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The Crystal Structure and Magnetic Property of Europium(II) Orthoborate

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The europium(II) orthoborate $Eu_3(BO_3)_2$ is trigonal, space group $R\bar{3}c$, with $a=9.069(1)$, $c=12.542(2)$ Å and $Z=6$. The structure has been refined to $R=0.082$ for 259 observed reflections with isotropic thermal parameters. The borate contains isolated and planar triangle BO_3^{3-} ions, the anions and Eu atoms being hexagonally packed along c. Each Eu atom is surrounded by 8 oxygens with Eu–O distances varying from 2.36 to 2.95 Å. The interatomic distances between Eu atoms are 3.509—4.200 Å for 8 nearest Eu neighbors and 4.831—5.450 Å for 6 second-nearest Eu neighbors. The 6 nearest Eu neighbors with the interatomic distances of 3.509 and 3.778 Å and the 4 second-nearest Eu neighbors with the Eu–O–Eu angle of 166.0° are effective for the magnetic exchange and superexchange interactions between Eu^{2+} ions, giving rise to ferromagnetism at low temperature.

Some europium(II) compounds have unique magnetic properties caused by the exchange and superexchange interactions between neighboring Eu^{2+} ions.[1] These interactions in oxides are closely related to the distances and angles *via* O^{2-} ions between the magnetic ions,[2] the arrangement of neighboring Eu^{2+} and O^{2-} ions around given Eu^{2+} ions being significant for interpreting their magnetic properties. For highly symmetrical compounds, *e.g.* EuO (rock salt type), $EuTiO_3$ (perovskite type) and Eu_2TiO_4 (K_2NiF_4 type), their magnetism has been discussed on the basis of their crystal structure.[3]

In a binary system EuO–B_2O_3, we have obtained a ferromagnetic compound, $Eu_3(BO_3)_2$, with $T_C=7.5$ K. This borate has been found to be isostructural with $Ca_3(BO_3)_2$,[4] which crystallizes in the trigonal system.[5] No three-dimensional structure analysis has been performed. The structures of other bivalent-cation orthoborates, $Zn_3(BO_3)_2$[6] and $Ni_3(BO_3)_2$,[7] have been determined. They consist of isolated triangle anions of BO_3 groups. Since the IR spectrum of $Eu_3(BO_3)_2$ is similar to that of zinc(II) and nickel(II) analogs,[8] $Eu_3(BO_3)_2$ is expected to contain BO_3^{3-} ions.

In this paper, we report the crystal structure of $Eu_3(BO_3)_2$ and discuss its magnetic property.

Experimental

Crystal Growth. The alkaline earth orthoborates [*e.g.* $Ca_3(BO_3)_2$ and $Sr_3(BO_3)_2$] have congruent melting points at 1400—1500 °C. However, $Eu_3(BO_3)_2$ has no melting point, decomposing into unknown compounds above 1400 °C. This might be due to the thermodynamic lability of Eu^{2+} ion.[9] The single crystals were prepared with use of a suitable flux: polycrystalline $Eu_3(BO_3)_2$ powder was mixed with a large excess of KCl, and the pelletized mixture was heated on a molybdenum boat at 1050 °C for 2 h in H_2 stream. The molten sample was allowed to cool to 750 °C at a rate of 3 °C/h, fine black hexagonal prisms being obtained by removing the flux with water.

Magnetic Susceptibility Measurements. The magnetic susceptibility of the powder sample was measured with a Shimadzu magnetic balance MB-11 (80—300 K) and a Faraday magnetic balance (2—80 K) constructed by Muneyuki Date and Ki-ichi Okuda (Department of Physics, Osaka University).

