mu \cdot \mathbf{H} = \mu_B (L + 2S) \cdot \mathbf{H}. \quad (3)$$
The paramagnetic susceptibility can be expressed using the Van Vleck theory,\(^1\)

\[
\chi_{\text{para}}(\text{free Eu}^{3+}) = \sum_{J=0}^{6} \chi_J(2J+1)e^{-\frac{E_J}{k_B T}}
\]

\[
= \sum_{J=0}^{6} \frac{[g^2\mu_B^2J(J+1)] + \alpha_J(2J+1)e^{-\frac{E_J}{k_B T}}}{[J(J+1)+l]}.
\]

Here \(N\) is the number of Eu\(^{3+}\) ion, \(k_B\) the Boltzmann constant, \(T\) the absolute temperature. The \(\chi_J\), the Lande’s \(g\)-factor, \(\alpha_J\), and \(F_J\) are written, with the Bohr magneton \(\mu_B\), as

\[
\chi_J = \frac{Ng^2\mu_B^2J(J+1)}{3k_B T} + N\alpha_J, \quad (5) \]

\[
g = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}, \quad (6) \]

\[
\alpha_J = \frac{\mu_B^2}{6(2J+1)} \left[ \frac{F_{J+1}}{E_{J+1} - E_J} - \frac{F_J}{E_J - E_{J-1}} \right], \quad (7) \]

\[
F_J = \frac{[(L+S+1)^2 - J^2][J^2 - (S-L)²]}{J}. \quad (8) \]

The explicit paramagnetic susceptibility of Eu\(^{3+}\) ions can be derived in the forms

\[
\chi_{\text{para}}(\text{free Eu}^{3+}) = \frac{N\mu_B^2}{Z} \left( \frac{A}{3\lambda} \right), \quad (9) \]

\[
Z = 1 + 3e^{-\frac{E_6}{k_B T}} + 5e^{-\frac{E_5}{k_B T}} + 7e^{-\frac{E_4}{k_B T}} + 9e^{-\frac{E_3}{k_B T}} + 11e^{-\frac{E_2}{k_B T}} + 13e^{-\frac{E_1}{k_B T}}, \quad (10) \]

\[
A = 24 + (13.5 \frac{\lambda}{k_B T} - 1.5)e^{-\frac{E_6}{k_B T}} + (67.5 \frac{\lambda}{k_B T} - 2.5)e^{-\frac{E_5}{k_B T}} + (189 \frac{\lambda}{k_B T} - 3.5)e^{-\frac{E_4}{k_B T}} + (405 \frac{\lambda}{k_B T} - 4.5)e^{-\frac{E_3}{k_B T}} + (742.5 \frac{\lambda}{k_B T} - 5.5)e^{-\frac{E_2}{k_B T}} + (1228.5 \frac{\lambda}{k_B T} - 6.5)e^{-\frac{E_1}{k_B T}}. \quad (11) \]

Since the formulae of Eqs. (9)-(11) include only one unknown parameter \(\lambda\), the value of \(\lambda\) can be determined uniquely in comparison with the experimental result of the temperature dependence of the susceptibility. In particular, the shift in the ground state energy is induced through the value of \(\alpha_J\). The \(\alpha_J\) connects and mixes the
III. EXPERIMENTAL METHODS

The polycrystalline specimens EuBO$_3$ and Gd$_2$O$_3$ were prepared by a solid-state reaction. Mixtures of high-purity fine powders of Eu$_2$O$_3$ (99.99 \%) and B$_2$O$_3$ (99.999 \%) were heated to 1473 K in air and kept at this temperature for 3 hours, where 0.3 wt \% excess B$_2$O$_3$ was added to compensate for possible volatility during heating. Subsequently, the sample EuBO$_3$ was quenched from 1473 K to the room temperature. The sample quality was not different from what was cooled down in the furnace after switching off the heating at 1473 K without the quenching. The prepared specimens with white in color were found to be stable under air after the synthesis. The specimens Eu$_2$O$_3$ (purity 99.99 \%) and EuF$_3$ (99.9 \%) used in this work were purchased from the Kishida Chemicals, Japan, which have extremely high purity. Impurity has not been detected for these three compounds within the X-ray measurements. The specimen of Gd$_2$O$_3$ was also prepared with the same method as EuBO$_3$, nevertheless the process of repeating was needed after reground. The identification of the crystal structure and the determination of the lattice constants were carried out by X-ray diffraction for powdered specimen using Cu Ka radiation at room temperature.

