The details of the association of coordination polyhedra around V atoms are shown in Fig. 1. Bond lengths and angles agree well with the Byström *et al.* (1950) and Bachmann *et al.* (1961) structural determinations. Compared with these fundamental models, the present result gives precise anisotropic thermal parameters and settles definitively the short O—O distance observed, 2·386 (4) Å.

The oxygenated coordination polyhedron around the V atoms should be described in terms of a square (SP) instead of a trigonal pyramid (TBP) as indicated by the previous authors. A calculation based on the dihedral angles of the polyhedron as proposed by Galy, Bonnet & Andersson (1979) gives $\Delta=0{\cdot}845$ (pure TBP and pure SP give $\Delta=0$ and 1, respectively) indicating a slight distortion of the square pyramid; it is also to be noticed that the base of V_2O_5, built up by the oxygen atoms O(21), O(31), O(23), O(23′), is quasi-planar [dihedral angle O(21)O(31)O(23)/O(21)O(31)O(23′) is 1·4°] and the distances of the atoms to the average plane are −0·013 (4), −0·010 (9), 0·011 (4) and 0·011 (4) Å for O(21), O(31), O(23) and O(23′), respectively. The V atom displaced towards the apex of the square pyramid O(11) is distant from this plane by 0·470 (1) Å. The short oxygen distance, 2·386 (4) Å, occurs between O(21)O(23) or O(21)O(23′), *i.e.* when VO_5 pyramids are edge-sharing; the shortening of this interatomic distance by some 0·3 Å shows the importance of the V^{5+}—V^{5+} repulsion. Such repulsion is also responsible for the fact that square VO_5 pyramids sharing edges always have opposite orientations (Bouloux & Galy, 1973).

The structure of V_2O_5 possesses layers built up of VO_5 square pyramids sharing edges and corners; the V—O = 2·791 (3) Å interlayer interaction cannot be treated as a real bond, the structure being, as a result of our recent investigations, easily intercalated by various molecular compounds or complexes (Savariault, 1985). V_2O_5 differs considerably in this case from the other sample sub-oxides, containing both V^{5+} and V^{4+} cations, all exhibiting three-dimensional networks: V_3O_7 (Andersson, Galy & Wilhelmi, 1970; Waltersson, Forslund, Wilhelmi, Andersson & Galy, 1974), V_4O_9 (Wilhelmi & Waltersson, 1970), and V_6O_{13} (Aebi, 1948; Waltersson, Wilhelmi & Kihlborg, 1971).

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Structure of the Body-Centered Tetragonal $ErRh_4B_4$

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Abstract. One of two known forms, $M_r = 622{\cdot}1$, tetragonal, $I4_1/acd$, $a = 7{\cdot}461$ (2), $c = 14{\cdot}804$ (2) Å, $V = 824{\cdot}1$ (6) Å^3, $Z = 8$, $D_x = 10{\cdot}03$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, μ(Mo $K\alpha$) = 35·72 mm^{-1}, $F(000) = 2144$, $T = 298$ K, $R = 0{\cdot}051$, 613 unique reflexions. Synthesized by induction heating. Isostructural with (RE)Ru_4B_4 (RE = rare earth). In contrast to the atomic arrangements of the other form, primitive tetragonal, Rh atom tetrahedra are rotated by 7° around the *c* axis and B atom tetrahedra are rotated in the same direction but by a slightly smaller amount (5°). The shortest connexion between Rh atoms forms zigzag chains running parallel to the a_1 and a_2 axes.

Introduction. $ErRh_4B_4$, known as a compound exhibiting both superconducting and ferromagnetic behavior,

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crystallizes in a primitive tetragonal (PT) $CeCo_4B_4$-type structure (Vandenberg & Matthias, 1977), on which a detailed X-ray structural study using single crystals was made (Watanabe, Iwasaki & Takei, 1984). Iwasaki, Ishino, Tsunokuni & Muto (1983) found that, under different growth conditions, that compound takes another form, a body-centered tetragonal (BCT) structure. Similarity of the lattice-parameter values measured on X-ray powder patterns suggests that this structure is isotypic with that of (RE)Ru_4B_4 (RE = rare earth) previously determined by Johnston (1977). $ErRh_4B_4$ in the BCT form also exhibits superconducting behavior, but, in contrast to the PT form, it becomes antiferromagnetic at lower temperatures. Extensive magnetic and superconductive measurements were carried out using single-crystal samples of the BCT form (Iwasaki, Ikebe & Muto, 1986; Iwasaki & Muto, 1986). It is of interest to determine precisely how the coordination and bonding distances differ in the BCT and PT forms. This kind of measurement will furnish data for understanding the difference in the magnetic property.