X-Ray Data Collection. Preliminary Weissenberg photographs showed that the crystals obtained belong to the trigonal system and that its space group is $R3c$ or $R\bar{3}c$ from the systematic absence (hkl, $-h+k+l=3n+1$ and $3n+2$; $h0l$, $l=2n+1$). The cell parameters (Table 1) were determined by a least-squares treatment of the X-ray powder pattern (Cu $K\alpha$) calibrated with high purity silicon as an internal standard. The intensity data were measured on a Rigaku Denki automated four-circle diffractometer with Mo $K\alpha$ radiation monochromated with graphite. The ω-2θ scan method was employed at a scanning rate of 4°/min, the dimension of the crystal used being 0.08 mm (side to side of hexagonal cross section) × 0.04 mm (thickness). All possible reflections with the indices of hkl and hkl were collected up to $2\theta=70°$. Three standard reflections were monitored every 60 reflections, no apparent decay in intensity being detected. The intensity values for equivalent reflections were averaged and 259 nonzero reflections were used for analysis. The Lorentz and polarization corrections were applied, but not the absorption correction.

Table 1. Crystal data

$F.W.=573.50$	$\lambda=0.71069$ Å
Trigonal	μ(Mo $K\alpha$)$=31.26$ mm^{-1}
Space group $R\bar{3}c$	$D_m=6.31$ g cm^{-3}
$a=9.069(1)$ Å	$D_x=6.40$
$c=12.542(2)$	$Z=6$
$V=893.3(3)$ Å^3	$F(000)=1482$

Structure Determination and Refinement. The structure was solved by the conventional heavy atom method and refined by the full-matrix least-square method (*FMLS* program[10]) based on the observed reflections, the minimized function being $\sum w(|F_o|-|F_c|)^2$ where $w=1$ for all $|F_o|$. From a three-dimensional Patterson synthesis, the centrosymmetric space group $R\bar{3}c$ was chosen and the coordinate of Eu atom determined to be at a special position (18e site). The remaining atoms (O and B) were located on the successive Fourier maps: O at the general position (36d site) and B at the 12c site on three-fold axis. Isotropic refinement for all atomic paramaters was carried out to give '$R=0.082$ for 259 observed reflections. The atomic scattering factors for Eu, O, and B atoms were those given in International Tables for X-Ray Crystallography.[11] The final positional and thermal param-

Table 2. Final positional and thermal parameters[a)] with their standard deviations in parentheses

Atom	x	y	z	B/Å^2
Eu	3075(18)	0	2500	0.45(4)
O	164(23)	33(23)	396(18)	0.88(27)
B	0	0	39(6)	1.3(8)

a) The coordinates are multiplied by 10^4 for Eu atom, 10^3 for O atom and 10^2 for B atom.

eters are given in Table 2.†

Results and Discussion

The crystal structure of $Eu_3(BO_3)_2$ is shown in Fig. 1, and the bond lengths and angles are given in Table 3. The borate contains isolated and planar triangles of BO_3 groups with a B–O distance of 1.36 Å like other orthoborates,[6,7] the crystal consisting of Eu atoms and BO_3 groups hexagonally packed along c. The triangle planes of BO_3 groups are perpendicular to the c axis. Each Eu atom is surrounded by 8 oxygens to form an EuO_8 polyhedron with Eu–O distances varying from 2.36 to 2.95 Å (Fig. 2). An Eu atom has 8 nearest and 6 second-nearest neighboring Eu atoms with the mean interatomic distances 3.816 and 5.244 Å, respectively.

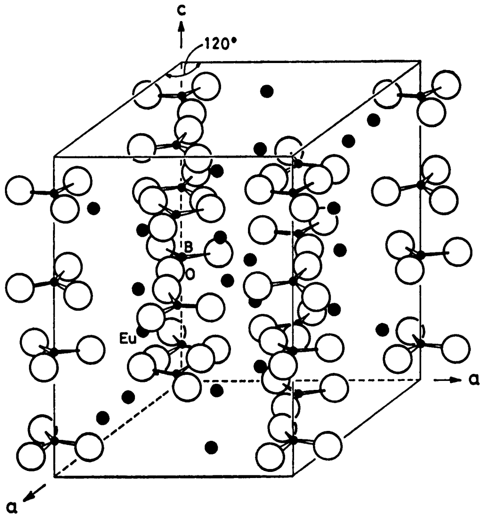

Fig. 1. Crystal structure of $Eu_3(BO_3)_2$.

