

The authors wish to express their gratitude to Professor S. Sugiura for his encouragement throughout this study and to Mr J. B. Parise for improvement of the manuscript. The computations were carried out at the Computation Centers of this University (FACOM 230-35), and Tokyo University (HITAC 8700/8800).

#### References

COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst. A* **26**, 71–83.

*Acta Cryst.* (1979). **B35**, 149–151

IMAMOV, P. M. & SEMILETOV, S. A. (1971). *Sov. Phys. Crystallogr.* **15**, 845–850.  
*International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.  
 KIHARA, K. & MATSUMOTO, T. (1978). *Z. Kristallogr.* In the press.  
 LANGE, P. W. (1939). *Naturwissenschaften*, **27**, 133–134.  
 NAKAJIMA, S. (1963). *J. Phys. Chem. Solids*, **24**, 479–485.  
 OZAWA, T. & SHIMAZAKI, H. (1974). Private communication.  
 VON HIPPEL, A. (1948). *J. Chem. Phys.* **16**, 372–380.

## Structure of Divalent-Europium Metaborate

BY K. MACHIDA, G. ADACHI\* AND J. SHIOKAWA

*Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita, Osaka 565, Japan*

(Received 17 July 1978; accepted 9 October 1978)

**Abstract.** EuB<sub>2</sub>O<sub>4</sub>, orthorhombic, *Pnca*;  $a = 6.593$  (1),  $b = 12.063$  (2),  $c = 4.343$  (1) Å,  $Z = 4$ ,  $D_x = 4.57$ ,  $D_m = 4.61$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 18.15$  mm<sup>-1</sup>. EuB<sub>2</sub>O<sub>4</sub> is isostructural with CaB<sub>2</sub>O<sub>4</sub>. The structural framework consists of endless chains of BO<sub>3</sub> groups, (BO<sub>2</sub>)<sub>∞</sub>, along the  $c$  axis. Each Eu atom is surrounded by eight O atoms to form an EuO<sub>8</sub> dodecahedron. The mean Eu–Eu distances between Eu nearest neighbors and between Eu next-nearest neighbors are 4.080 and 6.632 Å, respectively. The final  $R$  value was 0.029 for 334 observed reflections.

**Introduction.** Compounds containing divalent europium (Eu<sup>2+</sup>) have been of interest because of their magnetic and spectroscopic properties. The magnetic exchange interactions in highly symmetrical compounds such as rock salt-type EuO or perovskite-type EuTiO<sub>3</sub> have been evaluated on the basis of the Eu<sup>2+</sup>–Eu<sup>2+</sup> interactions, and Eu<sup>2+</sup>–O<sup>2-</sup>–Eu<sup>2+</sup> angles, 90 and 180°, between Eu nearest neighbors and next-nearest neighbors respectively. These exchange interactions are sensitive to the distances between Eu<sup>2+</sup> ions (Wolf, McGuire & Shafer, 1964; McGuire, Shafer, Joenk, Alperin & Pickart, 1966). Divalent-europium borates in the EuO–B<sub>2</sub>O<sub>3</sub> system, *i.e.* EuB<sub>4</sub>O<sub>7</sub>, EuB<sub>2</sub>O<sub>4</sub>, Eu<sub>2</sub>B<sub>2</sub>O<sub>5</sub> and Eu<sub>3</sub>B<sub>2</sub>O<sub>6</sub>, have been synthesized and EuB<sub>2</sub>O<sub>4</sub> is an antiferromagnet with the Néel temperature,  $T_N = 3$  K (Hata, Adachi & Shiohawa, 1977; Machida, Hata, Okuno, Adachi & Shiohawa, 1978).

The preparation of single crystals has been described in detail elsewhere (Machida *et al.*, 1978). They were grown in the form of light-yellow needles. Weissenberg photographs exhibited the following systematic absences:  $k + l = 2n + 1$  for  $0kl$ ,  $l = 2n + 1$  for  $h0l$  and  $h = 2n + 1$  for  $hk0$ .