IV. RESULTS AND DISCUSSION

A. Lattice constant

The dc magnetizations of powder specimens in a constant magnetic field of 10 kOe were measured for all the specimens with a SQUID magnetometer (MPMS, Quantum Design Inc.) over the temperature range 5.0-650 K. The magnetic susceptibility is defined as $\chi = (M/H)$. Since the value of the susceptibility is low, then the demagnetizing field corrections have not been applied to any of our magnetic data.

B. Gd$_2$O$_3$

Fig. 3 indicates the X-ray powder diffraction profile of EuBO$_3$, which gives an evidence that EuBO$_3$ has the vaterite-type structure. The X-ray data have been analyzed assuming a hexagonal structure with the space group P6$_3$/mmc (no.194). The lattice constant, $a$, is obtained by the least square method. As far as we know, all the crystallographic data of the specimens which have been reported so far, are summarized in Table 1.\textsuperscript{12} The specimens of the present work are specified in the symbols of (a), (f), (i), and (l) in Table 1.

Fig. 4 represents the temperature dependence of the magnetic susceptibility $\chi = (M/H)$ for Gd$_2$O$_3$. The result obeys well the Curie-Weiss law. The value of effective Bohr magneton number $p_{eff}$ Gd-ion$^{-1}$ is extracted. The value of $p_{eff}$ is obtained to be 7.79, which is close...
to the value of 7.94 as a free Gd$^{3+}$ ion. The asymptotic Weiss temperature $\theta$ has a value of -14.6 K, reflecting the nature of antiferromagnetic exchange interaction.

**C. Eu$_2$O$_3$, EuF$_3$ and EuBO$_3$**

Fig. 5 shows the temperature variation of the susceptibility of Eu$_2$O$_3$ in $H = 10$ kOe. The plateau at low temperature is less pronounced, but increasing, which will be discussed below. Fig. 6 shows the susceptibility of EuF$_3$. The used specimens of Figs. 5 and 6 were extremely pure, but the inclusion of Eu$^{3+}$ ions might be inevitable to preparation. The existence of small amount of Eu$^{3+}$ ions as impurity can be detected below 15 K, reflecting the rapid increase in $\chi$. Fig. 7 stands for the susceptibility of EuBO$_3$. As far as we know, the most typical and remarkable temperature independent paramagnetic susceptibility for Eu$^{3+}$ ions has been now found at low temperatures.

D. Comparison and analysis

Fig. 8 presents three susceptibilities for Eu$_2$O$_3$, EuF$_3$, and EuBO$_3$ in $H = 10$ kOe. The diamagnetic correction does not affect these magnitudes of the susceptibility as mentioned in the section of Introduction. In the first approximation, these three curves must coincide with each other with the same value of $\chi$ if these compounds would consist of sufficiently free paramagnetic Eu$^{3+}$ ions. Next consideration is that these three compounds have been imposed on the individual different situation: intrinsically (a) influence of crystalline field, (b) magnetic anisotropy, and (c) extrinsically the foreign magnetic impurity such as Eu$^{2+}$ ion.

Fig. 9 shows the enlargement of data at low temperature part below 150 K. Fig. 9 shows a manifest evidence of the existence of Eu$^{2+}$ ions for Eu$_2$O$_3$ and EuF$_3$, because the rapid increase due to the Curie-like behavior below 15 K. The previous workers also have detected the similar increase for Eu$_2$O$_3$ and EuF$_3$. In experimental study for the susceptibility at low temperatures, it is im-

FIG. 3: X-ray powder diffraction pattern for EuBO$_3$ at room temperature.

