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The Crystal Data of Ternary Rare Earth Borides, RCo_2B_2

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Compounds with the composition of RCo_2B_2 (R=La, Nd, Sm, Gd, Tb, Dy, and Y) were prepared by arc-melting methods. Their crystal structure was investigated by means of X-ray diffraction. These ternary rare earth borides crystallize in the tetragonal lattice. The lattice parameters are $a=3.616\pm0.003$ Å and $c=10.215\pm0.005$ Å for $LaCo_2B_2$ and $a=3.561\pm0.002$ Å and $c=9.358\pm0.005$ Å for YCo_2B_2. The good agreement between the X-ray diffraction intensities observed and those calculated shows that the ternary borides, $LaCo_2B_2$ and YCo_2B_2, crystallize in the $ThCr_2Si_2$-type structure. The crystallographic data obtained for $LaCo_2B_2$ and YCo_2B_2 are as follows: space group I4/mmm(D_{4h}^{17}); 2R in 2(a), 4Co in 4(d), and 4B in 4(e) with $z\sim3/8$. The boron atoms in this structure are situated at the center of a trigonal prism formed by four rare earth atoms and two cobalt atoms. We also found the RCo_2B_2 compounds to be isostructural with $LaCo_2B_2$ and YCo_2B_2, where R=Nd, Sm, Gd, Tb, and Dy. However, efforts to prepare $CeCo_2B_2$ and $ErCo_2B_2$ by arc-melting were unsuccessful.

In the binary systems of rare earth–cobalt and cobalt–boron, there exist a series of intermetallic compounds, (R_3Co, R_3Co_2, RCo, R_2Co_3, RCo_2, RCo_3, RCo_5, R_2Co_7, R_2Co_{17}, Co_3B, Co_2B, and CoB), many of which possess interesting magnetic properties.1—3) On the other hand, there are five compounds in the rare earth-boron system,4) (RB_2, RB_4, RB_6, RB_{12}, and RB_{66}), which are interesting for their possible electric and high-temperature uses. Taking into consideration the properties of these binary compounds, the ternary system of the rare earth–cobalt–boron combination seems quite interesting. Unfortunately, there have been few investigations concerning this ternary system.

While investigating the phase equilibria in the Y–Co–B system, we found a new ternary compound with a composition close to YCo_2B_2.5) The purpose of the present investigation is to prepare the ternary rare earth borides, RCo_2B_2 (R=rare earth elements), and to determine their crystal structures.

Experimental

Materials. All the rare earth metals6) 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. The purity of the metals obtained by these methods was 99.5%. Cobalt and crystalline boron were obtained from Wako Pure Chemical Industries, Ltd., Tokyo. The purities were 99.99% and 99.9% respectively.

Preparation of Samples. The ternary samples were synthesized by arc-melting mixtures of rare earth metal, cobalt, and boron in the atomic ratio of 1 : 2 : 2. Argon was used as a protective atmosphere in the arc-melting furnace, and the small amount of residual oxygen was eliminated prior to melting by fusing a button of titanium. The samples, weighing approximately 10 g, were melted three times to insure homogeneity. The fused samples were then wrapped with tantalum foil, sealed in quartz capsules under a vacuum, and annealed for 150 hr at 800°C. The samples were then pulverized in an agate motar under an inert gas atmosphere to prevent oxidation and examined by chemical and X-ray analyses. The chemical analyses for the content of rare earth metals and boron were preformed by a method previously reported.7) The cobalt content was determined by X-ray fluorescence analysis. The losses of the rare earth metals, cobalt, and boron during the melting process were negligible for the ternary systems of (La, Nd, Gd, Tb, Dy, and Y)-Co-B. In the case of the Sm-Co-B system, though 10—15 wt% of the Sm metal vaporized during the melting process. Therefore, mixtures containing an excess of the Sm metal were melted by means of an arc-furnace.

The density of the samples was determined at 20.5°C by a floatation technique, using CCl_4.

X-Ray Diffraction Measurements. The X-ray diffraction patterns of the samples were taken with a Debye-Scherrer camera 114.6 mm in diameter. The correction of the diameter of the Debye-Scherrer camera was performed 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 extrapolating the lattice parameters for $\cos^2\theta$ up to $\theta=90°$. The relative intensities were obtained by measuring the counts under the peaks which were produced using a diffractometer conbined with a scintillation counter and a pulse-height analyser. The scanning speed of the diffractometer was one-fourth degree (2θ) per minute.

