

## BRIEF COMMUNICATIONS

### Structural Investigation of $\text{CeRh}_3\text{B}_2$ by Single-Crystal X-Ray Diffractometry

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The crystal structure of  $\text{CeRh}_3\text{B}_2$  ( $P6/mmm$ ;  $a = 5.484(1)$  and  $c = 3.087(1)$  Å) has been analyzed by single-crystal X-ray diffractometry. It was corroborated that  $\text{CeRh}_3\text{B}_2$  crystallizes in the  $\text{CeCo}_3\text{B}_2$ -type structure. No partial occupation at the metal sites was found and thus the stoichiometric composition was established from both the X-ray and chemical analyses. Anisotropic thermal vibrations of atoms are discussed in connection with surrounding atoms. © 1987 Academic Press, Inc.

#### 1. Introduction

Although preparation and crystal chemistry of ternary rare-earth borides of the  $\text{CeCo}_3\text{B}_2$ -type structure (1) have been treated in a number of publications (1-4), no structural investigation by single-crystal counter data has been reported. In the present work, we report the result of an accurate single-crystal structure analysis of one of the representatives,  $\text{CeRh}_3\text{B}_2$ , which has attracted much interest because of its unusual magnetic properties (5-7). The proposed structure for this compound was corroborated, and anisotropic thermal vibrations of the atoms are discussed in connection with surrounding atoms.

#### 2. Experimental Procedures

A single crystal of  $\text{CeRh}_3\text{B}_2$  was successfully grown by using the Czochralski method with a triarc furnace under argon atmosphere (8). The crystal obtained was examined by preliminary X-ray diffraction work (by means of powder diffraction, Weissenberg and precession methods) and confirmed to be a single phase analogous to  $\text{CeCo}_3\text{B}_2$  (hexagonal,  $P6/mmm$ ;  $a = 5.057(3)$  and  $c = 3.036(2)$  Å) (1). The chemical composition was analyzed by inductively coupled plasma emission spectroscopy (9) and found to be  $\text{CeRh}_{2.94}\text{B}_{2.03}$  which is practically equal to the stoichiometric composition  $\text{CeRh}_3\text{B}_2$ . The lattice

constants were determined by the same diffractometer that was used for the intensity measurements; the wavelength employed was 0.71073 Å for MoK $\alpha$  radiation.

For intensity measurements an approximately spherical specimen with an average diameter of 0.08 mm was selected from the fragments obtained by crushing a CeRh<sub>3</sub>B<sub>2</sub> single crystal. All the reflections up to  $2\theta = 70^\circ$  and the reflections with  $0 \leq h \leq 13$ ,  $-13 \leq k \leq 13$  and  $0 \leq l \leq 7$ , for which  $70^\circ < 2\theta < 120^\circ$ , were measured by a Rigaku automated four-circle diffractometer, with graphite-monochromatized MoK $\alpha$  radiation. The  $\omega(2\theta \leq 30^\circ)$  or  $\omega - 2\theta(30^\circ < 2\theta < 120^\circ)$  scan mode was used at a rate of  $4^\circ \text{ min}^{-1}$  in  $\omega$ . Background counts were measured for 5 sec at each side of the scanning region,  $\Delta\omega = 1.2 + 1.5 \tan \theta$ . Three standard reflections were monitored every 100 reflections and no noticeable variation was observed. A total of 2272 reflections with  $F_o$  values greater than 2.5 times the standard deviation were collected. After Lorentz, polarization and absorption ( $\mu_r = 1.13$ ) corrections, equivalent reflections were averaged to give 258 unique reflections.

### 3. Structure Analysis and Discussion

Ku and Meisner (10) reported that the greater part of the ternary rare-earth borides designated  $\text{RE}_T\text{B}_2$  (RE = rare earth,  $T = \text{Rh, Ir}$ ) has monoclinic symmetry, slightly distorted from the hexagonal  $\text{CeCo}_3\text{B}_2$  type. The significant feature of the distorted structure is that the lattice constant  $\beta$  changes from  $90^\circ$  (in the hexagonal lattice) to  $90.8(1) - 92.8(1)^\circ$  (in the monoclinic lattice); the relationship between the two structures is  $\mathbf{a}_m = \mathbf{a}_h$ ,  $\mathbf{b}_m = 2\mathbf{b}_h + \mathbf{a}_h$ ,  $\mathbf{c}_m = \mathbf{c}_h$ . Furthermore, single crystals obtained from the Cu-flux method are not CeRh<sub>3</sub>B<sub>2</sub> but Ce<sub>0.67</sub>Rh<sub>3</sub>B<sub>2</sub> (11) with a distorted  $\text{CeCo}_3\text{B}_2$ -type structure different from the monoclinic crystals. Therefore particular

care was taken to check the symmetry by using single-crystal diffractometer data. It was confirmed that the CeRh<sub>3</sub>B<sub>2</sub> single crystal investigated in the present work had hexagonal symmetry with the lattice constants  $a = 5.484(1)$  and  $c = 3.087(1)$  Å, in agreement with published X-ray powder data for the CeRh<sub>3</sub>B<sub>2</sub> (4); the angle  $\alpha$  or  $\beta$  of the present crystal, which is the counterpart of the angle  $\beta$  in the distorted monoclinic structure, was measured to be  $90.01(2)$  or  $89.98(2)^\circ$ .