Table 1. *Atomic positional and thermal parameters of the BCT form of* $ErRh_4B_4$ (*space group* $I4_1/acd$; *origin at center of inversion*), *with standard deviations in parentheses*

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

	Atomic site	x	y	z	$B_{\rm eq}$(Å^2)
Er	8(*b*)	0	$\frac{1}{4}$	$\frac{1}{8}$	0·78 (1)
Rh	32(*g*)	0·11733 (8)	0·09915 (8)	0·93841 (4)	0·68 (1)
B	32(*g*)	0·8334 (14)	0·1092 (13)	0·9584 (6)	1·01 (15)

Experimental. Single crystals were grown by melting the pellet, prepared by pressing a mixed powder of rhodium and boron and heating at 1323 K for two days under argon gas atmosphere in the induction furnace and cooling slowly. A plate-shaped crystal (0·088 × 0·088 × 0·038 mm) with the *c* axis normal to the plate isolated by immersing bulk crystals in a mixture of *aqua regia* and ethyl alcohol was analyzed on a computer-controlled four-circle diffractometer (Rigaku AFC-5). Ten reflexions used for lattice-parameter determinations ($2\theta \sim 54°$). Intensity data collected with θ–2θ scan mode with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å), $\sin\theta/\lambda \leq 0{\cdot}89$ Å^{-1}, $|h|$, $|k| < 13$ and $|l| < 26$. Total of 9442 reflexions measured, of which 1726 were within the range of $F_o < 3\sigma$. 613 unique reflexions, $R_{\rm int} = \sum|F_o - \langle F_o\rangle|/\sum F_o = 0{\cdot}059$. Five standard reflexions, variation 7%. Systematic extinction of the reflexions led uniquely to the space group $I4_1/acd$ formerly assigned to (RE)Ru_4B_4. Measured integrated intensities were corrected for Lorentz and polarization effects and for absorption applying the method developed by Busing & Levy (1957), the maximum absorption correction being 3·65 and the minimum 1·79. 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 Johnston (1977) to (RE)Ru_4B_4, approximate locations of the B atoms could be recognized. Block-diagonal 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 reflexions and later a weighting scheme of the form $(98{\cdot}9 - 1{\cdot}379F_o + 0{\cdot}00744F_o^2)^{-1}$ was applied. In the refinement process, a correction for secondary extinction (value $1{\cdot}00 \times 10^{-6}$) (Zachariasen, 1967) was included. The extinction parameter and weighting function were determined using the program *SALS* (Nakagawa & Oyanagi, 1980). Final $R = 0{\cdot}051$ and $wR = 0{\cdot}064$ for 613 unique reflexions. For positional parameters $(\Delta/\sigma)_{\rm max} = 0{\cdot}04$. Excursions in the final $\Delta\rho$ map $< |2{\cdot}5|$ e Å^{-3} except the region within 0·9 Å around Er and Rh atom positions.

Discussion. The final structural parameters are given in Table 1.* The positional parameters of Rh atoms are in general agreement with those of Ru atoms in (RE)Ru_4B_4 determined by Johnston (1977) by X-ray powder diffractometry, while the positional parameters of B atoms have been considerably altered.