Results and Discussion

A new compound was prepared by the arc-melting method in the ternary system of Y–Co–B. This compound was in equilibrium with YCo_2, YB_2, YCo_3B_2,7) and $YCo_4B_4$8) at 800°C. It was found by chemical analyses that the samples in the single-phase region had compositions of 17.3—20.7 at% Y, 40.3—41.5at%

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8) This compound has a composition close to YCo_4B_4 and crystallizes in a tetragonal lattice. The lattice parameters are $a=5.07$ Å and $c=7.13$ Å, respectively.

Co, and 39.6—42.3 at% B. The stoichiometric composition of YCo_2B_2 was proposed on the basis of the results of X-ray and chemical analyses and the density measurements. The ternary compounds with the same composition were also prepared for La, Nd, Sm, Gd, Tb, and Dy.

Y was used as a crystal chemical stand-in for heavy rare earths since its atomic radius is located between those of Tb and Dy.[9] It may be assumed that the ternary compounds (RCo_2B_2) of the lanthanides will be structurally similar if $LaCo_2B_2$ and YCo_2B_2 are found to be isostructural. Therefore, particular emphasis in this experiment was placed on the investigation of the La–Co–B and Y–Co–B systems.

The Crystal Structures of $LaCo_2B_2$ and YCo_2B_2. The X-ray diffraction patterns of both ternary borides, $LaCo_2B_2$ and YCo_2B_2, could be indexed on the basis of the tetragonal lattices. The lattice parameters were $a=3.616\pm0.003$ Å and $c=10.215\pm0.005$ Å for $LaCo_2B_2$, and $a=3.561\pm0.002$ Å and $c=9.358\pm0.005$ Å for YCo_2B_2. The agreement between the observed and calculated d-values is excellent, as is shown in Tables 1 and 2. The unit-cell content is $2RCo_2B_2$, and the densities observed are in good agreement with those calculated, as is shown in Table 3.

TABLE 1. X-RAY DIFFRACTION DATA FOR $LaCo_2B_2$

hkl	d_{obsd}(Å)	d_{calcd}(Å)	I_{obsd}	I_{calcd}
002	5.11	5.11	13.8	16.9
101	3.410	3.409	53.7	43.0
110 004	2.555	2.557 2.554	45.0	8.6 29.4
103	2.478	2.479	26.4	26.4
112	2.285	2.286	102.6	98.8
200 114	1.808	1.808 1.807	27.9	25.1 6.9
105	1.775	1.779	6.5	9.5
202 006	1.703	1.704 1.703	2.0	3.2 0.7
211	1.598	1.597	8.0	7.8
204	1.475	1.476	22.5	18.9
213	1.460	1.461	5.8	10.0
116	1.417	1.417	22.5	21.1
107	1.353	1.353	1.0	2.1
220 008	1.277	1.278 1.277	6.6	4.2 4.3
215	1.269	1.268	10.5	6.9
222	n. obs.	1.240	0	1.9
206	n. obs.	1.240	0	1.9
301	1.200	1.197	1.5	2.4
310 224	1.144	1.144 1.143	16.2	1.4 12.4
118	1.141	1.142	1.3	1.3
303	1.135	1.136	5.0	3.7
312	1.116	1.116	30.5	29.7
217 109	1.084	1.083 1.083	5.6	5.9 2.9
314 208	1.043	1.044 1.043	28.2	5.9 21.7
305	1.039	1.043	5.3	5.2
226	1.022	1.022	2.4	2.6

$B=0.85$, $R=0.148$

TABLE 2. X-RAY DIFFRACTION DATA FOR YCo_2B_2

hkl	d_{obsd}(Å)	d_{calcd}(Å)	I_{obsd}	I_{calcd}
002	4.678	4.679	5.5	4.3
101	3.319	3.328	43.2	47.4
110	n. obs.	2.518	0	0.1
103 004	2.344	2.346 2.340	63.6	24.2 29.0
112	2.215	2.217	93.8	95.1
200	1.781	1.781	23.4	25.7
114	n. obs.	1.714	0	1.1
202	n. obs.	1.664	0	0.3
105	1.656	1.657	9.3	8.8
211	1.570	1.570	4.3	6.9
006	n. obs.	1.560	0	0.1
213 204	1.418	1.418 1.417	25.1	11.0 18.5
116	1.326	1.326	24.6	18.1
220	1.258	1.259	5.3	9.5
107	1.251	1.252	3.4	2.8
222	n. obs.	1.216	0	0.1
215	1.213	1.213	6.4	8.5
301	1.177	1.178	4.2	2.8
206	n. obs.	1.173	0	0.1
008	1.169	1.170	6.2	4.4
310	n. obs.	1.126	0	0.0
303 224	1.109	1.109 1.109	25.6	4.6 17.2
312	1.094	1.095	15.4	35.3
118	n. obs.	1.061	0	0.2
217	1.025	1.024	8.1	8.4
314	n. obs.	1.015	0	1.0
305	1.002	1.002	10.5	8.2
109	0.997	0.998	4.2	5.8
312	0.982	0.982	17.5	16.5
226	n. obs.	0.980	0	0.3
208	0.978	0.978	64.5	66.4

