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The Preparation and Crystal Structure of Ternary Rare Earth Borides, RCo_3B_2

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In the ternary system of rare earth-cobalt-boron, RCo_3B_2 compounds (R=rare earth elements) were prepared by arc-melting methods. Their crystal structure was investigated by X-ray diffraction methods. These ternary borides, RCo_3B_2, crystallize in a hexagonal lattice. The lattice parameters are $a=5.020\pm0.002$ Å and $c=3.027\pm0.002$ Å for YCo_3B_2 and $a=5.066\pm0.003$ Å and $c=3.022\pm0.002$ Å for $GdCo_3B_2$. The good agreement between the X-ray diffraction intensities observed and calculated shows that the ternary borides, YCo_3B_2 and $GdCo_3B_2$, crystallize in the $CaZn_5$-type structure. The space group and atomic positions are as follows: P6/mmm (D_{6h}^1), 1R in 1(a), 3Co in 3(g), and 2B in 2(c). It can be seen from these results that the ternary borides, RCo_3B_2, have a superstructure in which two Co atoms in the 2(c) site of intermetallic compounds, RCo_5, with the $CaZn_5$-type structure are replaced by two B atoms. The B atoms in this structure are situated at the center of a trigonal prism formed by six Co atoms. The interatomic distances between B and the six Co atoms are 2.11—2.10 Å and are fairly constant, although the radii of the rare earth atoms are changed according to the lanthanide contraction. We have also found RCo_3B_2 compounds to be isostructural with YCo_3B_2 and $GdCo_3B_2$, where R= Ce, Sm, Tb, Dy, Ho, and Er. Efforts to prepare $LaCo_3B_2$, $PrCo_3B_2$, and $NdCo_3B_2$ by arc-melting were unsuccessful.

Only recently have ternary metal-boron compounds been reported.[1-9] The most interesting borides are the family of the borides with the $Cr_{23}C_6$-type structure, found when the works that led to the perovskite carbides and nitrides were extended to include boron. The composition of the ternary boride varies from system to system and can best be symbolized by the $T_{23-m}M_mB_6$ formula. Here, T represents one of the d-transition metals, cobalt or nickel, M is a nontransitional metal or, a IVth or Vth-group transition metal, and B is boron. Roughly, m ranges from 2 to 3.5. There also exist some other ternary phases, such as Mo_2CoB_2,[10] Mo_2FeB_2,[11] W_2CoB_2,[12] $MoFeB_4$,[13] $ThWB_4$,[14] and $Mo_2Fe_{13}B_5$.[14] However, there have been few investigations concerning any ternary rare earth borides except $YCrB_4$.[15]

Recently we reported[16,17] that, in the system of rare earth-cobalt-boron, there exist two ternary compounds, RCo_2B_2 and $RCo_{12}B_6$, with tetragonal and rhombohedral structures respectively, where R represents a rare earth atom. In the present paper, we will describe the preparation and the crystal structure of another ternary rare earth boride, RCo_3B_2, of a hexagonal $CaZn_5$-type[18] structure in systems of rare earth-cobalt-boron.

Experimental

Materials. The cobalt metal and the crystalline boron were obtained from Wako Pure Chemical Industries, Ltd., Tokyo. The purities were 99.99 and 99.9% respectively. All the rare earth metals[19] except samarium were prepared in our laboratory by the calcium-metal reduction of rare earth trifluorides. The samarium metal was prepared from samarium oxide by lanthanum-metal reduction. These metal rods were refined by arc-melting. The purity of the metals obtained by these methods was 99.8%. The main impurities were oxygen and carbon.

Preparation of Alloys. The alloys were prepared by co-melting mixtures of the rare earth metal, the cobalt metal, and crystalline boron in an arc furnace under an inert gas atmosphere. Each sample was remelted three times to prove its homogeneity. After melting, some of the alloy buttons were analysed by chemical methods; it was found that the rare earth metals lost during the melting process were negligible except for samarium. In the case of samarium, 10—15 wt% of the samarium metals were vaporized during the melting process.