Fig. 1 shows the atomic arrangements in the BCT form of $ErRh_4B_4$ viewed along the *c* axis. For the sake of comparison, the arrangements in the PT form are also shown. There is a close relationship between the two forms: Er atoms have an f.c.c.-like arrangement and Rh and B atoms each bonded to form two kinds of tetrahedra occupy the octahedral interstices. Each Er atom is surrounded by twelve Rh and twelve B atoms. The lattice parameters of the 'f.c.c.-like' cell are $a_1 = a_2(=a) = 7{\cdot}461\ (2)$ and $a_3(=c/2) = 7{\cdot}402\ (1)$ Å for the BCT form and $a_1 = a_2(=\sqrt{2}a) = 7{\cdot}484$ and $a_3(=c) = 7{\cdot}379$ Å for the PT form.†

One can see, however, a significant difference in the orientation of the Rh atom tetrahedra (shown by the squares in Fig. 1): in the PT form the tetrahedra on the (001) plane have the same orientation and line up exactly in parallel, whereas in the BCT form they take

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* A list of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43150 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† Figures in parentheses are standard deviations calculated in a conventional way and do not necessarily represent true accuracy.

two orientations with their edge rotated by 7° around the *c* axis from the [110] or [1$\bar{1}$0] direction, the sense of the rotation being opposite for the tetrahedra with different orientations. This rotation may be interpreted as an adjustment of tetrahedron packing on the (001) plane. It results in the smaller a_1 (and a_2) parameter for the BCT form, the a_3 parameter slightly increasing to keep the cell volume of the two forms nearly equal. Boron atom tetrahedra slightly larger in size than Rh atom tetrahedra are also rotated in the same direction but by a smaller amount, 5°. The two kinds of tetrahedra are coupled to form a distorted cube. In the BCT form, this cube is twisted in addition to the distortion as a result of the different degrees of rotation.

Interatomic distances calculated for the BCT form are listed in Table 2 and compared with those in the PT form. Among the twelve Rh atoms surrounding an Er atom, four on the tetrahedra on the same (001) plane are located nearest (2·904 Å) to it, four on the tetrahedra immediately above and below are at a slightly longer distance (3·109 Å) and the remaining four at the greatest distance (3·209 Å). In the PT form, the nearest Rh atoms are found on the tetrahedra immediately above and below and the remaining eight Rh atoms at the longer distance are on the tetrahedra on the same (001) plane. This difference in the coordination around an Er atom may be the cause of the different magnetic behavior observed for the two forms. The shortest Rh—Rh atom distance in the BCT form, 2·692 Å, occurs between the atoms on the tetrahedra on adjacent (001) planes; the next shortest, 2·755 Å, occurs between the atoms on the same tetrahedron (one of the edge lengths). Thus the shortest connexion between Rh atoms forms zigzag chains running in the [100] and [010] directions. It is to be noted that in the PT form the shortest connexion between Rh atoms forms linear chains running in the [100] and [010] directions. The shortest B—B atom distance in the BCT form occurs, as in the PT form, not in the atom pair on the same tetrahedron, but between atoms (shown by filled small circles in Fig. 1) on the tetrahedron on adjacent (001) planes and the distance is as small as 1·75 Å, the corresponding distance in the PT form being 1·83 Å.

Table 2. *Interatomic distances* (Å) *in the BCT form of* $ErRh_4B_4$ *compared with those in the PT form*

Symmetry code: (i) $\frac{3}{4}-y, \frac{1}{4}-x, \frac{1}{4}+z$; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, 1+z$; (iii) $\frac{1}{4}+y, \frac{1}{4}+x, -\frac{3}{4}+z$; (iv) $\frac{1}{2}-x, y, 1-z$; (v) $-\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (vi) $\frac{1}{4}+y, -\frac{3}{4}+x, -\frac{3}{4}+z$; (vii) $1-x, \frac{1}{2}-y, z$; (viii) $-x, \frac{1}{2}-y, z$; (ix) $\frac{1}{4}-y, \frac{1}{4}+x, 1+\frac{3}{4}-z$; (x) $-x, -y, 2-z$; (xi) $\frac{1}{4}+y, -\frac{1}{4}+x, 1+\frac{3}{4}-z$; (xii) $-1+x, y, z$; (xiii) $\frac{1}{4}-y, -\frac{3}{4}+x, 1+\frac{3}{4}-z$; (xiv) $1-x, -y, 2-z$; (xv) $-\frac{1}{2}+x, -y, z$; (xvi) $2-x, \frac{1}{2}-y, z$; (xvii) $1+\frac{1}{4}-y, -\frac{3}{4}+x, 1+\frac{3}{4}-z$; (xviii) $1+\frac{1}{2}-x, y, 2-z$; (xix) $\frac{3}{4}-y, \frac{3}{4}-x, 1+\frac{3}{4}-z$; (xx) $2-x, -y, 2-z$.