Table3. Interatomic distances (Å) and bond angles (°)

(a) The BO_3 triangle			
B–O	1.36(6)	O–B–O	120(0)
(b) Eu–Eu distances			
Nearest neighbors		Second-nearest neighbors	
Eu–Eu^{i}	3.509(3)	Eu–Eu^{iv}	5.450(3)
–Eu^{ii}	3.778(3)	–Eu^{v}	4.831(3)
–Eu^{iii}	4.200(3)		
(c) Eu–O distances			
Eu–O^{i}	2.92(3)	Eu–O^{iii}	2.95(3)
–O^{ii}	2.58(3)	–O^{iv}	2.36(3)
(d) Eu–O–Eu angles			
Nearest neighbors		Second-nearest neighbors	
Eu–O–Eu^{i}	82.7(7)	Eu–O–Eu^{iv}	166.0(4)
–O–Eu^{ii}	80.1(6)		
	85.9(7)		
	99.8(8)		
–O–Eu^{iii}	103.9(8)		

Symmetry code: Eu^{i} ($1/3-x$, $-1/3$, $1/6+z$; $2/3-x$, $1/3$, $1/3-z$), Eu^{ii} ($1/3$, $2/3-x$, $1/6+z$; $1/3+x$, $-1/3+x$, $1/6+z$: $2/3$, $1/3-x$, $1/3-z$; $-1/3+x$, $-2/3+x$, $1/3-z$), Eu^{iii}($-1/3+x$, $1/3$, $1/3+z$; $1/3-x$, $2/3-x$, $-1/3+z$), Eu^{iv}($1-x$, $1-x$, z; 1, x, z; $1-x$, $-x$, z; 0, $-1+x$, z), Eu^{v}(0, x, z; $-x$, $-x$, z), O^{i} (x, y, z; $x-y$, $-y$, $1/2-z$), O^{ii} ($2/3-x+y$, $1/3+y$, $-1/6+z$; $1/3-x$, $-1/3-y$, $2/3-z$), O^{iii} ($2/3-y$, $1/3-x$, $-1/6+z$; $1/3+x-y$, $-1/3+x$, $2/3-z$), O^{iv} ($2/3-x$, $1/3-x+y$, $5/6-z$; $1/3-y$, $-1/3+x-y$, $1/3+z$).

The temperature dependence of magnetization and susceptibility of $Eu_3(BO_3)_2$ are shown in Fig. 3. The borate is a ferromagnetic with a Curie point (T_C) of *ca.* 7.5 K and a paramagnetic Curie temperature (θ_C) of *ca.* 8 K. The magnetization per Eu^{2+} ion below the Curie point is saturated to *ca.* 7 μB.

Kasuya[2)] suggested that the magnetism of europium(II) compounds is attributable to the magnetic exchange and superexchange interactions taking place *via* the overlap of 4f and 5d orbitals between neighboring Eu^{2+} ions. The magnetism of highly symmetrical compounds, EuO ($T_C=69$ K),[1d)] $EuTiO_3$ ($T_N=5.3$ K)[1f)] and Eu_2TiO_4 ($T_C=9$ K),[3)] has been interpreted in terms of the magnitude of the magnetic interactions between the nearest and second-nearest neighboring Eu^{2+} ions. The direct Eu^{2+}–Eu^{2+} interactions between the nearest Eu neighbors are responsible for the ferromagnetic interaction, the 90° Eu^{2+}–O^{2-}–Eu^{2+} superexchanging pairs undergoing the antiferromagnetic interaction *via*

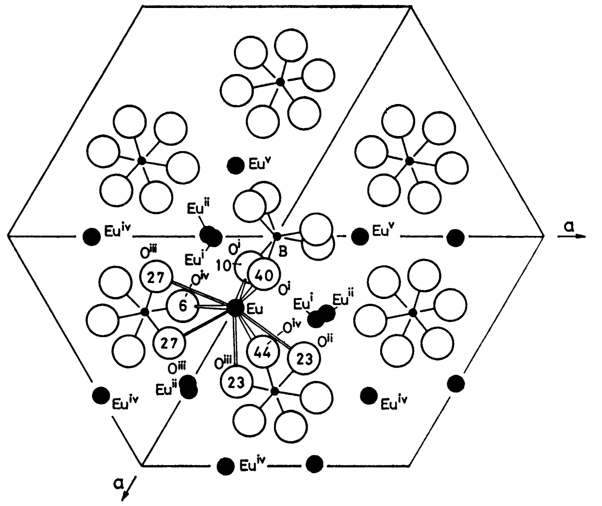

Fig. 2. A projection between $z=0$ and 0.5 of the $Eu_3(BO_3)_2$ structure viewed along the c axis. Numerical values give the fractional Z coordinates of O atoms.