In order to establish the thermal equilibrium, some of the alloy buttons were annealed at 1150°C for 96 hr in tantalum crucibles sealed into quartz tubes under a reduced pressure of purified argon.

The densities of the samples were determined at 24.5°C by the flotation technique using CCl_4.

X-Ray and Chemical Analytical Procedures. The samples

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1) H. H. Stadelmarer, *Z. Metallk.*, **52**, 758 (1961).

2) H. H. Stadelmarer and A. C. Fraker, *Metall.*, **16**, 212 (1962).

3) H. H. Stadelmarer and R. A. Gregg, *ibid.*, **16**, 407 (1962).

4) H. H. Stadelmarer, J. D. Schobel, and L. T. Jordon, *Metall.*, **16**, 752 (1962).

5) H. H. Stadelmarer and L. T. Jordon, *Z. Metallk.*, **53**, 719 (1962).

6) H. H. Stadelmarer and R. B. Fitts, *Metall.*, **16**, 773 (1962).

7) H. H. Stadelmarer, J. D. Schobel, and J. R. Sagmuller, *ibid.*, **18**, 23 (1964).

8) H. H. Stadelmarer and T. S. Yun, *Z. Metallk.*, **53**, 754 (1962).

9) H. H. Stadelmarer and F. M. Lee, *Metall.*, **18**, 111 (1964).

10) W. Rieger, H. Nowotony, and F. Benesovsky, *Mh. Chem.*, **97**, 378 (1966).

11) W. Rieger, H. Nowotony, and F. Benesovsky, *ibid.*, **95**, 1502 (1964).

12) W. Rieger, H. Nowotony, and F. Benesovsky, *ibid.*, **96**, 844 (1965).

13) H. Haschke, H. Nowotony, and F. Benesovsky, *ibid.*, **97**, 1461 (1966).

14) H. Haschke, H. Nowotony, and F. Benesovsky, *ibid.*, **97**, 1459 (1966).

15) Yu. B. Kuzma, *Soviet Physics-Crystallography.*, **15**, 312 (1970).

16) K. Niihara, T. Shishido, and S. Yajima, This Bulletin, **44**, 3214 (1971).

17) K. Niihara and S. Yajima, *Chem. Lett.*, **1972**, 875.

18) J. H. Wernick and S. Geller, *Acta Crystallogr.*, **12**, 662 (1959).

19) K. Niihara, K. Sasaki, and S. Konno, Tecknical Report, The Research Institute for Iron, Steel, and Other Metals, Tohoku University, **1**, 54 (1969).

for X-ray and chemical analyses were generally taken from the most homogeneous part of annealed specimens. They were crushed in an agate mortar under toluene in order to avoid unnecessary oxidation and then divided for X-ray and chemical analyses.

After the solution obtained by dissolving the samples into aqua regia was fumed with conc. $HClO_4$, the precipitates of RF_3 obtained by the addition of conc. HF were submitted to a gravimetrical determination of the rare earth content. The analyses of the Co metal were performed by means of X-ray fluorescence analysis. The boron content was determined by a method[20] previously reported.

All the X-ray powder patterns were taken with a Debye-Scherrer camera (114.6 mm in diameter) which corrected using standard silicon powder. Mn-filtered Fe ($K\alpha_1$=1.9360 Å, $K\alpha_2$=1.9399 Å, and $K\bar{\alpha}$=1.9373 Å) radiation was employed. The lattice parameters were determined by the Nelson-Riley extraporation method. The observed X-ray diffraction intensities were obtained by measuring the peak areas which were produced using a diffractometer in combination with an NaI(Tl) scintillation counter and a pulse-height analyser.

Results and Discussion

In investigating the phase equilibria in the system of Y–Co–B, a ternary compound was found by chemical and X-ray analyses. This compound was, at 1150°C, in equilibrium with YCo_2, YCo_5, and the ternary compounds YCo_2B_2[16] and $YCo_{12}B_6$.[17] The chemical analyses of the samples in the single-phase region showed that the new ternary compound existed in the region (at.%): Y(16.5—16.7), Co(50.0—50.4), and B(33.2—33.3). The stoichiometric composition of YCo_3B_2 was proposed on the basis of the results of X-ray and chemical analyses and density measurements. Ternary compounds with a similar composition were also prepared by the arc-melting method in the systems of (Ce, Sm, Gd, Tb, Dy, Ho, and Er)–Co–B. However, efforts to prepare $LaCo_3B_2$, $NdCo_3B_2$, and $PrCo_3B_2$ by arc-melting were unsuccessful.

