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A New Ternary Compound in Rare Earth-Cobalt-Boron System

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A new ternary boride $RCo_{12}B_6$ with a rhombohedral structure was synthesized by arc-melting in R-Co-B system, where R is a rare earth ion. From magnetic measurements, it was found that $CeCo_{12}B_6$ had a Curie temperature at 130°-140°K and exhibited a Curie-Weiss behavior in the paramagnetic region above 140°K.

It has been reported that only two of $RCrB_4$[1] and RCo_2B_2[2] existed in the ternary system of rare earth-transition metal-boron, where R is a rare earth ion. In the study of the phase equilibria in the R-Co-B system (R=Y or Ce), a new ternary compound with a rhombohedral unit cell was found to have a composition close to $RCo_{12}B_6$. This is the first compound in the metal-rich part of the ternary systems. The results of X-ray powder diffraction analyses and magnetic measurements of the new phases are reported in this paper.

The preparation of the samples was done by arc-melting of mixtures of Co and B with the stoichiometric amount of Y or Ce. The purities of Y, Ce, Co and B used were 99.9%, 99.9%, 99.99% and 99.9% (by weight), respectively. In order to establish thermal equilibrium, the alloy buttons were remelted in the Al_2O_3 crucible under Ar atmosphere of 20Kg/cm^2 pressure with a high frequency furnace. After remelting, the samples were ground in an agate mortar under inert gas atmosphere to prevent oxidation and then examined by chemical and X-ray analyses.

The X-ray patterns were taken using CrKα radiation with a Debye-Scherrer camera and a diffractometer equipped the pulse height analyser. The magnetic susceptibility was measured by a magnetic balance in the temperature range from liquid nitrogen to room temperature at magnetic fields of 5-8KOe.

The X-ray diffraction patterns of $YCo_{12}B_6$ and $CeCo_{12}B_6$ were indexed on the basis of hexagonal unit cell. As shown in Table 1, there is a good agreement between the observed and calculated interplanar spacings. The hexagonal lattice parameters for $YCo_{12}B_6$ and $CeCo_{12}B_6$ are a=9.435±0.006Å, c=7.435±0.005Å and a=9.469±0.006Å, c=7.433±0.006Å, respectively. The unit-cell content is $3RCo_{12}B_6$. The observed and calculated densities for $YCo_{12}B_6$ and $CeCo_{12}B_6$ are 7.48g/cm^3, 7.52 g/cm^3 and 7.81g/cm^3, 7.87g/cm^3, respectively. Consistent with the symmetry of the space group $R\bar{3}m$ (D_{3d}^6), we observed the following systematic extinction : -h+k+l=3n. The converted rhombohedral lattice parameters are a=5.985Å, α=104.05° and a=6.002Å, α=104.16° for $YCo_{12}B_6$ and $CeCo_{12}B_6$, respectively. The unit-cell content is $1RCo_{12}B_6$. Generally Y is used as a crystal chemical stand-in for heavier rare earths since its atomic radius is located between those of Tb and Dy[3]. From the

fact that there exist $RCo_{12}B_6$ compound in the Y-Co-B and Ce-Co-B systems, it may be thought that there exist ternary borides with the same structure in all rare earths-Co-B systems.

Fig.1 shows the reciprocal magnetic susceptibility plotted against temperature. It can be seen from this figure that $CeCo_{12}B_6$ follows the Curie-Weiss law in the paramagnetic region above 140°K and becomes ferromagnetic at low temperature. The Curie point exists between 130° and 140°K. The Curie constant per mole (C) obtained in the paramagnetic region is 5.43. It is shown from Curie-Weiss law that C can be written : $C=N\beta^2/3k(n_1^2 + 12n_2^2)$, where β is the Bohr magneton, N is Avogadro's number, and n_1 and n_2 are the magnitudes (in unit of β) of the magnetic moments of Ce and Co, respectively.