The intensity data were measured on a Rigaku automated four-circle diffractometer with a crystal of dimensions 0.15 × 0.15 × 0.30 mm. Reflections within  $(\sin \theta)/\lambda = 0.71$  Å<sup>-1</sup> were collected using the  $\omega$ – $2\theta$  scan technique with Mo  $K\alpha$  radiation ( $\lambda = 0.7107$  Å) monochromated by a graphite plate. 495 independent reflections were measured, among which 334 observed reflections were above background. The intensity data were corrected for Lorentz and polarization factors. No correction was made for absorption.

The location of the Eu atom was determined by a three-dimensional Patterson synthesis. Successive Fourier syntheses revealed the positions of the O and B atoms. All the atomic parameters were refined by the block-diagonal least-squares method with *HBL5-V*

Table 1. *Final positional parameters*

Standard deviations are given in parentheses.

	$x$	$y$	$z$
Eu	$\frac{1}{4}$	0	0.2610 (1)
B	0.1247 (13)	0.1944 (6)	0.8281 (18)
O(1)	0.0935 (9)	0.0914 (4)	0.7350 (9)
O(2)	0.1440 (9)	0.2111 (4)	0.1470 (12)

\* To whom correspondence should be addressed.

(Ashida, 1973) to give  $R = 0.029$  (weighted  $R = 0.039$ ). The final positional parameters are listed in Table 1.\* The atomic scattering factors for Eu, B and O atoms were those listed in *International Tables for X-ray Crystallography* (1974). The weighting scheme used was  $w = [\sigma(F_o)^2 + a|F_o|^2 + b|F_o|^2]^{-1}$ , and the values of  $a$  and  $b$  used in the final refinement were 0.1002 and 0.0004, respectively.

**Discussion.** The final parameters (Table 1) were found to agree with those of  $\text{CaB}_2\text{O}_4$  reported by Marezio, Plettinger & Zachariasen (1963). Therefore,  $\text{EuB}_2\text{O}_4$  is isostructural with  $\text{CaB}_2\text{O}_4$ . Projections of the  $\text{EuB}_2\text{O}_4$  structure viewed along the  $a$  and  $c$  axes are shown in Figs. 1 and 2, respectively.

The B—O distances are 1.32, 1.41 and 1.39 Å. The short bond B—O(1) involving the unshared O(1) atom in the  $(\text{BO}_2)_\infty$  chain may be ascribed to the next-nearest

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33949 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

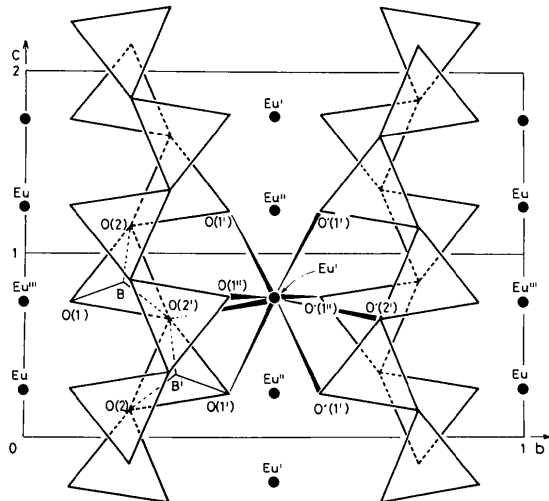


Fig. 1. A projection of the  $\text{EuB}_2\text{O}_4$  structure viewed along the  $a$  axis.

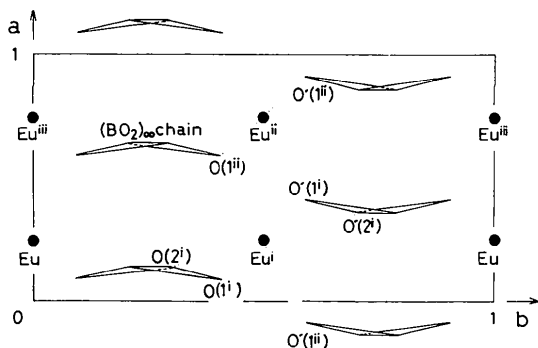


Fig. 2. A projection of the  $\text{EuB}_2\text{O}_4$  structure viewed along the  $c$  axis.