Table 1. X-ray diffraction data for YCo_3B_2

hkl	d_{obs}(Å)	d_{cal}(Å)	I_{obs}	I_{cal}
100	4.346	4.347	5.6	5.9
001	3.029	3.027	6.0	5.7
110	2.509	2.510	4.3	6.2
101	2.484	2.484	89.4	90.8
200	2.174	2.174	100.1	96.7
111	1.934	1.932	45.2	53.9
201	1.766	1.766	10.6	10.2
210	—	1.643	0	1.1
002	1.514	1.514	8.6	11.1
300	—	1.449	0	1.0
211	1.445	1.444	42.0	30.9
102	—	1.429	0	0.7
301	1.307	1.307	15.6	16.2
112	1.297	1.296	2.3	1.7
220	1.255	1.255	19.8	21.2
202	1.244	1.242	42.2	35.7
310	—	1.206	0	0.8
221	—	1.159	0	1.7
311	1.121	1.120	26.5	23.5
212	1.112	1.113	1.0	1.4
400	1.088	1.087	15.7	19.4
302	1.046	1.047	1.5	2.3
401	1.024	1.023	5.2	4.8

B (the temperature factor)=0.64, R=0.122

Table 2. X-ray diffraction data for $GdCo_2B_2$

hkl	d_{obs}(Å)	d_{cal}(Å)	I_{obs}	I_{cal}
100	4.388	4.387	38.6	39.8
001	—	3.022	0	0
110	2.530	2.533	15.3	18.2
101	2.488	2.489	98.7	96.6
200	2.193	2.194	75.8	77.9
111	1.940	1.941	55.2	53.5
201	—	1.775	0	0.1
210	1.658	1.658	6.5	5.8
002	1.512	1.511	7.9	8.5
300	1.460	1.462	3.2	2.9
211	1.453	1.454	30.9	34.5
102	1.429	1.429	21.5	18.5
301	1.318	1.316	19.8	16.5
112	1.300	1.298	6.0	4.6
220	1.268	1.267	14.2	16.7
202	1.244	1.244	26.6	28.7
310	1.217	1.217	21.8	14.2
221	—	1.168	0	0.1
311	1.129	1.129	24.0	25.9
212	1.117	1.117	5.0	6.5
400	1.097	1.097	17.4	15.4
302	1.052	1.051	8.1	5.9
401	—	1.031	0	0
320	1.007	1.007	7.3	5.8
003		1.007		0
103	0.983	0.982	35.2	38.3

B (the temperature factor)=0.87, R=0.130

The Crystal Structure of YCo_3B_2 and $GdCo_3B_2$. The X-ray powder pattern for YCo_3B_2 was indexed on the basis of a hexagonal unit cell. The *d*-values are shown in Table 1. As is shown in this table, the observed *d*-values are in good agreement with those calculated. The lattice parameters for YCo_3B_2 were $a=5.020\pm0.002$ Å, $c=3.027\pm0.002$ Å, and $c/a=0.603$. The calculated and measured densities were 4.35 g/cm³ and 4.29 g/cm³ respectively. Therefore, the unit cell contains one formula unit of YCo_3B_2.

The crystal structure of the YCo_3B_2 compound was considered to be of a type similar to that of the intermetallic compound $CaZn_5$,[18] because the X-ray diffraction pattern of YCo_3B_2 appeared to be similar. $CaZn_5$ has the following atomic positions, according to the International Table for X-ray Crystallography:[21] space group P6/mmm (D_{6h}^1), 1Ca in 1(a), 3Zn in 3(g), and 2Zn in 2(c). Therefore, it was assumed that the Y, Co, and B atoms of YCo_3B_2 occupy the following positions: 1Y in 1(a), 3Co in 3(g), and 2B in 2(c). The X-ray diffraction intensities were calculated according to the formula;

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[20] K. Niihara, This Bulletin, **44**, 963 (1971).

