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Structure of the Primitive Tetragonal $ErRh_4B_4$

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Abstract. One of two known forms, $M_r = 622{\cdot}1$, tetragonal, $P4_2/nmc$, $a = 5{\cdot}292\ (4)$, $c = 7{\cdot}379\ (3)$ Å, $V = 206{\cdot}7\ (4)$ Å^3, $Z = 2$, $D_m(293\ \text{K}) = 10{\cdot}21$, $D_x = 10{\cdot}00$ Mg m^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}7107$ Å, $\mu(\text{Mo}\ K\alpha) = 35{\cdot}58$ mm^{-1}, $F(000) = 536$, $T = 290$ K, $R = 0{\cdot}049$, 379 unique reflections. Isostructural with $CeCo_4B_4$. Rh-atom tetrahedra are connected into sheets perpendicular to the c axis and linear chains of atoms running parallel to the a_1 and a_2 axes are formed. B atoms lie almost exactly on the top and bottom surfaces of the sheet.

Introduction. The title compound is known to exhibit both superconducting and ferromagnetic behavior and has been the subject of extensive investigations (Tachiki, Matsumoto & Umezawa, 1979; Gray, Zasadzinski, Vaglio & Hinks, 1983). The first structural study of this compound was carried out by Vandenberg & Matthias (1977) using an X-ray powder method. They found it to be isostructural with the tetragonal $CeCo_4B_4$ and gave lattice-parameter data. The atomic positional parameters were determined, however, not on the title compound but on its cognate YRh_4B_4 and the values obtained were considered as representative of the $M\text{Rh}_4\text{B}_4$ (M = rare-earth element) series of compounds.

We report here a refinement of the structure using good-quality single crystals of $ErRh_4B_4$.

Experimental. Using Cu metal as a solvent, the single crystals were grown by the flux method, the details of the method and some of their physical properties being described elsewhere (Takei, Shishido, Iwasaki & Muto, 1983). D_m determined pycnometrically using H_2O. A well developed needle-shaped crystal elongated along **c** ($0{\cdot}096 \times 0{\cdot}096 \times 0{\cdot}688$ mm) was selected and analysed on a computer-controlled four-circle diffractometer (Rigaku AFC-5). Six reflections used for lattice parameters. Total of 5410 reflections measured with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å), θ–2θ scan mode, $\sin\theta/\lambda \le 0{\cdot}91$ Å^{-1}; $|h| \le 9$, $|k| \le 9$, $|l| \le 13$. 379 unique reflections, $R_{\text{int}} = \sum|F_o - \langle F_o\rangle| / \sum F_o = 0{\cdot}087$, 495 unobserved [$F_o \le 2{\cdot}5\sigma(F_o)$]. Three standard reflections, variation 7%. Multiple-reflection effects led to difficulty in confirming the space-group extinction, but application of convergent-beam electron diffraction method (Tanaka, Sekii & Nagasawa, 1983) led uniquely to the formerly assigned space group $P4_2/nmc$. Measured integrated intensities were corrected for Lorentz and polarization effects and for absorption applying the method developed by Busing & Levy (1957). Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). In the difference Fourier map calculated using the positional parameters of the metal atoms given by Vandenberg & Matthias (1977), approximate locations of the B atoms could be recognized. Least-squares refinement (on F) of all positional and thermal parameters then performed using the program *UNICS*III (Sakurai & Kobayashi, 1979) on the Tohoku University ACOS computer. First equal weight was given to all reflections and later a weighting scheme of the form $(23 - 0{\cdot}86F_o + 0{\cdot}01F_o^2)^{-1}$ was applied. In the refinement process, a correction for secondary extinction (value $2{\cdot}2 \times 10^{-5}$) (Zachariasen, 1967) was included. Final $R = 0{\cdot}049$ and $R_w = 0{\cdot}051$ for 379 unique reflections. For positional parameters $(\Delta/\sigma)_{\max} = 0{\cdot}3$. Excursions in final $\Delta\rho$ map $\le |1{\cdot}2|$ e Å^{-3}.

Discussion. The final structural parameters are given in Table 1.*

The positional parameters of the B atoms are in good agreement with those determined by Vandenberg & Matthias (1977) on the basis of geometrical considerations. For the parameters of the Rh atoms the single-crystal intensity data have significantly altered the z value. A list of interatomic distances is given in Table 2. For comparison, those in the $C15$-type compound $ErRh_2$ (Crangle & Ross, 1964) and the $B8_1$-type compound $RhB_{\sim 1.1}$ (Aronsson, Stenberg & Aselius, 1960) are also shown. The Er—Er distance in $ErRh_4B_4$ is substantially longer than that in the ferromagnetic $ErRh_2$, while the Er—Rh distances are approximately the same as the corresponding distance in $ErRh_2$. More notable are the distances between Rh atoms. These atoms form tetrahedra in the structure and the edge length along the a_1 (or a_2) axis is 2·634 Å,

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39509 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic positional and thermal parameters of* $ErRh_4B_4$ (*space group $P4_2/nmc$; origin at center of inversion*), *with standard deviations in parentheses*

$B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$, where β_{ij} is defined by $T = \exp[-(\beta_{11}h^2 + ... + 2\beta_{12}hk + ...)]$.