FIG. 4: Temperature dependence of magnetic susceptibility $\chi = (M/H)$ of Gd$_2$O$_3$ and the inverse susceptibility $\chi^{-1} = (M/H)^{-1}$ in a constant magnetic field of 10 kOe. This specimen is considered as a standard material.
important to eliminate from the specimen even trace quantities of foreign paramagnetic impurities, because they can exhibit severely the Curie-like increase.

The Eu$^{2+}$ ion is equivalent magnetically with Gd$^{3+}$ ion, in which extremely large moment arises with $S = 7/2$. The valence mixing problem concerned with Eu$^{2+}$ and Eu$^{3+}$ is discussed, for example, in Refs. 13,14.

Some Eu-based intermetallic compounds are known to have intermediate valence between Eu$^{3+}$ (4f$^6$) and Eu$^{2+}$ (4f$^7$) configurations. Valence fluctuations in Eu intermetallic compounds have attracted much attention because of the interest in hybridization between Eu$^{2+}$ and Eu$^{3+}$ ions for quantum mechanical mixing. The intrinsic hybridization between Eu$^{2+}$ and Eu$^{3+}$ ions may take place in these intermetallic compounds. However, the present compounds of Eu$_2$O$_3$ and EuF$_3$ are not intermetallic, but are well defined ionic compounds. Therefore the possibility of the hybridization between Eu$^{2+}$ and Eu$^{3+}$ ions is exclusive.

We have carried out the estimation of the magnitude of the Curie contribution to the susceptibility for Eu$_2$O$_3$ and EuF$_3$. Our evaluation leads definitely that the number of Eu$^{2+}$ ions does not exceed 0.01 percent in the two compounds.

Fig. 10 indicates the comparison with the theoretical prediction for Eu$_2$O$_3$. The discrepancy between the experiment and the theory cannot be attributed to the influence from the existence of the small amount of the Eu$^{2+}$ ions.

Fig. 11 indicates the comparison with the theoretical prediction for EuF$_3$. The best fit of Eq. (9) to the experimental data gives the value of $\lambda = 490$ K. The susceptibility of EuF$_3$ has been studied in rather detail by Jayasankar et al., Our present experimental data are in good agreement with the reported data by them. They have taken into account the crystalline field even though the spin-orbit interaction is comparatively larger than crystalline field for lanthanides. It should be stressed that the fitting is in agreement sufficiently with Eq. (9) as seen in Fig. 11, without the influence from the crystalline field.

Fig. 12 indicates the comparison with the theoretical prediction for EuBO$_3$. The best fit of Eq. (9) to the experimental results leads to the value $\lambda = 471$ K. Now, the
FIG. 7: Variation of the magnetic susceptibility with temperature for EuBO$_3$ in $H = 10$ kOe.

wide temperature range observation has been performed up to 650 K. As can be seen in Fig. 12, however, the little deviation from Eq. (9) is appreciated, which is pronounced between 200-500 K. The experimental data are slightly larger than that of expected value in Eq. (9).

E. Temperature-dependent effective moment

Since the excited state induces the magnetic combination to the ground state in the external magnetic field, the temperature independent permanent moment does not make sense for Eu$^{3+}$ ion. Nevertheless the phenomenological temperature dependent effective Bohr magneton number is defined by the equation

$$ p_{\text{eff}} = \sqrt{\frac{3\chi k_B T}{N \mu_B^2}}. \quad (12) $$

Only when Curie’s law is obeyed and is valid, the permanent moment $p_{\text{eff}}$ is identified, therefore Eq. (12) is a simplified interpretation by means of a kind of artificial form. Here, the experimental values of $p_{\text{eff}}$ through Eq. (12) are listed in Table 2 at only 300 K in order to compare them of the past bibliography.\(^1\) These values of $p_{\text{eff}}$ correspond with the moment induced by the Zeeman energy. It is noted that the $p_{\text{eff}}$ approaches zero in Eq. (12) at $T = 0$ because $\chi$ is constant below 100 K and then $p_{\text{eff}}$ is proportional to $\sqrt{T}$. However, this does not mean that the susceptibility $\chi$ of Eu$^{3+}$ vanishes at absolute zero. The first term of Eq. (5) disappears when $J=0$ as in the component in Fig. 1, nevertheless the second term of $N \alpha J$ becomes abnormally large. Thus, in the vicinity of $T = 0$, the susceptibility $\chi$ of Eu$^{3+}$ is not zero.