[21] International Tables for X-ray Crystallography., Vol. 1, p. 298. The Kynoch Press, Birmingham, England 1968.

TABLE 3. CRYSTALLOGRAPHIC DATA FOR YCo_3B_2 AND $GdCo_3B_2$ COMPOUNDS.

	YCo_3B_2	$GdCo_3B_2$
Symmetry	Hexagonal	Hexagonal
Lattice	$a=5.020+0.002$	$a=5.066+0.003$
parameters	$c=3.027+0.002$	$c=3.022+0.002$
(Å)	$c/a=0.603$	$c/a=0.597$
Molecules per unit cell	1	1
Density	$\rho_{obsd}=4.29$	$\rho_{obsd}=5.25$
(g/cm³)	$\rho_{calcd}=4.35$	$\rho_{calcd}=5.30$
Space group	$P6/mmm(D^1_{6h})$	$P6/mmm(D^1_{6h})$
Atom position	1Y in 1(a) (0,0,0)	1Gd in 1(a) (0,0,0)
	3Co in 3(g) $(\frac{1}{2}0\frac{1}{2})$ $(0\frac{1}{2}\frac{1}{2})$ $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$	3Co in 3(g) $(\frac{1}{2}0\frac{1}{2})$ $(0\frac{1}{2}\frac{1}{2})$ $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$
	2B in 2(c) $(\frac{1}{3}\frac{2}{3}0)$ $(\frac{1}{3}\frac{2}{3}0)$	2B in 2(c) $(\frac{1}{3}\frac{2}{3}0)$ $(\frac{2}{3}\frac{1}{3}0)$
Interatomic	6Co–B=2.10	6Co–B=2.10
distance in	3Y–B=2.90	3Gd–B=2.93
coordination	4Co–Co=2.51	4Co–Co=2.53
polyhedron of B.	2Co–Co=3.03	2Co–Co=3.02
(Å)		

$$\mathbf{I}_{cal} = A\cdot|\mathbf{F}|^2\cdot M\cdot Lp\cdot\theta$$

in which A, $\mathbf{F}$, Lp, M, and θ represent the scaling factor, the structure factor, the multiplicity, the Lorentz polarization factor, and the overall temperature factor respectively. In the structure-factor calculation, the atomic scattering factor for the neutral atoms listed in the International Table for X-ray Crystallography and the anomalous dispersion corrections for the Y and Co atoms of Cromer[22] were employed.

In this structure, the positions of all the atoms are fixed by symmetry. Thus, the only variable parameter is the temperature factor.

The temperature factors were found by a least-squares solution of the plot of log $|I_c/I_0|$ $vs.(\sin/\lambda)^2$. Using an overall temperature factor of 0.64, the calculated and observed X-ray diffraction intensities obtained for YCo_3B_2 are given in Table 1. The reliability factor, $R=\sum_{hkl}|I_{cal}-I_{obs}|/\sum_{hkl}I_{obs}$, amounts to 0.122 for this structure. From this result, it can be considered that the Y and Co atoms occupy the 1(a) and 3(g) sites respectively. However, from only the value of the R-factor it cannot be evaluated accurately whether or not the assumption concerning the positions of the B atoms is reasonable because of the small atomic scattering factor of the B atoms. It is impossible, however, that B atoms occupy the 2(d) and 2(e) sites in the P6/mmm space group, considering the atomic sizes of Y, Co, and B, and the coordination of the B atoms. Generally, B atoms of metal-rich borides, such as Re_3B, Pd_3B, Cr_5B_3, and Pd_5B_3,[23] are surrounded by nine metal atoms, situated at the six corners of a trigonal prism and outside the three lateral faces of this prism. Thus, with these simple geometrical arguments it is reasonable to think that the B atoms in YCo_3B_2 occupy the 2(c) site. In the ternary system of Gd–Co–B, a ternary boride $GdCo_3B_2$ with the $CaZn_5$-type structure was synthesized by arc-melting. The lattice parameters and densities are shown in Table 3. In order to calculate the X-ray diffraction intensities for $GdCo_3B_2$, it was assumed that the crystal structure of this compound was the same as that of YCo_3B_2. The final results are compared with the observed intensities in Table 2, using a temperature factor of 0.87. The