Although the  $\text{CeCo}_3\text{B}_2$ -type structure model (Fig. 1) seems reasonable for the ternary rare-earth borides producing powder X-ray patterns similar to that of  $\text{CeCo}_3\text{B}_2$ , it is almost impossible to determine the boron position in the presence of such heavy metal atoms as cerium and rhodium using only powder X-ray diffraction. To establish the structure model, therefore, a difference Fourier synthesis was calculated by using  $F_o - F_{\text{CeRh}_3}$  coefficients. The difference map showed a strong peak with the density of  $33e^- \text{ \AA}^{-3}$ , and this established the boron position at the  $2(c)$  site ( $\frac{1}{3}, \frac{2}{3}, 0$ ;  $\frac{2}{3}, \frac{1}{3}, 0$ ); the positions of Ce and Rh are at the  $1(a)$  site (0, 0, 0) and the  $3(g)$  site ( $\frac{1}{2}, 0, \frac{1}{2}$ ;  $0, \frac{1}{2}, \frac{1}{2}$ ;  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ ), respectively (Fig. 1). Adding the boron site to the CeRh<sub>3</sub>

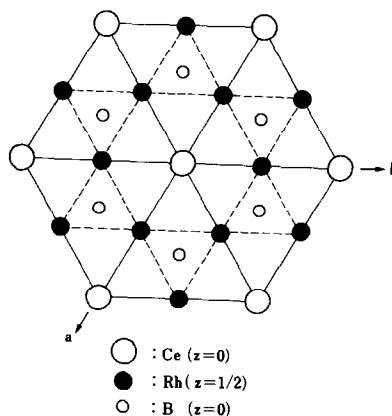


FIG. 1. Structure of CeRh<sub>3</sub>B<sub>2</sub> as seen along the  $c$  axis.

TABLE I  
REFINEMENT OF PARAMETERS AND  
R VALUES OBTAINED

Refinement No.	Structure	Refined parameters <sup>a</sup>	R(Rw) <sup>b</sup>
1	CeRh <sub>3</sub>	SC, $B_{\text{iso}}$ (Ce, Rh)	0.11(0.11)
2	CeRh <sub>3</sub> B <sub>2</sub>	SC, $B_{\text{iso}}$ (Ce, Rh, B)	0.098(0.093)
3	CeRh <sub>3</sub> B <sub>2</sub>	SC, $B_{\text{iso}}$ (B), $\beta_{i,j}$ (Ce, Rh)	0.055(0.052)
4	CeRh <sub>3</sub> B <sub>2</sub>	SC, $B_{\text{iso}}$ (B), $\beta_{i,j}$ (Ce, Rh), $G_{\text{iso}}$	0.050(0.047)
5	CeRh <sub>3</sub> B <sub>2</sub>	SC, $\beta_{i,j}$ (Ce, Rh, B), $G_{\text{iso}}$	0.049(0.046)
6	CeRh <sub>3</sub> B <sub>2</sub>	SC, $\beta_{i,j}$ (Ce, Rh, B), $G_{\text{iso}}$ , $P(\text{Rh})^c$	0.049(0.046)

<sup>a</sup> SC, scale factor;  $B_{\text{iso}}$ , isotropic temperature factors;  $\beta_{i,j}$ , anisotropic temperature factors;  $G_{\text{iso}}$ , parameter for isotropic extinction corrections;  $P$ , occupancy factor.

$$^b R = \frac{\sum(|F_o| - |F_c|)/\sum|F_o|}{Rw} = \frac{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2}{1/2}$$

<sup>c</sup> Occupancy of the Rh site was refined fixing those of Ce and B at 100% without any decrease of the  $R$  value; the occupancy obtained was 99.1(7)%, indicating practically full occupation.

arrangement, the full structure was then refined by using the full-matrix least-squares program RADIEL (12). In the final stage of the refinement, anisotropic temperature factors were applied to all the atoms and isotropic secondary extinction corrections were made. The function minimized was  $\sum w(|F_o| - |F_c|)^2$  where the weights  $w$  were  $1/\sigma^2(F_o)$ . Table I shows how the  $R$  value was decreased in successive stages of refinements. The results of the final least-squares refinement (Refinement No. 5 in Table I) are presented; interatomic distances are given in Table II. The atomic scattering factors and anomalous dispersion correction factors were taken from Ref. (13). The data processing and crystallographic computations other than the least-squares calculations were made with the program UNICS-III (14).