$B=0.74$, $R=0.142$

It may be seen from Tables 1 and 2 that there is systematic absence of reflections when $h+k+l=2n+1$. Therefore, the possible space groups are 14, $1\bar{4}$, 14/m, 1422, 14 mm, 14 m2, and 14/mmm. The structures of $LaCo_2B_2$ and YCo_2B_2 were considered to be similar to that of $ThCr_2Si_2$ because the lattice parameters and X-ray diffraction intensities of these three compound appeared to be similar to one another. The structure of $ThCr_2Si_2$[10–13] belongs to the $BaAl_4$ type, whereby the two nonequivalent sites of aluminium are occupied by crominum and silicon. The X-ray diffraction intensities were calculated on the assumption, by analogy with the $ThCr_2Si_2$ structure, that the atomic

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configurations of $LaCo_2B_2$ and YCo_2B_2 are as follows: space group 14/mmm (D_{4h}^{17}), 2R in 2(a), 4Co in 4(d), and 4B in 4(e). In this structure, the positions of the rare-earth and cobalt atoms are fixed by symmetry and the only variable parameter is z, which defines the positions of the boron atoms. The value of the z-parameter was assumed to be 3/8 from the geometrical argument for $LaCo_2B_2$ and YCo_2B_2.

The calculated intensities were derived from:

$$\mathbf{I}(\mathrm{cal})\alpha p\frac{1+\cos^2 2\theta}{\sin^2\theta\cdot\cos}|\mathbf{F}|^2$$

where p is the multiplicity, θ is the Bragg diffraction angle, and **F** is a structure factor. The structure factors were calculated from the atomic coordinates (x_n, y_n, z_n) and the total atomic scattering factors, f_n:

$$\mathbf{F}=\sum_n f_n \exp 2\pi i(hx_n+ky_n+lz_n)$$

$$f_n=f_0+\Delta f_n'+i\Delta f_n''$$

where f_0 is the atomic scattering factor for radiation with a frequency much higher than any absorption edge, and where $\Delta f_n'$ and $\Delta f_n''$ are the real and imaginary dispersion corrections respectively. The respective values of $\Delta f_n'$ for Y, La, Co, and B were −0.56, −7.09, −1.74, and 0, while those of $\Delta f_n''$ were 3.08, 12.45, 0.84, and 0.[14] The correction of the absorption by the sample was not employed because the absorption does not depend on the diffraction angle in the case of the diffractometer. The temperature factor was found by a least-squares solution of the plot of log $|\mathbf{I}_{cal}/\mathbf{I}_{ob}|$ *vs* $(\sin\theta/\lambda)^2$.

In the calculation of the X-ray diffraction intensities for YCo_2B_2[5] previously reported, we did not employ any corrections for the abnormal dispersion in the structure factor or for the temperature dependence. Therefore, the calculation in present paper is more accurate.

The observed and calculated intensities of $LaCo_2B_2$ and YCo_2B_2 are summarized in Tables 1 and 2. The temperature factors for $LaCo_2B_2$ and YCo_2B_2 were 0.85 and 0.74 respectively. The reliability factor, $R=\sum_{hkl}|I_{obs}-I_{cal}|/\sum_{hkl}I_{obs}$, is 0.148 and 0.142 for $LaCo_2B_2$ and YCo_2B_2 respectively.

From these results, it can be considered that the rare earth and cobalt atoms occupy the 2(a) and 4(d) sites respectively. The variable parameter, z, however, could not be evaluated with sufficient accuracy because of the small atomic scattering factor of the boron atoms. In general, the boron atoms of the binary borides,[15] such as Re_3B, Pd_3B, Cr_5B_3, and Pd_5B_3, are situated at the center of the trigonal prism formed by six metal atoms. In the ternary borides,[16] such as Mo_2CoB_2, Mo_2NiB_2, W_2FeB_2, W_2CoB_2, and W_2NiB_2, with U_3Si_2-type structure, the boron atoms are also situated at the center of the trigonal prism formed by two kinds of metals. On the other hand, it is impossible to consider that the boron atoms occupy the 4(c) site in the 14/mmm space group with respect to the atomic sizes of rare earth, cobalt, and boron, and the coordination of the boron atoms.