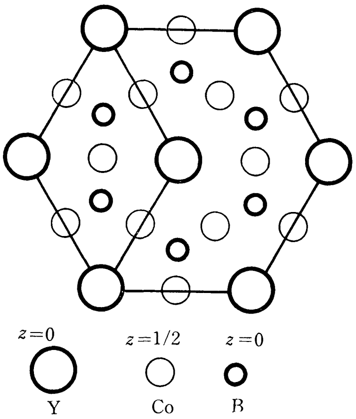

Fig. 1. The projection of YCo_3B_2 structure on (001).

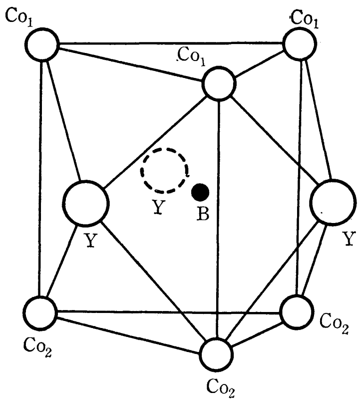

Fig. 2. The coordination polyhedron of boron atom in YCo_3B_2 structure.

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[22] D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

[23] B. Aronsson, "Borides, Silicides and Phosphides," Edited by B. Aronsson, Methuen and Co. Ltd., London (1965), p. 46.

Table 4. The X-ray diffraction data for $CeCo_3B_2$, $SmCo_3B_2$, $TbCo_3B_2$, $DyCo_3B_2$, $HoCo_3B_2$, and $ErCo_3B_2$

hkl	Int	$CeCo_3B_2$		$SmCo_3B_2$		$TbCo_3B_2$		$DyCo_3B_2$		$HoCo_3B_2$		$ErCo_3B_2$	
		d_{obsd}	d_{cald}	d_{obsd}	d_{cald}	d_{obsd}	d_{cald}	d_{obsd}	d_{cald}	d_{obsd}	d_{cald}	d_{obsd}	d_{cald}
100	m	4.376	4.380	4.398	4.398	4.377	4.373	4.359	4.357	4.344	4.346	4.332	4.335
001	vvw	—	3.040	3.029	3.031	—	3.009	—	3.021	—	3.023	—	3.024
110	m	2.528	2.529	2.536	2.539	2.523	2.525	2.514	2.516	2.506	2.509	2.503	2.503
101	s	2.497	2.497	2.495	2.496	2.476	2.479	2.480	2.483	2.483	2.482	2.482	2.480
200	vs	2.189	2.190	2.200	2.199	2.187	2.187	2.178	2.178	2.174	2.173	2.168	2.168
111	s	1.943	1.944	1.945	1.947	1.933	1.934	1.932	1.933	1.930	1.931	1.927	1.928
201	m	1.777	1.777	1.783	1.780	1.768	1.769	1.765	1.767	—	1.764	—	1.762
210	vvw	1.654	1.656	1.663	1.662	1.652	1.653	1.647	1.647	1.640	1.643	1.638	1.639
002	m	1.520	1.520	1.514	1.516	1.504	1.503	1.511	1.511	1.513	1.512	1.512	1.512
211	s	1.454	1.454	1.459	1.458	1.450	1.449	1.447	1.446	1.445	1.443	1.441	1.441
102	vw	—	1.436	1.433	1.433	1.422	1.423	1.425	1.427	—	1.428	—	1.428
301	m	1.317	1.316	1.318	1.320	1.312	1.312	1.310	1.309	1.307	1.306	1.304	1.304
112	w	—	1.303	1.302	1.301	1.291	1.292	1.295	1.295	1.294	1.295	—	1.294
220	m	1.266	1.265	1.270	1.270	1.262	1.263	1.259	1.258	1.255	1.255	1.252	1.252
202	s	1.249	1.249	1.250	1.248	1.239	1.239	1.241	1.241	1.242	1.241	1.240	1.240
310	vw	—	1.215	1.220	1.220	1.213	1.213	1.211	1.208	1.204	1.205	—	1.156
221	vvw	—	1.168	—	1.171	—	1.164	—	1.161	—	1.159	1.202	1.202
311	m	1.129	1.128	1.134	1.132	1.125	1.125	1.123	1.122	1.120	1.120	1.118	1.117
212	w	—	1.120	1.122	1.120	1.113	1.113	1.111	1.113	1.113	1.112	—	1.111
400	m	1.095	1.095	1.100	1.100	1.093	1.093	1.089	1.089	1.086	1.086	1.084	1.084
302	vw	—	1.053	1.053	1.054	1.047	1.047	1.047	1.047	1.046	1.046	1.044	1.045