	Atomic site	x	y	z	B_{eq}(Å^2)
Er	2(*b*)	$\frac{3}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0·75 (1)
Rh	8(*g*)	$\frac{1}{4}$	−0·0011 (1)	0·3953 (1)	0·70 (1)
B	8(*g*)	$\frac{1}{4}$	0·0772 (21)	0·0971 (16)	1·00 (16)

Table 2. *Interatomic distances* (Å) *in* $ErRh_4B_4$, *compared to those in* $ErRh_2$ *and* $RhB_{\sim 1.1}$

Standard deviations are in parentheses.

$ErRh_4B_4$		$ErRh_2$*		$RhB_{\sim 1\cdot 1}$†	
Er–4 Er	5·255 (2)	–4 Er	3·222		
–4 Rh	2·930 (1)	–12 Rh	3·085		
–8 Rh	3·149 (2)				
–8 B	3·02 (1)				
–4 B	3·09 (1)				
Rh–1 Rh	2·634 (2)				
–1 Rh	2·658 (2)	–6 Rh	2·631	–6 Rh	2·85
–2 Rh	2·840 (1)				
–2 Rh	3·064 (2)				
–2 B	2·18 (1)				
–2 B	2·20 (1)			–6 B	2·18
–1 B	2·24 (1)				
B–1 B	1·83 (2)			–2 B	2·11‡
–2 B	3·12 (1)				
–2 B	3·33 (1)				
–1 B	3·46 (2)				

* Crangle & Ross (1964).

† Aronsson, Stenberg & Aselius (1960).

‡ The value 2·21 in the original paper has been corrected.

which is almost equal to the Rh—Rh distance in $ErRh_2$. The tetrahedra are connected edge by edge with the slightly longer distance of 2·658 Å, so that a sheet consisting of the connected tetrahedra contains linear chains of Rh atoms running parallel to the a_1 and a_2 axes. This structural feature has some resemblance to that found in the *A*15-type structure, known as a typical structure for superconducting compounds, in which metal-atom chains are considered to be responsible for the high superconducting transition temperature. The short B—B distance in $ErRh_4B_4$ suggests that the B atoms exist as dimers (Yvon & Johnston, 1982).

There is an alternative view of the $CeCo_4B_4$-type structure; it can be regarded as a *B*1 (NaCl) like array of Ce atoms and $(CoB)_4$ units, which, in an idealized model, form a cube (Woolf, Johnston, MacKay, McCallum & Maple, 1979). The real shape of the unit in $ErRh_4B_4$ is shown in Fig. 1. It can be seen that the face diagonals [B(1)—B(2) and B(3)—B(4)] are considerably longer than the face diagonals [Rh(1)—Rh(2) and Rh(3)—Rh(4)], and therefore the shape is a distorted cube. It is to be noted, however, that the *z* coordinates of atoms B(1) and B(2) are nearly the same as those of Rh(1) and Rh(2), *i.e.* these four atoms are coplanar, and the same is true for B(3), B(4) and Rh(3), Rh(4).

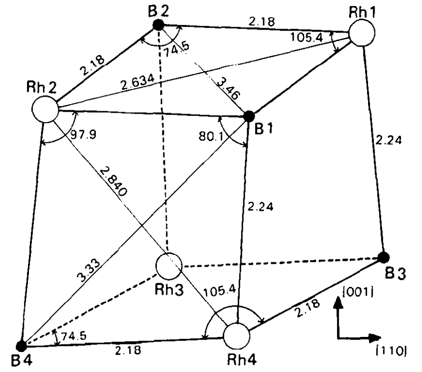

Fig. 1. A $(RhB)_4$ unit contained in the structure of $ErRh_4B_4$. The lengths are in Å and the angles in degrees [e.s.d.'s for distances are given in Table 2; for angles e.s.d.'s are 0·3° for B(1)—Rh(1)—B(2), 0·4° otherwise]. B(1), B(2), Rh(1) and Rh(2) as well as B(3), B(4), Rh(3) and Rh(4) are coplanar, while B(1), B(3), Rh(1) and Rh(4) as well as B(1), B(4), Rh(2) and Rh(4) are not coplanar.