Table 2. *Interatomic distances (Å) and angles (°) in  $\text{EuB}_2\text{O}_4$*

Standard deviations are given in parentheses.

(a) The  $(\text{BO}_2)_\infty$  chain

Distances			
B—O(1)	1.32 (1)	O(1)—O(2)	2.323 (8)
—O(2)	1.41 (1)	—O(2')	2.435 (8)
—O(2'')	1.39 (1)	O(2)—O(2')	2.365 (8)
B—B <sup>i</sup>	2.55 (1)		
Angles			
O(1)—B—O(2)	116.7 (7)	O(1)—B—O(2')	127.7 (7)
O(2)—B—O(2')	115.6 (7)	B—O(2)—B <sup>i</sup>	131.8 (7)

(b) Eu—Eu distances

Nearest neighbors		Next-nearest neighbors	
Eu <sup>i</sup> —Eu <sup>ii</sup>	4.342 (1) (×2)	Eu <sup>i</sup> —Eu <sup>iii</sup>	6.593 (1) (×2)
—Eu <sup>ii</sup>	4.001 (1) (×2)	—Eu	6.410 (1) (×4)
—Eu <sup>iii</sup>	3.896 (1) (×2)	Eu <sup>iii</sup>	6.874 (1) (×4)
Average	4.080	Average	6.632

(c) Eu—O distances

Eu <sup>i</sup> —O(1 <sup>i</sup> )	2.738 (6) (×2)	Eu <sup>i</sup> —O(1 <sup>ii</sup> )	2.519 (6) (×2)
—O(2')	2.687 (6) (×2)	Eu <sup>ii</sup> —O(1 <sup>iii</sup> )	2.553 (6) (×2)
Average	2.624		

(d) Eu—O—Eu angles

Eu <sup>i</sup> —O(1 <sup>i</sup> )—Eu <sup>ii</sup>	110.3 (2)	Eu <sup>i</sup> —O(1 <sup>i</sup> )—Eu <sup>iii</sup>	100.4 (2)
Eu <sup>i</sup> —O(1 <sup>i</sup> )—Eu <sup>iii</sup>	99.0 (2)	Eu <sup>ii</sup> —O(1 <sup>ii</sup> )—Eu <sup>iii</sup>	100.4 (2)
Eu <sup>i</sup> —O(1 <sup>ii</sup> )—Eu <sup>ii</sup>	99.0 (2)		

Symmetry transformations: Eu<sup>i</sup> ( $\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + z$ ), Eu<sup>ii</sup> ( $\frac{1}{2}, \frac{1}{2}, -\frac{1}{2} + z$ ;  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + z$ ), Eu<sup>iii</sup> ( $-\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + z$ ;  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + z$ ), Eu<sup>iv</sup> ( $\frac{1}{2}, \frac{1}{2}, \frac{1}{2} - z$ ), Eu<sup>v</sup> ( $-\frac{1}{2}, \frac{1}{2}, \frac{1}{2} - z$ ;  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2} - z$ ), Eu<sup>vi</sup> ( $\frac{1}{2}, 0, \bar{z}$ ), B<sup>i</sup> ( $x, \frac{1}{2} - y, \frac{1}{2} + z$ ), O(1<sup>i</sup>) ( $x, \frac{1}{2} - y, \frac{1}{2} + z$ ;  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$ ), O(1<sup>ii</sup>) ( $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$ ;  $x, \frac{1}{2} + y, \frac{1}{2} - z$ ), O(2') ( $x, \frac{1}{2} - y, \frac{1}{2} + z$ ;  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$ ).

neighbor interaction between Eu and B atoms since O(1) is shared between the  $\text{BO}_3$  triangle and the  $\text{EuO}_8$  dodecahedron (Table 2, Fig. 1). The B—O(2)—B<sup>i</sup> angle ( $131.8^\circ$ ) closely agrees with the corresponding angle ( $131.5^\circ$ ) in a pyroborate group,  $\text{B}_2\text{O}_5$ , of  $\text{Mg}_2\text{B}_2\text{O}_5$  reported by Takeuchi (1952).

