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Ytterbium and terbium dodecaborides.* By SAM LA PLACA and DANIEL NOONAN,† *Brookhaven National Laboratory, Upton, N. Y., U.S.A.* and BEN POST, *Polytechnic Institute of Brooklyn, Brooklyn 1, N. Y., U.S.A.*

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The synthesis of several rare earth dodecaborides, isomorphous with UB_{12} (Bertaut & Blum, 1949) and ZrB_{12} (Post & Glaser, 1952), and crystallographic data for these phases, were reported recently (La Placa, Binder & Post). The unit cells are face-centered cubic with four formula weights of MeB_{12} per unit cell. The structures may be visualized in terms of boron atoms linked in a rigid three-dimensional network, with the metal atoms in large cubo-octahedral holes.

The rare earth dodecaborides were prepared by heating the metal oxides with amorphous boron in a protective helium atmosphere at 1400–1500 °C. Efforts were made to carry out this reaction with yttrium and all the rare earth metals (except promethium), but the dodecaborides of Y, Dy, Ho, Er, Tm and Lu were the only ones that could be prepared. The atomic radii of these metals are the smallest in the rare earth series. The preparative results indicated that the stability of these phases was sensitively dependent on the effective sizes of the metal atoms, and that metal atoms with radii greater than that of Y ($r_m = 1.77 \text{ \AA}$), the largest of the six listed above, could not be accommodated in the dodecaboride structure.

A similar sensitivity to the size of the metal atom, at the other extreme of the size scale, had been indicated previously by repeated failures to prepare HfB_{12} contrasted with the relative ease with which ZrB_{12} was prepared (Glaser, Moskowitz & Post, 1953). The atomic radius of zirconium in the elementary state is 1.59 Å compared with 1.565 Å for hafnium.

In terms of size factors, the failure to prepare TbB_{12} was somewhat puzzling, since the Tb atom is generally considered to be slightly smaller than Y. On the other hand, the failure to prepare YbB_{12} could be plausibly accounted for on this basis; its atomic radius in the metallic state is anomalously large (1.935 Å), more than 10% larger than Tm or Lu, the elements immediately adjacent to Yb in the rare earth series.

Recently, in the course of studies of other borides of rare earth metals, signs of the possible presence of YbB_{12} as a minor component, in some of the preparations, were detected. Efforts were then made to prepare pure YbB_{12} . The appropriate amounts of ytterbium metal and

crystalline boron (99.9% and 99.0% pure respectively) were arc melted under a one atmosphere blanket of argon. X-ray diffraction patterns of the product revealed that it consisted almost entirely of the face-centered cubic phase which was sought. A lattice constant of $7.469 \pm 0.001 \text{ \AA}$ was computed from measurements of sharp high angle lines of the diffractometer pattern, obtained with Ni-filtered $Cu K\alpha$ radiation. Similar reaction conditions were used in efforts to prepare the dodecaborides of gadolinium and terbium. The former yielded only the hexaboride: GdB_6 . The latter formed the face-centered cubic TbB_{12} with a lattice constant of $7.504 \pm 0.001 \text{ \AA}$.

Crystallographic data for other dodecaborides have been listed by La Placa *et al.* (1961). The unit-cell dimensions of these compounds decrease monotonically with increasing atomic number of the metal. This is in contrast to the analogous unit-cell dimensions of the rare earth hexaborides; in that series the unit cells of both EuB_6 and YbB_6 are anomalously large.

It is tempting to ascribe the successful preparations of YbB_{12} and TbB_{12} to the use of the pure metals as starting materials, in place of the metal oxides used in previous, unsuccessful, efforts. The two sets of preparations are, unfortunately, not directly comparable. In the earlier efforts the reactants were heated only to about 1400–1500 °C. In the successful preparations the starting materials were arc melted at much higher temperatures. There is, however, some independent evidence that the use of the pure metals as starting materials is desirable. In earlier efforts to prepare lanthanum tetraboride, repeated attempts, using lanthanum oxide and boron as starting materials, were unsuccessful. When lanthanum metal was used in place of the oxide under similar reaction conditions, the tetraboride was readily prepared (Felton, Binder & Post, 1958).

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