Thus, from these geometrical arguments it is reasonable to think that the boron atoms in $LaCo_2B_2$ and YCo_2B_2 occupy the 4(e) site and that the z-parameter is about 3/8. The crystallographic data for $LaCo_2B_2$ and YCo_2B_2 are summarized in Table 3.

TABLE 3. CRYSTALLOGRAPHIC DATA FOR $LaCo_2B_2$ AND YCo_2B_2

	$LaCo_2B_2$	YCo_2B_2
Symmetry	Tetragonal	Tetragonal
Lattice parameter (Å)	$a=3.616\pm0.003$ $c=10.215\pm0.005$ $c/a=2.825$	$a=3.561\pm0.003$ $c=9.358\pm0.005$ $c/a=2.628$
Molecule per unit cell	2	2
Density (g/cm³)	$\rho_{obsd}=6.88$ $\rho_{calcd}=6.92$	$\rho_{obsd}=6.30$ $\rho_{calcd}=6.39$
Space group	14/mmm(D_{4h}^{17})	14/mmm(D_{4h}^{17})
Atom position	$\left(0,0,0;\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)+$ 2La in 2(a) (0, 0, 0) 4Co in 4(d) $\left(0,\frac{1}{2},\frac{1}{4}\right)$ $\left(\frac{1}{2},0,\frac{1}{4}\right)$ 4B in 4(e) $(0,0,z)$ $(0,0,\bar{z})$ $z\sim3/8$	$\left(0,0,0;\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)+$ 2Y in 2(a) (0, 0, 0) 2Co in 4(d) $\left(0,\frac{1}{2},\frac{1}{4}\right)$ $\left(\frac{1}{2},0,\frac{1}{4}\right)$ 4B in 4(e) $(0,0,z)$ $(0,0,\bar{z})$ $z\sim3/8$
Interatomic distances (Å)	La–Co=3.13 La–B=2.86 Co–B=2.21 B–B=2.55	Y–Co=2.94 Y–B=2.78 Co–B=2.13 B–B=2.34

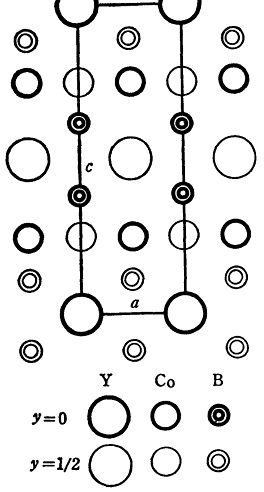

Fig. 1. The projection of RCo_2B_2 structure on (010).

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Table 4. X-Ray diffraction data for $NdCo_2B_2$, $SmCo_2B_2$, $GdCo_2B_2$, $TbCo_2B_2$, and $DyCo_2B_2$

hkl	Int.	$NdCo_2B_2$		$SmCo_2B_2$		$GdCo_2B_2$		$TbCo_2B_2$		$DyCo_2B_2$	
		d_{obsd}	d_{calcd}	d_{obsd}	d_{calcd}	d_{obsd}	d_{calcd}	d_{obsd}	d_{calcd}	d_{obsd}	d_{calcd}
002	m	4.865	4.837	4.823	4.815	4.718	4.769	—	4.710	—	4.667
101	s	3.342	3.351	3.340	3.340	3.347	3.346	3.326	3.328	3.320	3.317
110	w	2.518	2.523	—	2.519	2.520	2.526	—	2.515	2.506	2.509
004	s	2.437	2.437	2.410	2.408	2.386	2.385	2.355	2.355	2.340	2.339
103	m	2.403	2.402	2.386	2.385	2.375	2.376		2.354		2.342
112	vs	2.243	2.241	2.232	2.232	2.233	2.233	2.219	2.219	2.210	2.210
200	m	1.786	1.784	1.782	1.782	1.784	1.787	1.777	1.779	1.774	1.773
105	w	1.710	1.711	1.695	1.694	1.684	1.683	1.663	1.665	1.652	1.655
211	w	1.574	1.575	1.572	1.572	1.575	1.576	1.568	1.569	1.563	1.564
204	m	1.439	1.440	1.431	1.432	1.427	1.430	1.418	1.419	1.415	1.413
213	w	1.432	1.432	1.429	1.427		1.428		1.419		1.414
116	m	1.366	1.366	1.353	1.354	1.345	1.346	1.334	1.322	1.323	1.324
107	vvw	1.299	1.297	1.257	1.260	1.271	1.273	1.258	1.259	1.249	1.251
220	vw	1.252	1.262		1.253	1.262	1.263		1.258	1.254	1.254
215	vvw	1.233	1.235	1.227	1.228	1.224	1.225	1.215	1.215	1.212	1.210
222	vw	1.220	1.221	1.221	1.219		1.221		1.215		1.211
008	vw		1.218	1.203	1.204	1.191	1.193	1.177	1.177	1.169	1.169
301	vvw	1.181	1.181	1.179	1.179	1.182	1.182		1.176	1.173	1.173
310	vvw	1.126	1.128	—	1.127	—	1.130	1.126	1.125	1.121	1.121
224	m	1.121	1.120	1.116	1.116	1.116	1.116	1.109	1.109	1.105	1.105
303	w	1.117	1.117	1.113	1.114		1.115		1.109		1.105
312	m	1.101	1.099	1.096	1.097	1.099	1.100	1.094	1.094	1.090	1.090
217	w	1.050	1.049	1.044	1.041	1.037	1.037	1.029	1.027	1.021	1.022