	BCT	PT*	
Er—8 $\mathrm{Er^{i}}$	5·255 (1)	5·255 (2)	
Er—4 $\mathrm{Er^{ii}}$	5·276 (1)	5·292 (4)	
Er—4 Rh	3·109 (1)	2·930 (1)	
Er—4 $\mathrm{Rh^{iii}}$	2·904 (1)	3·149 (2)	
Er—4 $\mathrm{Rh^{iv}}$	3·209 (1)		
Er—4 $\mathrm{B^{v}}$	2·97 (1)	3·02 (1)	
Er—4 $\mathrm{B^{vi}}$	3·20 (1)		
Er—4 $\mathrm{B^{vii}}$	2·95 (1)	3·09 (1)	
Rh—1 $\mathrm{Rh^{viii}}$	2·851 (1)	2·634 (2)	Intra-Rh tetrahedron
Rh—2 $\mathrm{Rh^{ix}}$	2·755 (1)	2·840 (1)	
Rh—1 $\mathrm{Rh^{iv}}$	2·692 (1)	3·064 (2)	Inter-Rh tetrahedron
Rh—1 $\mathrm{Rh^{x}}$	2·929 (1)		
Rh—1 $\mathrm{Rh^{xi}}$	3·084 (1)	2·658 (2)	
Rh—1 $\mathrm{B^{xii}}$	2·14 (1)	2·18 (1)	Intra-$(RhB)_4$ unit
Rh—1 $\mathrm{B^{vii}}$	2·23 (1)		
Rh—1 $\mathrm{B^{xiii}}$	2·18 (1)	2·24 (1)	
Rh—1 $\mathrm{B^{xiv}}$	2·21 (1)	2·20 (1)	Inter-$(RhB)_4$ unit
Rh—1 $\mathrm{B^{xv}}$	2·26 (1)		
B—1 $\mathrm{B^{xvi}}$	3·25 (1)	3·46 (1)	Intra-B tetrahedron
B—2 $\mathrm{B^{xvii}}$	3·38 (1)	3·33 (2)	
B—1 $\mathrm{B^{xviii}}$	1·75 (1)	1·83 (2)	Inter-B tetrahedron
B—1 $\mathrm{B^{xix}}$	3·20 (1)	3·12 (1)	
B—1 $\mathrm{B^{xx}}$	3·22 (1)		

Figures in parentheses are standard deviations calculated in a conventional way and do not necessarily represent true accuracy.

* Watanabe, Iwasaki & Takei (1984).

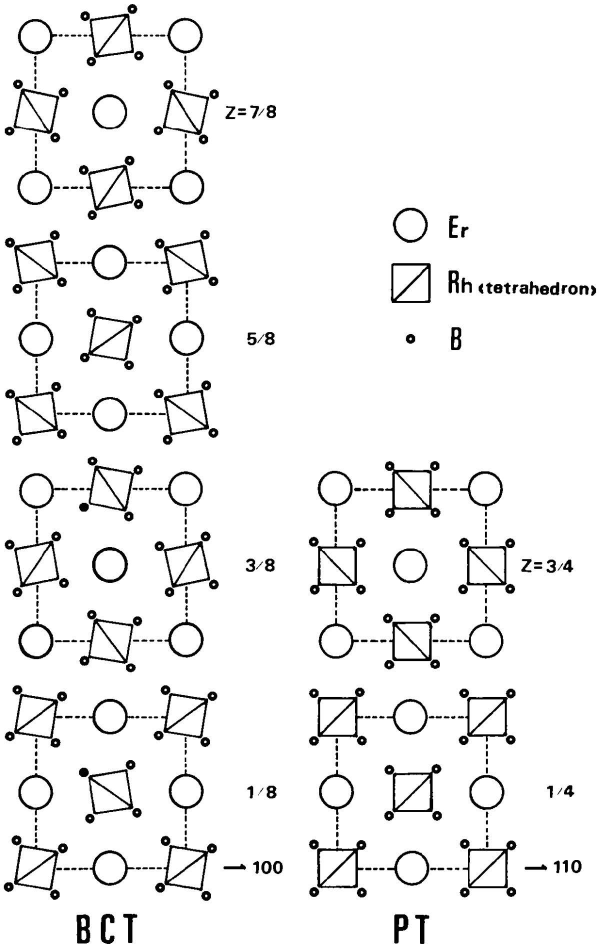

Fig. 1. Atomic arrangements of $ErRh_4B_4$ in the BCT form (left) and PT form (right) viewed along the *c* axis. Large open circles represent Er atoms, squares Rh atom tetrahedra and small circles B atoms. Small solid circles represent one of the B atom pairs with the shortest interatomic distance.