reliability factor, R, is 0.130. The crystallographic data for YCo_3B_2 and $GdCo_3B_2$ are summarized in Table 3. Figure 1 indicates the projection of the YCo_3B_2 structure on the (001) plane. The coordination polyhedron of the B atoms was formed by the combination of a trigonal prism and three rectangular pyramids on its lateral faces. In other words, the boron atom is surrounded by six Co atoms and three Y atoms, situated at the corners of a trigonal prism and outside the lateral faces of the prism respectively. Figure 2 shows the polyhedron of the B atom in the 2(c) site of the YCo_3B_2 structure. The ternary boride YCo_3B_2 has a superstructure in which two Co atoms in the 2(c) site of the intermetallic compound YCo_5[24] with the $CaZn_5$-type structure are replaced by two B atoms.

The interatomic distances between the B and the six nearest Co stoms are 2.10 Å for both YCo_3B_2 and $GdCo_3B_2$. This distance is closer to the sum of the Goldschmidt metallic radii[23] for the 12-coordination of B (0.88 Å) and Co (1.16 Å) than to the sum of the Pauling metallic radii[25] for the 12-coordination of B (0.98 Å) and Co (1.25 Å). The distances between the B atom and three rare earth atoms in the next-nearest neighbor are 2.90 and 2.93 Å for YCo_3B_2 and $GdCo_3B_2$ respectively.

The Structure of Ternary Rare Earth Borides, RCo_3B_2 (R=Ce, Sm, Tb, Dy, Ho, and Er). The crystal structure of RCo_3B_2 compounds (R=Ce, Sm, Tb, Dy, Ho, and Er) is isostructural with YCo_3B_2 and $GdCo_3B_2$. The powder X-ray data are shown in Table 4 for $CeCo_3B_2$, $SmCo_3B_2$, $TbCo_3B_2$, $DyCo_3B_2$, $HoCo_3B_2$, and $ErCo_3B_2$. As is shown in this Table, there is a good agreement between the observed and calculated interplanar spacings. The lattice parameters of RCo_3B_2 compounds are summarized in Table 5. The change in the a parameter against the atomic number of the rare earth elements plotted in Fig. 3 is characteristic of the well-known lanthanide contraction. The c para-

Table 5. The lattice parameters for RCo_3B_2 compounds (R=Y, Ce, Sm, Gd, Tb, Dy, Ho, Er)

R	Lattice parameters (Å)		Density (g/cm³)	
	a	c	ρ_{obsd}	ρ_{cald}
Y	5.020±0.002	3.027±0.002	4.29	4.35
Ce	5.058±0.002	3.040±0.002	4.96	5.03
Sm	5.079±0.003	3.031±0.002	5.20	5.28
Gd	5.066±0.003	3.022±0.002	5.25	5.30
Tb	5.050±0.003	3.009±0.002	5.32	5.38
Dy	5.031±0.003	3.021±0.002	5.45	5.45
Ho	5.018±0.003	3.023±0.002	5.50	5.51
Er	5.006±0.003	3.024±0.002	5.57	5.57