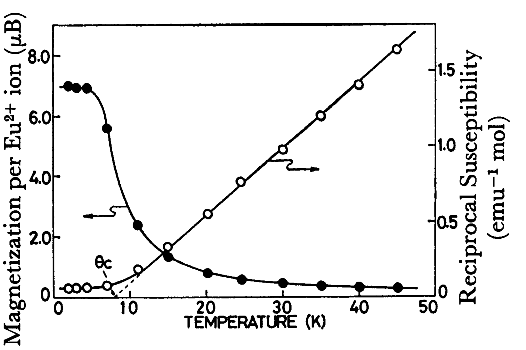

Fig. 3. Temperature dependences of magnetization and reciprocal susceptibility of $Eu_3(BO_3)_2$.

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† The F_o-F_c Table is kept as Document No. 8115 at the Chemical Society of Japan.

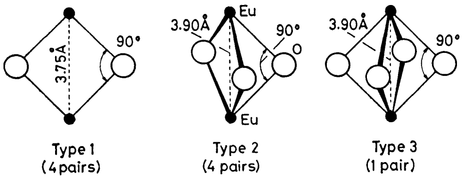
the O^{2-} ions at an angle of 90°. The 180° Eu^{2+}–O^{2-}–Eu^{2+} superexchange interactions between the second-nearest Eu neighbors contribute to the overall magnetism, ferromagnetically or antiferromagnetically, as the case may be. The difference among the magnetic properties of europium(II) compounds results from the difference in magnitude for the above-mentioned interactions.

From the Heisenberg model and molecular field approximation, McGuire *et al.*[1b,1d,1f] expressed the θ_C value as follows:

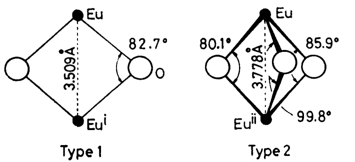
$$\theta_C = \frac{2}{3k} S\,(S+1)\,(Z_1 J_1 + Z_2 J_2), \tag{1}$$

where J_1 and J_2 denote the effective exchange integrals between the nearest and second-nearest neighboring Eu^{2+} ions, respectively, and Z_1 and Z_2 the numbers of the nearest and second-nearest Eu neighbors, respectively. For the oxides, EuO, $EuTiO_3$, and Eu_2TiO_4, the direct Eu^{2+}–Eu^{2+} exchange and indirect 90° Eu^{2+}–O^{2-}–Eu^{2+} superexchange interactions are responsible for J_1, positively and negatively, respectively. The 180° Eu^{2+}–O^{2-}–Eu^{2+} superexchange interactions contribute to the value of J_2. The magnitude of direct exchange interactions is strongly influenced by the Eu–Eu distance, but that of superexchange interactions is not.

Each Eu^{2+} ion in $Eu_3(BO_3)_2$ has 8 nearest and 6 second-nearest neighboring Eu^{2+} ions. The nearest Eu neighbors with the interatomic distances of 3.509 and 3.778 Å contribute as the exchanging and superexchanging pairs, but not the nearest Eu neighbors with 4.200 Å, the distance of 4.200 Å appearing to be too great to interact with the neighboring Eu^{2+} ions as judged by the cases of other europium(II) compounds. For example, the mean distance between the nearest Eu neighbors in EuB_4O_7 (paramagnetic) is 4.338 Å and insufficient for the magnetic interactions.[12] In the nearest Eu neighbors, therefore, we can point out two kinds of effective exchanging pairs (Fig. 4). Type 1: the Eu–Eu^{i} pair with two 82.7° Eu^{2+}–O^{2-}–Eu^{2+}; Type 2: the Eu–Eu^{ii} pair with three 80.1—99.8° Eu^{2+}–O^{2-}–Eu^{2+}.



