tion is about 200 μsec and is dependent on both concentrations and temperature. An Arrhenius plot of the longitudinal relaxation rate gives a value of 3.8 kcal/mol. This value is consistent with a correlation time, τ_c, produced by diffusional translation or reorientation.[7] The decrease in T_2 with increasing salt concentration is probably due to ion pairing at higher concentrations. Ion pairing would tend to distort the tetrahedral symmetry of the tetramethylantimony cation and reduce T_2. Ion pairing would also explain the relatively small T_2 value of tetramethylantimony cation in methanol, since the reduced dielectric constant of this solvent would tend to enhance the equilibrium concentration of ion pairs. Solutions of tetraphenylantimony sulfate in water and tetraphenylantimony fluoride and chloride in methanol were also studied but signals were not observed because of extremely short T_2's in these solutions. An upper limit of 10 μsec can be placed on the T_2 values for these ions. The octahedral structure of $SbCl_6^-$ is reflected in its relatively long relaxation time. The short T_2 of $SbCl_4^-$, on the other hand, indicates a nontetrahedral geometry for this anion as expected from the lone pair in the antimony valence shell.[9]

The extremely short relaxation found for tetraphenylantimony cations in aqueous solution demonstrates that the geometry of these ions deviates significantly from tetrahedral in aqueous solution. This result confirms the inferences made from a study of the vibrational spectra of tetraphenylantimony cation in aqueous solution.[3] From limited Raman evidence the authors also proposed that tetraphenylantimony chloride is tetracoordinate in methanolic solution. If tetraphenylantimony chloride were tetrahedral in methanolic solution, one would expect to observe a ^{121}Sb relaxation time comparable to that observed for the tetramethylantimony cation in methanol. Our data, therefore, do not support the previous interpretation of the Raman data.

Registry No. $(CH_3)_4SbI$, 2185-78-6; $SbCl_6^-$, 17949-89-2; ^{121}Sb, 14265-72-6; tetraphenylantimony cation, 15912-81-9.

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[9] The $SbCl_6^-$ resonance was observed at 780 ppm to the high field of tetramethylantimony cation.

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Erbium Hectoboride

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This note reports the preparation and characterization of single-phase erbium hectoboride, together with the electron microprobe and wet chemical analyses that were performed to determine more exactly the erbium to boron ratio. Previously, binary borides of composition MB_{50-100} (historically labeled as hectoborides) have been reported for yttrium,[1] ytterbium,[2,3] gadolinium,[2] holmium,[3] and plutonium.[4] In fact, Spear and Solovyev[5] have found that all of the lanthanide rare earth metals with the exception of lanthanum, cerium, and praseodymium form a hectoboride compound. However, the exact metal to boron ratio of this class of compounds has never been established with certainty. This uncertainty may simply result from the complexity of the structure and reflect variations in the degree of metal and/or boron occupancy of equivalent lattice sites. On the other hand, a reliable chemical analysis of this type of compound had never been performed prior to the investigation described in this note. Instead, the chemical compositions of MB_{50}, MB_{66}, MB_{70}, and MB_{100} have been inferred from less accurate means. For example, Smith and Gilles[2] have established the composition as GdB_{100} on the strength of relative intensities of X-ray diffraction maxima from patterns obtained on samples of overall compositions GdB_{49}, GdB_{99}, and GdB_{199}. In the case of YB_{66} the formula was inferred on the basis of the crystal structure analysis, as significant boron impurity precluded a meaningful direct chemical analysis.[6] Formulas have also been approximated from the known compositional makeup of the starting materials before synthesis; however, the final synthesized composition is almost certainly altered due to the preferential loss of one constituent.

Experimental Section

An assortment of arc-melted erbium–boron samples were prepared using β-rhombohedral boron of 99.98% purity and erbium sponge of 99.9% purity as the starting materials. Spectrographic analysis of the boron showed a total metal impurity level of less than 300 ppm, the major impurities in the erbium were calcium (<200 ppm), oxygen (300–700 ppm), and total rare earths (<400 ppm).

Using a water-cooled copper crucible, the samples were arc-melted in a glove box that had been evacuated to less than 10^{-5} Torr and back-filled with argon. Prior to each melt, a zirconium button was melted as an oxygen getter. Each erbium–boron button was flipped and remelted 4 times to ensure sample homogeneity. The resulting arc-melted buttons were of the order of 2–4 g, with compositions ranging from 93 to nearly 100 mole % boron. A button single phased with respect to erbium hectoboride was sought, upon which a reliable wet chemical analysis could be made.