F. Deviation from free ions in Eu$_2$O$_3$

Eq. (9) cannot fit very well the data of $\chi$ of Eu$_2$O$_3$. The appreciable deviation from the Van Vleck formula of Eq. (9) is seen in Fig. 10. On the other hand, the fittings of Eq. (9) to the data of EuF$_3$ (Fig. 11) and EuBO$_3$ (Fig. 12) are fairly good over wide temperature range. The comparison between Fig. 2 and Fig. 8 is interesting
FIG. 9: An enlargement of data of Fig. 8. The Curie-like increase is seen below 15 K for Eu₂O₃ and EuF₃.

and instructive. The analysis of Fig. 2 indicates no-crossing in curves of χ each other with the variation of λ. Fig. 8 shows that χ of Eu₂O₃ crosses that of EuBO₃ around 180 K, and furthermore that of EuF₃ around 600 K. On the contrary, the temperature variations of EuF₃ and EuBO₃ have a reasonable difference without crossing in χ as seen in Fig. 8. The intrinsic mechanism to cause the deviation exists in Eu₂O₃. A plausible interpretation for this deviation should be required.

Possible origin of the deviation for Eu₂O₃ comes from the influence of the crystalline field. Table 3 proves compelling evidence for the rather strong influence of the crystalline field in Eu₂O₃ in comparison with EuF₃ and EuBO₃. The bond length between Eu³⁺ and the O²⁻ ions is the shortest in Eu₂O₃. Eu³⁺ has two different sites of 1 and 2 and these bond lengths of Eu³⁺ - O²⁻ are shorter than those of EuF₃ and EuBO₃, as can be seen in Table 1. These crystal structure data might support the stronger influence from the crystalline field for Eu₂O₃.

The other indirect evidence is that the melting point of Eu₂O₃ is highest in the three compounds, reflecting the ionic bond is strongest and then the crystalline field could not be negligible. The detailed calculation of χ, taking into account of the crystalline field, has not been done in the present study because this is not main subject.

G. Higher-order corrections

A slight discrepancy is seen between the experimental and the calculated values over the temperature region 200–500 K in Fig. 12 for EuBO₃. The present analysis has confined to the original one parameter theory according to the theory of Van Vleck. Further detailed theoretical investigation for the rare-earth ions is available for understanding the result. The Russell-Saunders coupling might be incomplete, which have been provided by Judd. The partial breakdown of the Russell-Saunders coupling is introduced and discussed in this theory. Unfortunately we cannot judge correctly the validity of this theory at the present. We do not discuss this problem in this paper.

There is another different approach to solve the seri-
FIG. 11: Temperature dependence of $\chi$ for EuF$_3$. The solid circles show experimental data and the solid curves indicate calculated $\chi$ for three values of $\lambda$. The best fit is given by $\lambda = 490$ K except the region below 20 K.

FIG. 12: Temperature dependence of $\chi$ for EuBO$_3$. Much emphasis is placed on the better fit to the low temperature data below 100 K. The results agree well with $\lambda = 471$ K using Eq. (9).

one issue mentioned above. The higher order perturbation correction is the valuable tool of the theory. We have extended the formula of the magnetization to the third power of the field strength $H$. It is reasonable that the deviation should be attributed to the lacking of the higher-order corrections in the perturbation theory. This treatment can lead to the susceptibility depending on field of which strength is sufficiently large. The derivation have been carried out systematically by means of the perturbation theory, following the same procedure by Van Vleck.\(^1\)

The energy level $E_{J,m}$ for each $J$ in Fig. 1 is expressed as a power series in a field $H$ of the form,

$$E_{J,m} = E_{J}^{(0)} + HE_{J,m}^{(1)} + H^2 E_{J,m}^{(2)} + H^3 E_{J,m}^{(3)} + \cdots$$  \hspace{1cm} (13)

Here the quantum number $m$ specifies the degeneracy for $J > 1$. The $E_{J}^{(0)}$ is the energy in zero field and $E_{J,m}^{(i)}$ is the $i$-th order small correction in the field from the perturbation by Zeeman energy.