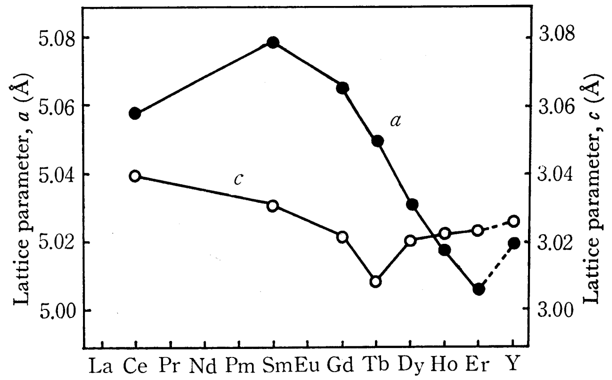

Fig. 3. The lattice parameters of the hexagonal RCo_3B_2 compounds as a function of atomic number of rare earth elements. ○: the c parameter, ●: the a parameter.

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[24] J. Schweizer and F. Tasset, *Mat. Res. Bull.*, **4**, 369 (1969).

[25] L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, (1960), Chap. 11.

meter is fairly constant, increasing slightly with the atomic number of the rare earth element from the $TbCo_3B_2$ compound onwards.

The parameters of the $CeCo_3B_2$ compound are an exception. They are similar to those of the compound at the second series of lanthanides. It may be seen that the Ce atom has a relatively small radius in this structure. Various authors[26–28] have attributed this contraction of the Ce atom to the loss of the 4f electron to the compound's conduction band.

A similar variation in the *c* parameter has been observed in the case of RCo_5,[29] which has the $CaZn_5$-type structure. The *c* parameters of the RCo_3B_2 compounds do not indicate the lanthanide contraction, probably because of: (a) the effect of the nonstoichiometric composition in RCo_3B_2 compounds and (b) the fairly constant interatomic distances between the B and Co atoms in the trigonal prism. With reference to (b), the interatomic distances, B–6Co, in the trigonal prism of RCo_3B_2 (Fig. 2) are 2.11—2.10 Å and are fairly constant, although one rare earth is replaced by another small rare earth. Figure 4 shows the variation in the interatomic distances in the coordination polyhedron of the B atom in the RCo_3B_2 structure (Fig. 2) against the atomic number of the rare earth elements and the variation in the corresponding distances of RCo_5 compounds. As is shown in Fig. 4, the interatomic distances of B–3R, Co_1–Co_1, and R–4Co indicate an acceptable lanthanide contraction. The Co_1–Co_2 distance has its minimum at $TbCo_3B_2$. From these results, it may be seen that, in the compounds at the end of the second rare earth series, the Co_1–Co_1 distance decreases and the Co_1–Co_2 distance increases in order to preserve the stable Co–B interatomic distance (2.11—2.10) in the trigonal prism of the RCo_3B_2 structure, when one rare earth element is replaced by other small rare earth elements.

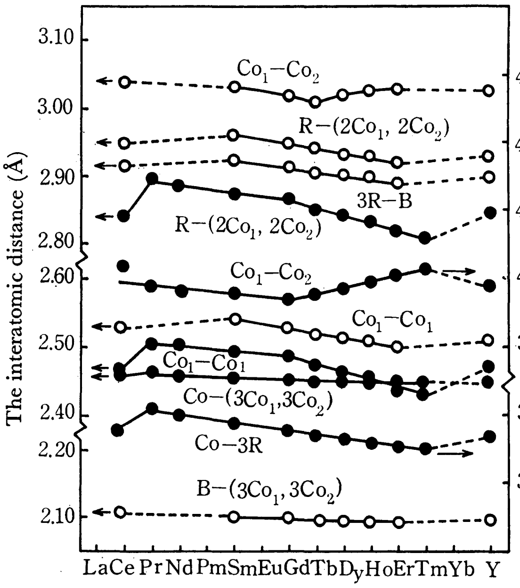

Fig. 4. The interatomic distances in the coorinatidon polyhedron of B and Co atoms situated at the 2(c) sites of RCo_3B_2 and RCo_5 structure, respectively (Ref. Fig. 2).
○: RCo_3B_2; ●: RCo_5.

Similar phenomena were observed in the RCo_5 compounds,[29] as is shown in Fig. 4. The nonstoichiometric and magnetic properties of these borides will provide additional data which may be useful in the interpretation of the nature of bonding. These data will be the subject of a separate paper.

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