Table 5. Lattice parameters of tetragonal RCo_2B_2

R	Lattice parameters (Å)		Density (g/cm³)	
	a	*c*	ρ_{obsd}	ρ_{calcd}
La	3.616±0.003	10.215±0.005	6.88	6.92
Nd	3.586±0.005	9.747±0.007	7.49	7.52
Sm	3.563±0.003	9.630±0.007	7.70	7.83
Gd	3.573±0.003	9.540±0.005	8.02	8.09
Tb	3.557±0.004	9.419±0.007	8.25	8.31
Dy	3.546±0.004	9.354±0.006	8.50	8.53
Y	3.561±0.003	9.358±0.005	6.30	6.39

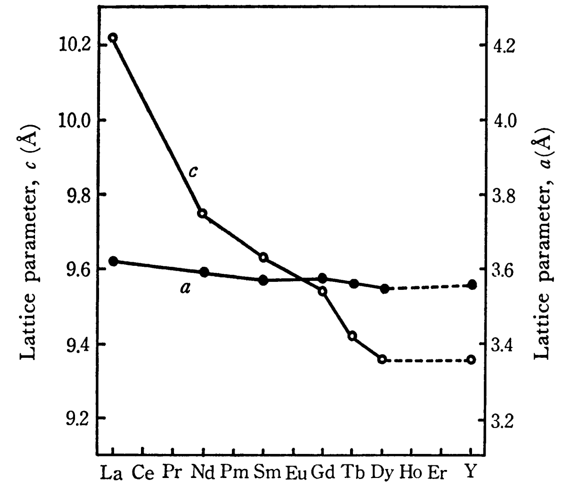

Fig. 2. The variation of the lattice parameters for RCo_2B_2 with the atomic number.
The open circles: the *c* parameter, The closed circles: the *a* parameter.

Figure 1 shows the projection of the RCo_2B_2 structure on the (010) plane. As is shown in Fig. 1, each boron atom is situated at the center of a trigonal prism formed by the four rare earth atoms and the two cobalt atoms. The interatomic distances of 4R–B and 2Co–B in the trigonal prism are 2.86 and 2.21 for $LaCo_2B_2$, and 2.78 and 2.13 for YCo_2B_2. These values are close to the sum of the corresponding Pauling metallic radii for the 12-coordination of La(1.87 Å), Y(1.78 Å), Co(1.25 Å), and B(0.98 Å).

The X-Ray Diffraction Data for RCo_2B_2 (R=Nd, Sm, Gd, Tb, and Dy). The RCo_2B_2 compounds were found to be crystallized isostructurally with $LaCo_2B_2$ and YCo_2B_2, since the X-ray diffraction data of these samples were similar to those of $LaCo_2B_2$ and YCo_2B_2. The X-ray diffraction data are shown in Table 4 for $NdCo_2B_2$, $SmCo_2B_2$, $GdCo_2B_2$, $TbCo_2B_2$, and $DyCo_2B_2$. As is shown in this table, there is a good agreement between the observed and calculated *d*-spacings. Efforts to prepare $CeCo_2B_2$ and $ErCo_2B_2$ by arc-melting were unsuccessful. The failure to obtain these compounds may be caused by a decomposition process occurring during the arc-melting.

The lattice parameters of the RCo_2B_2 compounds obtained in this study are summarized in Table 5, while their variation with the atomic number is plotted in Fig. 2. The contraction in the *c* parameter against the atomic number of the rare earth elements is approximately 10 percent, about the same as that of the rare-earth metals. On the other hand, the *a* parameter is fairly constant, decreasing only slightly with the atomic number of the rare earth elements,