Initially the calculation of the structure factors of the "CeRh<sub>3</sub>" arrangement with refined temperature factors gave the  $R$  value of 0.11 (Refinement No. 1 in Table I), which is next decreased to 0.098 by adding the B atom to the metal arrangement. Subsequently the  $R$  value was greatly reduced by applying anisotropic temperature factors to the metal atoms (Refinement No. 3).

Isotropic secondary extinction corrections and the application of anisotropic temperature factors to the B atom also contributed to the lowering of the  $R$  value in a certain extent (Refinement Nos. 4 and 5). In order to examine the presence of a partial occupation of metal sites as in a related compound CeRh<sub>3</sub>B (15), occupational refinement for the Rh site was tested fixing those of Ce and B at 100% (Refinement No. 6). In this stage, however, the  $R$  value could not be reduced; the occupancy obtained was 99.1(7)%, indicating practically full occupation. A final difference synthesis showed no significant residual peaks.

The anisotropy of the thermal vibration of each atom (Fig. 2) is thought to reflect the geometry of the surrounding atoms. The thermal vibration of the Ce atom in the  $c$  axis direction is less prominent than in the plane perpendicular to the  $c$  axis because of the unusually short Ce-Ce distances (3.087 Å). The Rh atom vibrates, in the case of the atom at  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ , for example (Figs. 1 and 2), less prominently in the [110] direction than in the direction perpendicular to it, possibly

TABLE II  
ATOMIC COORDINATES, TEMPERATURE FACTORS,  
AND INTERATOMIC DISTANCES (Å) OF CeRh<sub>3</sub>B<sub>2</sub>

Atom	Site	$x$	$y$	$z$	$B_{\text{eq}}$ (Å <sup>2</sup> )	
Ce	1(a)	0	0	0	0.99(4)	
Rh	3(g)	$\frac{1}{2}$	0	$\frac{1}{2}$	0.85(3)	
B	2(e)	$\frac{1}{2}$	$\frac{2}{3}$	0	1.7(6)	
Atom <sup>a</sup>	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
Ce	103(4)	U <sub>11</sub>	51(3)	$\frac{1}{2}U_{11}$	0	0
Rh	81(3)	71(3)	72(2)	$\frac{1}{2}U_{22}$	0	0
B	173(64)	U <sub>11</sub>	58(35)	$\frac{1}{2}U_{11}$	0	0
Interatomic distances						
Ce-2Ce	3.087(1)	Rh-4Ce	3.1468(5)	B-3Ce	3.1664(6)	
Ce-12Rh	3.1468(5)	Rh-4Rh	2.742(1)	B-6Rh	2.2111(4)	
Ce-6B	3.1664(6)	Rh-2Rh	3.087(1)	B-B	3.087(1)	
		Rh-4B	2.2111(4)	B-B	3.1664(4)	

<sup>a</sup> Anisotropic temperature factors. The expression is  $\exp[-10^{-4} \times 2\pi^2 (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ .

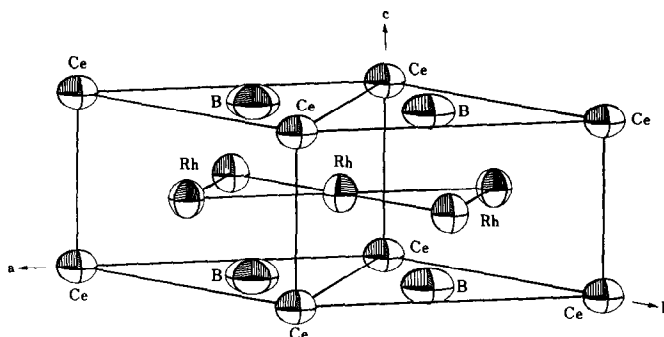


FIG. 2. Perspective view of the structure of  $\text{CeRh}_3\text{B}_2$ . Thermal ellipsoids are drawn at the 99.9% probability level.

due to closer contact between Rh atoms (Rh–Rh: 2.742 Å). As to the B atom, although the thermal parameters have large standard deviations (Table II), it seems likely that the thermal vibration is less prominent in the  $c$  axis direction, because the atom is tightly bonded to six Rh atoms (Rh–B = 2.211 Å) forming a trigonal prism with its two triangular faces parallel to the  $c$  plane (Fig. 2). (Interatomic distances Ce–Ce and Rh–Rh in the elements are 3.63 and 2.684 Å, respectively (16), and usual Rh–B bond length is 2.22 Å (17).) It is of interest to note that the Ce atoms form chains along the  $c$  axis and the chains are isolated from each other (Figs. 1 and 2), this being consistent with the fact that the measured electrical resistivity along the  $c$  axis is one order of magnitude smaller than that within the  $c$  plane (8).

In conclusion, the present single-crystal study has demonstrated that  $\text{CeRh}_3\text{B}_2$  crystallizes in the  $\text{CeCo}_3\text{B}_2$ -type structure. The validity of the structure analysis is based on a reasonably low  $R$  value, a featureless final difference synthesis, normal values of the thermal parameters for all the atoms, and excellent agreement in the chemical composition between the structure and the chemical analyses.

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