Each Eu atom is surrounded by eight O atoms to form a distorted  $\text{EuO}_8$  dodecahedron with individual Eu—O distances varying from 2.519 to 2.738 Å (Table 2).

The mean Eu—Eu distance between Eu nearest neighbors (4.080 Å) is similar to that in  $\text{EuTiO}_3$  (3.90 Å) which has been found to be an antiferromagnet with the  $T_N = 5.3$  K by McGuire, Shafer, Joenk, Alperin & Pickart (1966). Consequently, the  $\text{Eu}^{2+}$ — $\text{Eu}^{2+}$  and  $90^\circ$   $\text{Eu}^{2+}$ — $\text{O}^{2-}$ — $\text{Eu}^{2+}$  interactions seem to contribute to the magnetic properties of  $\text{EuB}_2\text{O}_4$ , although the Eu—O—Eu angles ( $110.3, 99.0$  and  $100.4^\circ$ ) somewhat deviate from the value of  $90^\circ$ . The mean Eu—Eu distance between Eu next-nearest neighbors (6.632 Å) is so long that the  $180^\circ$   $\text{Eu}^{2+}$ — $\text{O}^{2-}$ — $\text{Eu}^{2+}$  interaction may be very weak.

Therefore it seems that the magnetism of  $\text{EuB}_2\text{O}_4$  results mainly from the  $\text{Eu}^{2+}$ — $\text{Eu}^{2+}$  and  $90^\circ$   $\text{Eu}^{2+}$ — $\text{O}^{2-}$ — $\text{Eu}^{2+}$  interactions between Eu nearest neighbors.

The authors wish to thank Mr K. Okuno and Mr H. Hata for their assistance and Drs M. Nakane and N. Kamijo for the measurements on the four-circle X-ray diffractometer, and also wish to express their gratitude to Drs N. Kasai and N. Yasuoka, and Mr K. Miki for their helpful discussions and encouragement.

## References

ASHIDA, T. (1973). *The Universal Crystallographic Computing System - Osaka*, pp. 55-61. The Computation Center, Osaka Univ., Japan.

HATA, H., ADACHI, G. & SHIOKAWA, J. (1977). *Mater. Res. Bull.* **12**, 811-814.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.  
 MCGUIRE, T. R., SHAFER, M. W., JOENK, R. J., ALPERIN, H. A. & PICKART, S. J. (1966). *J. Appl. Phys.* **37**, 981-982.  
 MACHIDA, K., HATA, H., OKUNO, K., ADACHI, G. & SHIOKAWA, J. (1978). To be published.  
 MAREZIO, M., PLETTINGER, H. A. & ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 390-392.  
 TAKÉUCHI, Y. (1952). *Acta Cryst.* **5**, 574-581.  
 WOLF, W. P., MCGUIRE, T. R. & SHAFER, M. W. (1964). *J. Appl. Phys.* **35**, 984-988.

*Acta Cryst.* (1979). **B35**, 151-152

Structure du Monophosphate de Potassium-Zinc:  $\text{KZn}_4(\text{PO}_4)_3$ 

PAR M. T. AVERBUCH-POUCHOT ET A. DURIF

Laboratoire de Cristallographie, CNRS, 166 X, 38042 Grenoble CEDEX, France

(Reçu le 27 juin 1978, accepté le 16 octobre 1978)

**Abstract.**  $\text{KZn}_4(\text{PO}_4)_3$ , orthorhombic, *Pccn*,  $a = 13.81$  (1),  $b = 8.166$  (8),  $c = 9.675$  (8) Å,  $D_x = 3.56$  Mg m<sup>-3</sup>,  $Z = 4$ . The crystal structure has been solved with 1260 independent reflexions. The final  $R$  value is 0.062 (0.045 for 1113 reflexions with  $|F_o| - |F_c|/\sigma < 5$ ). The atomic arrangement is a three-dimensional chain involving  $\text{PO}_4$  and  $\text{ZnO}_4$  tetrahedra and  $\text{KO}_{10}$  polyhedra.