On the assumption of 2.54β of the free Ce^{3+} ion moment, the magnetic moment of Co can be found to be 1.76. This value is as large as that derived from the saturation moment for pure Co. The preparation, the analysis of crystal structure and magnetic measurements of other ternary borides $RCo_{12}B_6$ are in progress.

Table 1. The X-ray Diffraction Data for $YCo_{12}B_6$ and $CeCo_{12}B_6$.

hkl	Int.	$YCo_{12}B_6$		$CeCo_{12}B_6$	
		$d_{obs.}$	$d_{cal.}$	$d_{obs.}$	$d_{cal.}$
101	vvw	5.497	5.499	5.504	5.507
021	vw	3.582	3.580	3.586	3.590
211	w	2.855	2.852	2.858	2.861
202	s	2.752	2.750	2.753	2.754
300	s	2.724	2.724	2.734	2.734
220	vvw	2.359	2.359	2.367	2.367
113	s	2.194	2.194	2.194	2.195
131	vs	2.167	2.168	2.173	2.175
401	vvw	1.971	1.970	—	1.976
312	m	1.935	1.935	1.939	1.940
303	m	1.831	1.833	1.836	1.836
321	vvw	—	1.818	1.822	1.824
104	vw	1.813	1.812	1.812	1.812
042	m	1.789	1.790	1.795	1.795
410			1.784		1.790
223	w	1.707	1.709	1.712	1.712
024	w	1.692	1.692	1.693	1.693
232	w	1.673	1.674	1.681	1.679
214	vw	1.593	1.593	1.594	1.594
330	m	1.574	1.573	1.579	1.578
241	vw	1.512	1.512	1.517	1.517
502	m	1.496	1.496	1.501	1.501
015	w	1.463	1.463	1.462	1.463
143	m	1.448	1.447	1.452	1.451
134	vw	1.437	1.437	1.440	1.439
205	vvw	1.401	1.397	—	1.398
152	w	1.364	1.365	1.370	1.369
600			1.362		1.367
324	vvw	1.320	1.320	—	1.322
250	w	1.310	1.308	1.315	1.313
315	m	1.244	1.243	1.246	1.244
006	vvw	—	1.239	1.238	1.239
054	vvw	1.228	1.227	—	1.230
612	w	1.180	1.182	1.187	1.185

hkl : hexagonal axis

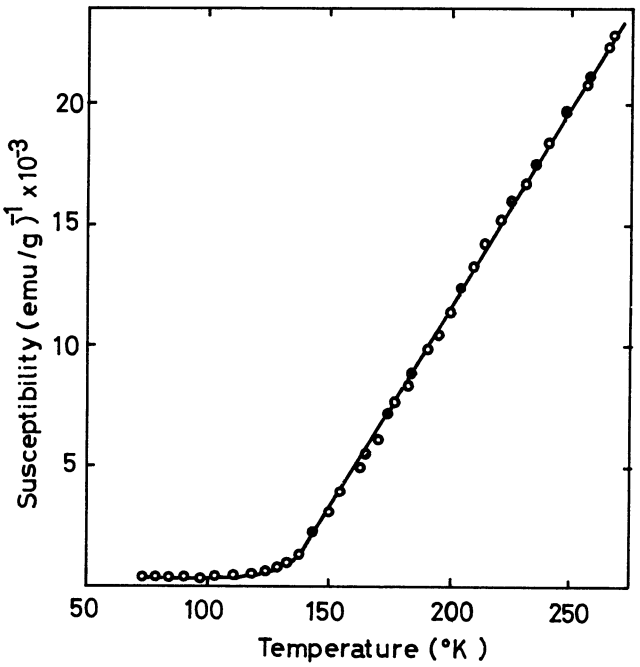

Fig.1 The variation of the reciprocal susceptibility with temperature for $CeCo_{12}B_6$. The open circles: H=7.5KOe, the closed circles: H=4.7KOe.

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