Results and Discussion

Seven ingots with compositions ranging from 93 to nearly 100 mole % boron were prepared and cursorily examined by metallographic analysis. Six ingots were two phased, composed of either ErB_{12} and what appeared to be the hectoboride or the hectoboride and free boron. One sample was single phase, and because the starting composition was ErB_{70}, this ingot was felt to be pure erbium hectoboride. X-Ray diffraction analysis confirmed the single-phase nature of this button. The indexed pattern for this button is given in Table I [nickel-filtered copper radiation (λ_α 1.54178, λ_{α_1} 1.54051) and a Debye–Scherrer camera (diameter 114.6 mm) were used]. The lattice parameter was determined using selected back-reflection lines and a combination of Nelson–Riley and least-squares procedures. The structure is face-centered cubic with $a_0 = 23.440$, $\sigma = 0.003$ Å, com-

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Table I. Indexed X-Ray Diffraction Pattern for ErB_{65}

$h^2 + k^2 + l^2$	I/I_0[a]	d_{obsd}, Å	d_{calcd}, Å
4	4	11.707	11.720
12	9	6.757	6.767
16	10	5.857	5.860
18	2	5.242	5.241
24	4	4.782	4.785
32	3	4.150	4.144
35	6[b]	3.925	3.962
40	1	3.710	3.706
44	6	3.533	3.534
52	7	3.246	3.251
68	2	2.835	2.843
72	7	2.759	2.762
75	1	2.700	2.707
83	2	2.563	2.573
88	4	2.499	2.499
91	2	2.458	2.457
96	3	2.390	2.392
100	6	2.345	2.344
104	7	2.298	2.299
107	3	2.260	2.266
116	5	2.179	2.176
128	1	2.067	2.072
132	6	2.041	2.040
136	4	2.009	2.010
140	1	1.983	1.981
144	3	1.953	1.953
152	8	1.902	1.901
164	3	1.828	1.830
172	4	1.787	1.787
184	2	1.729	1.729
212	3	1.610	1.610
216	2	1.591	1.594
	plus 14 lines to 1.2153 Å		

[a] Visual estimates. [b] Broad.

pared to Spear and Solovyev's[5] value of $a_0 = 23.438 \pm 0.003$ Å for ErB_{66}.

To verify further that this sample was single phase, an electron microprobe was used to scan the entire surface for erbium. The composition was found to be $ErB_{65 \pm 4}$ using an Er standard of 99.9% purity and determining boron by difference. The erbium content did not vary by more than ±0.01 atom % over the entire cross section. Having firmly established that the sample was single-phase hectoboride, the chemical composition was further established by wet chemical analysis for erbium and boron.[7] These results showed the composition of this erbium hectoboride button to be $Er_{1.0 \pm 0.01}B_{65 \pm 1.0}$.

The composition limits of the erbium hectoboride phase were determined by microprobe analysis of two buttons. One button, which contained the dodecaboride and hectoboride phases, was richer in erbium that the single-phase hectoboride; the other, composed of the hectoboride and free boron, contained more boron than the single-phase hectoboride. The erbium rich composition was found to be 21.72 ± 1.1 wt % erbium, and the boron-rich limit, 17.34 ± 0.9 wt % erbium. Assuming the boron concentration by difference, the corresponding compositions are $ErB_{56 \pm 4}$ and $ErB_{73 \pm 4}$, respectively. The upper and lower extremes of the composition limits and their temperature dependence have not been established; the maximum stoichiometric variation may certainly be greater than the 0.4 atom % erbium found in this investigation.

To the authors' knowledge, the only other explicit assessment of the chemical composition of such a hectoboride phase was by Schwetz, *et al.*[8] They reported the compositions DyB_{95} and ThB_{76}, as determined by microprobe analysis.

Two other ingots in this series of melts contained a compound with a composition intermediate between ErB_{12} and ErB_{60}. Preliminary electron microprobe data indicate a composition of $ErB_{\sim 45}$. Microscopic examination of polished sections of the ingot showed that this intermediate compound occurred as the matrix in which large primary crystals of ErB_{12} were found. Preliminary X-ray diffraction results for this matrix phase indicate a cubic pattern having a simple cubic lattice parameter tentatively set at $a_0 = 27.0$. Since this cubic pattern is significantly different from any others reported in the Er–B system, further studies are being made to characterize the nature of this phase more completely.

Registry No. ErB_{65}, 37341-96-1; erbium hectoboride, 37341-97-2.

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