(a) Eu_2TiO_4



(b) $Eu_3(BO_3)_2$

Fig. 4. Anions environments around exchanging pairs between nearest neighboring Eu^{2+} ions in Eu_2TiO_4 and $Eu_3(BO_3)_2$.

For the second-nearest Eu neighbors, four Eu–Eu^{iv} pairs *via* an O^{2-} ion at 166.0° correspond to the 180° Eu^{2+}–O^{2-}–Eu^{2+} superexchanging pairs in EuO, $EuTiO_3$ and Eu_2TiO_4, although the Eu–O–Eu angle somewhat deviates from the value of 180°. The remaining two Eu–Eu^{v} pairs can not be regarded as the superexchanging pairs because no oxygen occupies the position between them.

Greedan and McCarthy[3] estimated the values of exchange integrals J_1/k and J_2/k of Eu_2TiO_4 to confirm agreement with the experimental value ($\theta_C = 10$ K) using Eq. 1: $J_1/k = 0.07$ and $J_2/k = 0.04$ K (Table 4). An Eu^{2+} ion in Eu_2TiO_4 is surrounded by 9 nearest and 8 second-nearest neighboring Eu^{2+} ions with the interatomic distances of 3.75 to 3.90 Å and 5.51 Å, respectively. The Eu–Eu distances and Eu–O–Eu angles in Eu_2TiO_4 are closely similar to those of $Eu_3(BO_3)_2$.

In Eu_2TiO_4, there are three kinds of exchanging pairs between the nearest Eu neighbors, Types 1 and 2 correspond to those of $Eu_3(BO_3)_2$, the Eu–Eu distances in the borate being smaller than those in the titanate (Fig. 4). The exchanging pair (Type 3), not existing in $Eu_3(BO_3)_2$, is the pair with four 90° Eu^{2+}–O^{2-}–Eu^{2+} and contributing antiferromagnetically to the overall magnetism in a simillar manner to that of the exchanging pairs in $EuTiO_3$.[1f,3] Thus, $Eu_3(BO_3)_2$ is expected to give the greater values of J_1/k than Eu_2TiO_4. The superexchanging pairs between the second-nearest Eu neighbors in Eu_2TiO_4 and $Eu_3(BO_3)_2$ should give similar values of J_2/k from the similarity of the Eu–Eu distances and Eu–O–Eu angles. From the observed θ_C value of 8 K, we can estimate the values of J_1/k and J_2/k to be 0.10 and 0.04 K, substituting $S=7/2$,

TABLE 4. MAGNETIC EXCHANGE AND SUPEREXCHANGE INTERACTIONS IN Eu_2TiO_4 AND $Eu_3(BO_3)_2$

	Eu_2TiO_4[a]	$Eu_3(BO_3)_2$
T_c/K	9	7.5
θ_c/K[b]	10	8
Nearest neighbors	5 Eu^+ at 3.90 Å 4 Eu^+ at 3.75	2 Eu^+ at 3.509 Å 4 Eu^+ at 3.778
Second-nearest neighbors	8 Eu^+ at 5.51	4 Eu^+ at 5.450
Interactions contributing to J_1	Eu^{2+}–Eu^{2+}(+) 90°Eu^{2+}–O^{2-}–Eu^{2+}(−)	Eu^{2+}–Eu^{2+}(+) 80.1—99.8°Eu^{2+}–O^{2-}–Eu^{2+}(−)
Resultant J_1k^{-1}/K	0.07	0.10
Interactions contributing to J_2	180°Eu^{2+}–O^{2-}–Eu^{2+}	166.0°Eu^{2+}–O^{2-}–Eu^{2+}
Resultant J_2k^{-1}/K	0.04	0.04

a) Ref. 8. b) θ_c=paramagnetic Curie temperature.

$Z_1=6$ and $Z_2=4$ into Eq. 1. It is concluded that the 166.0° Eu^{2+}–O^{2-}–Eu^{2+} superexchanging pairs contribute ferromagnetically and the ferromagnetism of $Eu_3(BO_3)_2$ is attributable to the direct Eu^{2+}–Eu^{2+} and the 166.0° Eu^{2+}–O^{2-}–Eu^{2+} ferromagnetic interactions.

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