

## RARE EARTH METAL "DISILICIDES"<sup>1</sup>

BY JOHN A. PERRI, IRA BINDER AND BEN POST

*Polytechnic Institute of Brooklyn, Brooklyn, N. Y.*

Received October 2, 1958

Disilicides of Ce, Pr, Nd, Sm, Eu, Gd, Dy and Y have been prepared. The Ce, Pr and Nd compounds are tetragonal as previously reported; the Sm, Gd, Dy and Y compounds are orthorhombic, space group *Imma*. Their structures are slightly distorted versions of the tetragonal  $\text{MeSi}_2$  structure. The magnitude of the distortion appears to increase with decreasing size of the metal atom. Chemical and X-ray diffraction studies of " $\text{GdSi}_2$ " indicate that the composition is actually close to  $\text{GdSi}_{1.4}$ .  $\text{EuSi}_2$  crystallizes in the tetragonal system apparently due to the anomalously large size of the metal atom.

### Introduction

Brauer and Haag<sup>2</sup> have described the isomorphous disilicides formed by La, Ce, Pr and Nd. The unit cells are tetragonal; there are four formula weights per unit cell, and the space group is  $I4_1/amd$ . Dimensions of the unit cells, as given by Brauer and Haag, are listed in Table I.

The structure may be described in terms of linear arrays of atoms of the type Si-Me-Si-Si-Me-Si-, parallel to the "*c*"-axis. One such line is placed at  $x = 0$  and  $y = 1/4$ ; the operation of the fourfold screw axis generates three additional lines at  $x = 0, y = 3/4$ ;  $x = 1/2, y = 1/4$ ; and  $x = 1/2, y = 3/4$ . This arrangement is shown schematically in Fig. 1.

In terms of a unit cell whose origin is at a center of symmetry, atomic positions are

4 metal atoms in 4b:

$$0, 1/4, 3/8; 0, 3/4, 5/8; 1/2, 3/4, 7/8; 1/2, 1/4, 1/8$$

8 silicon atoms in 8c:

$$0, 1/4, z; 0, 3/4, \bar{z}; 1/2, 3/4, 1/2 + z; 1/2, 1/4, 1/2 - z; 0, 3/4, 1/4 + z; 0, 1/4, 3/4 - z; 1/2, 1/4, 3/4 + z; 1/2, 3/4, 1/4 - z$$

There are two types of Si-Si bonds in this structure, *i.e.*

(a) from  $0, 1/4, z$  to  $0, 1/4, 3/4 - z$

(b) from  $0, 1/4, 3/4 - z$  to  $0, 3/4, 1/4 + z$

Brauer and Haag postulated an "ideal"  $\text{MeSi}_2$  structure in which both types of Si-Si bonds are equal in length. Simple geometrical considerations show that in this "ideal" structure the variable positional parameter of the silicon atoms is  $z = 0.792$ . Brauer and Haag found that calculated and observed diffraction intensities showed fairly good agreement in the cases of  $\text{LaSi}_2$  and  $\text{CeSi}_2$  when  $z$  was assumed equal to this value. They also reported the doubling of some weak reflections on the powder diffraction patterns of  $\text{SmSi}_2$  and  $\text{YSi}_2$  and suggested the possibility that the symmetry of the unit cell deviated from tetragonal in these compounds, and that it was possibly orthorhombic.

The present investigation was undertaken to study more closely the structures of these and other rare earth disilicides.

**Sample Preparation.**—Disilicides of La, Ce, Pr, Nd, Sm, Eu, Gd, Dy and Y were prepared. These compounds were produced readily by direct silicon reduction of the metal oxides, either *in vacuo* or in a protective atmosphere such as hydrogen. Some reductions also were carried out using mixtures of carbon and silicon with the metal oxides. The oxides were 99–99.9% pure except in the case of neodymium where an oxide of 95% purity was used.

Reactions carried out in alumina boats under vacuum (with continuous pumping) generally gave the best products. The silicon monoxide which was formed in the reaction between the metal oxide and the silicon was quickly and completely removed from the reaction mass. When reactions were carried out under a protective layer of hydrogen, the silicon oxides appeared to form coatings about the silicide particles. These coatings were never completely removed and all lots produced in reactions carried out in hydrogen contained some oxygen. For this reason each of the disilicides also was prepared *in vacuo*.