**Introduction.** Un certain nombre de molécules d'eau du monophosphate acide de potassium-zinc [ $\text{K}_2\text{Zn}_2\text{H}(\text{PO}_4)_2 \cdot \frac{5}{2}\text{H}_2\text{O}$  (Tordjman, Durif, Averbuch-Pouchot & Guitel, 1975)] présentent des propriétés zéolithiques intéressantes.

Au cours d'une étude physico-chimique de ce sel, Barbou des Courières & Simonot-Grange (1978) ont constaté que dans certaines conditions sa décomposition thermique permet de mettre en évidence un nouveau monophosphate de potassium-zinc anhydre.

Les analyses effectuées par les auteurs conduisent à attribuer à ce nouveau monophosphate une formule  $\text{K}_2\text{Zn}_5(\text{PO}_4)_4$  ou très voisine. Des monocristaux préparés par fusion et refroidissement lent d'un mélange correspondant à un rapport Zn/K = 5/2 ont été utilisés pour l'étude cristallographique de ce sel. L'étude structurale de ce monophosphate qui fait l'objet de ce travail montre que sa formule chimique exacte est  $\text{KZn}_4(\text{PO}_4)_3$ .

Le cristal utilisé avait très approximativement la forme d'un parallélépipède rectangle, dont les trois côtés avaient respectivement pour dimensions: 0,22, 0,16 et 0,16 mm.

Les intensités de 1260 réflexions indépendantes ont été mesurées à l'aide d'un diffractomètre automatique Philips PW 1100, fonctionnant à la longueur d'onde  $K\alpha_1$  de l'argent (monochromateur de graphite). Le domaine angulaire de ces mesures est compris entre 3 et 25° ( $\theta$ ). Chaque réflexion est balayée à la vitesse de 0,02° s<sup>-1</sup> dans un domaine de 1,20°. Le fond continu est mesuré 10 s à chaque extrémité du domaine d'intégration qui était exploré en balayage  $\omega$ .

La structure a été résolue par la méthode de l'atome lourd. L'exploitation de la fonction de Patterson a permis de localiser les atomes de zinc, de potassium et de phosphore. Une synthèse de Fourier, réalisée en utilisant la position des atomes précédemment cités, met en évidence tous les atomes d'oxygène de l'arrangement. Une série d'affinements (Prewitt, 1966) amène le

Tableau 1. Paramètres des positions atomiques ( $\times 10^4$ ) et  $B_{\text{éq}}$  (Å<sup>2</sup>) ( $R = 0,045$ )

	$x$	$y$	$z$	$B_{\text{éq}}$
Zn(1)	504,9 (6)	1055 (1)	1931,6 (9)	1,2
Zn(2)	1455,6 (6)	867,1 (9)	4974,2 (9)	1,2
K	7500 (0)	2500 (0)	1930 (3)	1,8
P(1)	5655 (1)	2454 (2)	4338 (2)	0,9
P(2)	2500 (0)	2500 (0)	2538 (3)	1,0
O(1)	2630 (4)	4022 (6)	3415 (6)	1,6
O(2)	3396 (4)	2356 (6)	1556 (5)	1,5
O(3)	4712 (4)	3420 (6)	3930 (6)	1,6
O(4)	4129 (4)	6182 (6)	1767 (6)	1,8
O(5)	1501 (4)	6327 (6)	636 (6)	1,6
O(6)	4482 (4)	8297 (7)	4250 (5)	1,9