Recently it has been found that $ErRh_4B_4$ crystallizes in another form which is identified as being of the $LuRu_4B_4$-type (body-centered tetragonal) structure (Iwasaki, Ishino, Tsunokuni & Muto, 1983). It is, however, not yet certain whether this form can be transformed into the other.

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Note on the Structure of Ba_2CaMoO_6

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Abstract. That the O atoms in Ba_2CaMoO_6 are sited at the corners of regular octahedra, centered at Mo atoms, is confirmed by comparing the near-edge shape of its Mo *K*-edge absorption spectrum with those of MoS_2 and $Mo_2O_5(pq)_2$ (pq = 9,10-phenanthrenequinone). The structure parameter of Ba_2CaMoO_6 was then directly determined from its EXAFS spectrum, calibrated by that of K_2MoO_4.

Introduction. To calibrate EXAFS spectra of a series of $Mo/Co/Al_2O_3$ supported catalysts (which are amorphous), we were fortunate in obtaining a sample of Ba_2CaMoO_6 from Dr A. W. Sleight (Du Pont Experimental Station, Wilmington, Delaware). Of the many compounds at our disposal which incorporated 'octahedral' MoO_6 moieties, the Ba/Ca molybdate is the only one in which the O atoms occupy the corners of *regular* octahedra; in all the others the octahedra are grossly distorted. The reported structure of Ba_2CaMoO_6 is based on the similarity of its X-ray powder diffraction pattern to those of a series of homologous tungstates and molybdates (pseudocubic), analyzed by Steward & Rooksby (1951). They reported a value for the cubic cell dimension (8·335 Å), and stated that no detectable deformation from cubic symmetry is apparent in the molybdate. However, no value for the Mo—O distance could be derived other than one based on an *estimate* of the structure parameter ($u = 0{\cdot}23$) for Ba_2CaWO_6. If this is accepted for the molybdate, then (Mo—O) $\approx 1{\cdot}92$ Å. In Ba_2NdMoO_6 the quoted value is 1·86 Å (Brandle & Steinfink, 1971).

Discussion. The X-ray absorption data we recorded at the CHESS facility confirm that in Ba_2CaMoO_6 the octahedra are regular, and we are able to determine directly the magnitude of the Mo—O distance. The first conclusion follows from the shape of the near-edge spectrum, recorded at 1 eV ($1\text{ eV} = 1{\cdot}60 \times 10^{-19}$J) intervals in the vicinity of the *K* edge of Mo. Refer to Fig. 1 for comparison of the absorption functions for MoS_2 (regular octahedra of S atoms around the Mo atoms) (Takeuchi & Nowacki, 1964), $Mo_2O_5(pq)_2$ (typical for distorted octahedra of oxygens) (Pierpont & Buchanan, 1976), K_2MoO_4 (regular tetrahedra) (Gatehouse & Leverett, 1969), and for Ba_2CaMoO_6. For the tetrahedral and distorted octahedral structures these curves have been resolved into three overlapping Gaussian distributions (as indicated), after the $\{\mu(E).x\}$ values were normalized by dividing them by the magnitude of the total jump from the pre-edge level to the background level, extrapolated from the high-energy side. The assignment sequence for the resolved Gaussian distributions is based on a pseudo-atomic model: $1s\rightarrow 4d$; $1s\rightarrow 5s$; $1s\rightarrow 5p$ (Shulman, Yafet, Eisenberger & Blumberg, 1976). The first transition is dipole forbidden in spherical or regular octahedral symmetry, but the selection rule breaks down when the octahedra are distorted. In Fig. 1, the relative areas for K_2MoO_4 are $A_1 = 16$; $A_2 = 25$; $A_3 = 360$ and for $Mo_2O_5(pq)_2$, $A_1 = 14$; $A_2 = 29$; $A_3 = 353$, whereas for Ba_2CaMoO_6 they are $A_1 = 0$; $A_2 = 8$; $A_3 = 155$, and for MoS_2, $A_1 = 0$; $A_2 = 33$; $A_3 = 308$. A detailed analysis is presented by Chiu, Bauer & Johnson (1984).

A value for the Mo—O distance was derived from a Fourier transform of EXAFS spectra, Fig. 2. K_2MoO_4 was used for the reference species; it incorporates regular tetrahedra of O atoms about the Mo atoms, and thus calibrates the phase-shift correction in the first coordination shell. We previously checked the validity of this procedure for known structures with distorted MoO_6 octahedra (Chiu *et al.*, 1984). Thus in Ba_2CaMoO_6, (Mo—O) $= 1{\cdot}86 \pm 0{\cdot}02$ Å, which is in general agreement with the proposed value for the *u* parameter (0·223). The second peak in the radial distribution curve is due to an unresolved superposition

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