The magnetic moment $(\mu_{2})_{J,m}$ in the direction of the applied field is

$$ (\mu_{2})_{J,m} = -\partial E_{J,m}/\partial H. \hspace{1cm} (14) $$

The magnetization $M$ is given, using a Boltzmann distribution.

$$ M = N \sum_{J,m} (\mu_{2})_{J,m} e^{-E_{J,m}^{(0)}/k_B T} / (\sum_{J,m} e^{-E_{J,m}^{(0)}/k_B T}). \hspace{1cm} (15) $$

The final results can be written in the forms

$$ M = \frac{N}{Z} \sum_{J,m} [W_1 H + W_3 H^3] e^{-E_{J,m}^{(0)}/k_B T}, \hspace{1cm} (16) $$
\[ W_1 = \frac{|E_{J,m}^{(1)}|^2}{k_B T} - 2E_{J,m}^{(2)}, \quad (17) \]

\[ W_3 = \frac{1}{k_B T} \left( 2 |E_{J,m}^{(2)}|^2 + 4E_{J,m}^{(1)}E_{J,m}^{(3)} \right) \]

\[ -\frac{1}{(k_B T)^2} \left( |E_{J,m}^{(1)}|^2 E_{J,m}^{(2)} \right) \]

\[ + \frac{1}{(k_B T)^3} |E_{J,m}^{(1)}|^4 \]

\[ -4E_{J,m}^{(4)}. \quad (18) \]

It should be noticed that the magnetization does not have the second power of \( H \), because it is an odd function of \( H \) without the residual magnetization in the absence of field. When the extension of the third power of magnetic field \( H \) inclusive, the susceptibility depends on the field. The resultant form of Eq. (16) is applicable for all the rare earth ions, where \( N \) is the number of ions and the denominator \( Z \) is the partition function.

For example, the expressions of the first-order correction \( E_{0,m}^{(1)} \) and the second-order correction \( E_{0,m}^{(2)} \) (omitting the long expressions for \( E_{0,m}^{(3)} \) and \( E_{0,m}^{(4)} \)) are given by using eigenfunctions,

\[ E_{0,m}^{(1)} = \langle \psi_{0,m} | \mu_z | \psi_{0,m} \rangle. \quad (19) \]

\[ E_{0,m}^{(2)} = \sum_{J,m} \frac{|\langle \psi_{0,m} | \mu_z | \psi_{J,m} \rangle|^2}{E_0 - E_J}, \quad (20) \]

If we take only the lowest term of \( W_1 \) in Eq. (16), then the Van Vleck formula of the susceptibility is obtained. Here the first term of \( |E_{J,m}^{(1)}|^2/k_B T \) in Eq. (17) corresponds to the first term of Eq. (5), and the second term of \( -2E_{J,m}^{(2)} \) in Eq. (17) corresponds exactly to the \( \alpha_J \) in Eq. (5). The temperature independent susceptibility of Eu\(^{3+} \) ions originates from the numerical value of 24 for the leading term in Eq. (11), which is caused by the correction of \( E_{0,m}^{(2)} \). In this way, Eq. (4) to (11) are given without \( W_3H^3 \) term in Eq. (16).

The inclusion of \( W_3 \) term has been now formulated and established in the present study as Eq. (18) even though the calculation itself is extremely complicated. Unfortunately the actual calculations of the matrix elements for the higher-order corrections via \( W_3 \) term have never been made.

V. SUMMARY

In summary, a systematic study of the Van Vleck paramagnetism for Eu\(^{3+} \) ions has been carried out. The most typical temperature independent susceptibility at low temperatures has been demonstrated for the compound EuBO\(_3 \) with \( \lambda = 471 \text{ K} \).

Acknowledgment

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Table 1
Crystallographic data of the specimens [12].