The relative stability of the two forms in $ErRh_4B_4$ has not been established. Chemical analysis made using single-crystal samples of the BCT form suggested a slight deficiency in the boron content from the stoichiometry, but the poor accuracy of the analysis (owing to the small quantity of the sample) did not permit measurement of the degree of the deficiency. However, the closeness of the cell volume (per chemical formula) of the two forms, 103·0 Å^3 for the BCT and 103·3 Å^3 for the PT, indicates that the deficiency, if any, is small. Further study will be necessary to elucidate the relation between the boron content and the relative stability.

X-ray diffraction measurements were carried out using the diffractometer at the Department of Applied Physics, Faculty of Engineering, Tohoku University. We express thanks to Professors T. Ikeda and N. Yamada for providing an opportunity to use the apparatus and Dr S. Kawano for his technical assistance in the diffraction experiments.

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Dineodymium Magnesium Titanate(IV). A Rietveld Refinement of Neutron Powder Diffraction Data

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Abstract. Nd_2MgTiO_6, $M_r = 456{\cdot}69$, monoclinic, $P2_1/n$, $a = 5{\cdot}4661\,(2)$, $b = 5{\cdot}5905\,(2)$, $c = 7{\cdot}7768\,(3)$ Å, $\beta = 90{\cdot}010\,(9)^\circ$, $V = 237{\cdot}65\,(2)$ Å^3, $Z = 2$, $D_x = 6{\cdot}382\,(2)$ Mg m^{-3}, $\mu R = 0{\cdot}59$. The structure has been refined by Rietveld analysis of neutron powder diffraction data recorded at room temperature [$\lambda = 2{\cdot}5790\,(3)$ Å, $R_I = 2{\cdot}02$, $R_p = 6{\cdot}30$, $R_{wp} = 6{\cdot}93\%$]. The structure is of a monoclinic $GdFeO_3$-type perovskite with a high degree of order between Mg and Ti. The mean Nd—O, Mg—O and Ti—O distances are 2·552 (7), 2·068 (6) and 1·961 (6) Å, respectively. An analysis of octahedra tilting is given.

Introduction. In a research program covering the suitability of oxides as a host lattice for nuclear waste, we have investigated compounds with the general formula $Ln_2M_1M_2O_6$ (M_1 = Mg, Ni; M_2 = Ti, Ru; Ln = lanthanide ion). These compounds have a perovskite-type structure with a high degree of order for M_1 and M_2. Raman spectra (Macke, 1977) indicate that the order is not complete. The same conclusion can be drawn from luminescence experiments on Ti perovskites (Macke & Blasse, 1976). Nd_2MgTiO_6, with Nd as an average lanthanide ion, deserves special attention because Nd constitutes a substantial part of nuclear waste. Nd_2MgTiO_6 has been mentioned already by German & Kovba (1983), but they did not describe the structure. Calculations of the rotation of octahedra are given, based on the work of Megaw (1972), Glazer (1972), O'Keeffe & Hyde (1977) and Lelieveld & IJdo (1980).

Experimental. AR starting materials Nd_2O_3, MgO, TiO_2 thoroughly mixed in an agate mortar in the appropriate ratio; mixture heated to 1673 K for a total of 50 d in air, followed by repeated grindings at 295 K.

X-ray powder diffraction patterns obtained with a Philips PW 1050 diffractometer. No other phases observed in the diffraction pattern. Systematic absences $h0l$ $h + l = 2n + 1$ and $0k0$ $k = 2n + 1$ indicating the space group $P2_1/n$. Since no single crystals were available, Rietveld's (1969) method was used for refinement of neutron powder diffraction data on the powder diffractometer at the Petten High-Flux Reactor;

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