JAN 4 1966

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PREPARATION AND CELL PARAMETERS OF $\text{Lu}_{12}^{\text{B}}\text{C}_2$

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Livermore, California

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Contract No. W-7405-eng-48

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Gordon S. Smith
Quintin Johnson

November 19, 1964

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Preparation and Unit Cell Parameters of LuB_2C_2 *

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November 19, 1964

In a recent investigation of the ternary compounds formed between rare earth elements and boron and carbon, Smith (1964) has reported the occurrence of a stable, high-melting compound MB_2C_2 for $\text{M} = \text{Nd, Gd, Tb, Dy, Ho, Er and Yb}$. Two lanthanides, La and Sm, did not form this borocarbide phase under the method of synthesis; the other metals were not studied. X-ray powder patterns indicated that this phase is identical with the one previously thought to be either a pure boride (Post, Moskowitz and Glaser, 1956) or a boride stabilized by carbon (Binder, 1960). In their method of preparation Post, Moskowitz and Glaser (1956) were in fact able to obtain the lanthanum compound.

Smith (1964) also noted an unusual trend in the tetragonal lattice parameters across the MB_2C_2 series, viz. as compared to a 1 percent decrease in a from La through Yb, c decreases sharply and exhibits an anomalously high value at Yb. The percent change in c from La through Er is ~11%, and easily exceeds twice the change of either a or c in the tetragonal MB_4 series (see Gschneidner, 1961). This disparity in the behavior of a and c is explicable in terms of the layered structure proposed. It is accordingly of interest to determine whether the smallest lanthanide, lutetium, also

forms this compound and whether the lattice parameters conform to the trend established by the earlier members.

The preparations were made by arc-melting ~ 0.5 g lutetium metal filings with appropriate amounts of boron and carbon powders in a Th-gettered argon atmosphere. Prior to this, the starting materials had been well-mixed and pressed into pellet form. After melting, the ingot was turned and re-melted. A tungsten electrode was used, and by controlling the power the sample was kept as close to the melting point as possible to inhibit vaporization losses. The ingots were then annealed at ~ 2000° C by induction heating in a graphite crucible for 1/2 hour under a vacuum of 10^{-5} torr.

The lutetium metal was supplied by Semi-Elements, Inc., and was reported to be 99.9% pure. Crystalline boron, reported as 99.1% pure, was obtained from U.S. Borax Research. Spectroanalyses showed it to contain 0.24-2.4% impurities consisting mainly of Ca, Cr, Cu, Fe, Mg, Mn, Mo, Ni and Si. Grade SP-1C graphite powder from National Carbon Company was used. Maximum spectroscopic impurities were certified to be 6 ppm by weight.

The powder pattern was recorded using a standard Norelco camera of 57.3 mm radius and Ni-filtered $\text{CuK}\alpha$ radiation. The diffraction spectrum was readily indexed, and the lattice parameters determined by a least-squares technique using the IBM 7094 program of Mueller and Heaton (1962).

The lattice parameters thus obtained are: $a = 5.321 \pm 0.001$, $c = 3.447 \pm 0.001 \text{ \AA}$ (based on $\lambda \text{ CuK}\alpha_1 = 1.54050 \text{ \AA}$). Parameters obtained from single-crystal photographs are in excellent agreement with these values, although of lower accuracy. The a parameter fits nicely on the very nearly linear a vs atomic number plot. The overall decrease in a from La through Lu is 1.5%; the corresponding decrease in c is 12.9%. Even excepting

the anomalous behavior at Yb, the $\underline{c}$ parameter plot is not linear. With the final point at Lu now established it is clear that the overall decline is less rapid than for a linear plot.

Thus in $\underline{MB}_2C_2$ we have the unusual situation of a lanthanide contraction being taken up almost entirely in one unit-cell direction only. Nonetheless, the smaller change in $\underline{a}$ across the series carries its own implications. In terms of the proposed structure (Smith, 1964) where the bond distances are determined solely by cell dimensions, the small change in $\underline{a}$ corresponds to a shortening of the B-C bond distances from $1.58_2 \text{ \AA}$ in LaB_2C_2 to $1.55_6 \text{ \AA}$ in LuB_2C_2 , and hence, formally to a progressive change in the bond-character of the B-C bonds.

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*This work was performed under the auspices of the U.S. Atomic Energy Commission.

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