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<td>Gd$_2$O$_3$</td>
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<td>a</td>
<td>$\overline{I}a3$ (No.206) Cubic $\begin{align*} a &amp;= 10.810 \text{ Å} \end{align*}$</td>
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<tr>
<td>b</td>
<td>$\overline{I}a3$ (No.206) Cubic $\begin{align*} a &amp;= 10.813 \text{ Å} \end{align*}$</td>
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<td>c</td>
<td>Hexagonal $\begin{align*} a &amp;= 3.86 \text{ Å} \ c &amp;= 6.16 \text{ Å} \end{align*}$</td>
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<tr>
<td>d</td>
<td>C2/m (No.12) Monoclinic $\begin{align*} a &amp;= 14.095 \text{ Å} \ b &amp;= 3.5765 \text{ Å} \ c &amp;= 8.7692 \text{ Å} \end{align*}$</td>
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<td>Monoclinic $\begin{align*} a &amp;= 14.1126 \text{ Å} \ b &amp;= 3.6025 \text{ Å} \ c &amp;= 8.8089 \text{ Å} \end{align*}$</td>
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<td>EuF$_3$</td>
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<td>i</td>
<td>Pnma (No.62) Orthorhombic $\begin{align*} a &amp;= 6.622 \text{ Å} \ b &amp;= 7.020 \text{ Å} \ c &amp;= 4.398 \text{ Å} \end{align*}$</td>
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<tr>
<td>j</td>
<td>Pnma (No.62) Orthorhombic $\begin{align*} a &amp;= 6.6105 \text{ Å} \ b &amp;= 7.0157 \text{ Å} \ c &amp;= 4.3959 \text{ Å} \end{align*}$</td>
</tr>
<tr>
<td>k</td>
<td>P3c1 (No.165) Hexagonal $\begin{align*} a &amp;= 6.9204 \text{ Å} \ c &amp;= 7.0856 \text{ Å} \end{align*}$</td>
</tr>
<tr>
<td>EuBO$_3$</td>
<td></td>
</tr>
<tr>
<td>l</td>
<td>P65/mmc (No.194) Hexagonal (Quenched specimen) $\begin{align*} a &amp;= 3.850 \text{ Å} \ c &amp;= 8.950 \text{ Å} \end{align*}$</td>
</tr>
<tr>
<td>m</td>
<td>Hexagonal $\begin{align*} a &amp;= 3.845 \text{ Å} \ c &amp;= 8.94 \text{ Å} \end{align*}$</td>
</tr>
<tr>
<td>n</td>
<td>P6c2 (No.188) Hexagonal $\begin{align*} a &amp;= 6.671 \text{ Å} \ c &amp;= 8.945 \text{ Å} \end{align*}$</td>
</tr>
</tbody>
</table>

The specimens of the present work are specified in (a), (f), (i), and (l).
Table 2
Effective magneton numbers $p_{\text{eff}}$ at 300 K.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\chi$ 10$^{-3}$ emu (mol-Eu$^{3+}$)$^{-1}$</th>
<th>$p_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu$_2$O$_3$</td>
<td>4.66</td>
<td>3.34</td>
</tr>
<tr>
<td>EuF$_3$</td>
<td>4.52</td>
<td>3.29</td>
</tr>
<tr>
<td>EuBO$_3$</td>
<td>4.89</td>
<td>3.43</td>
</tr>
</tbody>
</table>

Table 3
Bond length between Eu$^{3+}$ and O$^{2-}$ ions. The last column indicates the melting point.

<table>
<thead>
<tr>
<th>Material</th>
<th>Space group</th>
<th>Bond</th>
<th>Bond length (Å)</th>
<th>Melting point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu$_2$O$_3$</td>
<td>Ia$\bar{3}$</td>
<td>Eu1 – O</td>
<td>2.309</td>
<td>1646</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Eu2 – O</td>
<td>2.330</td>
<td></td>
</tr>
<tr>
<td>EuF$_3$</td>
<td>Pnma</td>
<td>Eu – F</td>
<td>2.333</td>
<td>1276</td>
</tr>
<tr>
<td>EuBO$_3$</td>
<td>P6$_3$/mmc</td>
<td>Eu – O</td>
<td>2.345</td>
<td>1540 ± 20</td>
</tr>
</tbody>
</table>