Reaction temperatures of the order of 1100 to 1600° were used. Preparations fired at temperatures above 1600° usually yielded relatively impure products due to chemical attack on the container. In the case of yttrium and dysprosium, reactions were carried out most successfully in the temperature range 1400–1550°; for  $\text{SmSi}_2$ , a temperature range of 1200–1300° was found most suitable. The exact temperatures did not appear to be critical in other cases.

As a check on the procedure, lanthanum metal was heated with silicon *in vacuo*; a pure disilicide was obtained identical with that produced in the reaction between the metal oxide and silicon.

**X-Ray Results. Powder Data.**—X-Ray diffraction examination of the powdered products indicated that the La, Ce and Pr compounds were tetragonal with lattice constants differing slightly from those reported by Brauer and Haag (see Table I). It should be noted that Brauer and Haag's measurements were made on films taken in a small (57.3 mm. diameter) Debye-Scherrer camera. Our measurements were made with a Geiger counter diffractometer, making possible far better precision of measurement and resolution of lines than are generally obtainable with small film cameras.

| Brauer and Haag <sup>2</sup> |          | —The present work— |          |          |       |
|------------------------------|----------|--------------------|----------|----------|-------|
| <i>a</i>                     | <i>c</i> | <i>a</i>           | <i>b</i> | <i>c</i> |       |
| 4.272                        | 13.72    | $\text{LaSi}_2$    | 4.31     | ...      | 13.80 |
| 4.148                        | 13.81    | $\text{CeSi}_2$    | 4.27     | ...      | 13.88 |
| 4.140                        | 13.64    | $\text{PrSi}_2$    | 4.29     | ...      | 13.76 |
| 4.103                        | 13.53    | $\text{NdSi}_2$    | 4.18     | 4.15     | 13.56 |
|                              |          | $\text{SmSi}_2$    | 4.105    | 4.035    | 13.46 |
|                              |          | $\text{GdSi}_2$    | 4.09     | 4.01     | 13.44 |
|                              |          | $\text{DySi}_2$    | 4.04     | 3.95     | 13.34 |
|                              |          | $\text{YSi}_2$     | 4.04     | 3.95     | 13.23 |

The powder patterns of Nd, Sm, Gd, Dy and Y disilicides could be indexed only on the basis of a slightly distorted (orthorhombic) version of the  $\text{LaSi}_2$  tetragonal type. (The europium disilicide preparation will be discussed separately below.) Unit cell dimensions of these compounds are included in Table I; powder data are listed in Table II.

(1) Supported by Air Force Office of Scientific Research.

(2) V. G. Brauer and H. Haag, *Z. anorg. allgem. Chem.*, **267**, 198 (1952).



TABLE II

PARTIAL POWDER DIFFRACTION DATA FOR ORTHORHOMBIC DISILICIDES

| hkl | NdSi <sub>2</sub> |     | SmSi <sub>2</sub> |      | GdSi <sub>2</sub> |      | DySi <sub>2</sub> |      | YSi <sub>2</sub> |                |
|-----|-------------------|-----|-------------------|------|-------------------|------|-------------------|------|------------------|----------------|
|     | d(Å.)             | I   | d(Å.)             | I    | d(Å.)             | I    | d(Å.)             | I    | d(Å.)            | I <sup>b</sup> |
| 101 | 4.00              | 35  | 3.93              | 30   | 3.91              | 25   | 3.86              | 30   | 3.89             | ..             |
| 011 | 3.97              |     | 3.86              | 25   | 3.84              | 25   | 3.77              | 30   | 3.79             | ..             |
| 004 | 3.39              |     | 35                | 3.37 | 50                | 3.36 | 30                | 3.33 | 35               | 3.33           |
| 103 | 3.06              | 65  | 3.03              | 35   | 3.02              | 25   | 2.99              | 35   | 3.00             | ..             |
| 013 |                   |     | 3.01              | 40   | 2.99              | 30   | 2.95              | 40   | 2.96             | ..             |
| 112 | 2.70              | 100 | 2.65              | 100  | 2.62              | 100  | 2.60              | 100  | 2.60             | ..             |
| 105 | 2.274             | 50  | 2.252             | 35   | 2.25              | 20   | 2.225             | 30   | 2.23             | ..             |
| 015 |                   |     | 2.241             | 35   | 2.23              | 20   | 2.21              | 25   | 2.21             | ..             |
| 200 | 2.048             | 18  | 2.052             | 25   | 2.047             | 14   | 2.021             | 20   | 2.021            | ..             |
| 020 | 2.074             | 18  | 2.017             | 20   | 2.005             | 12   | 1.974             | 15   | 1.975            | ..             |

<sup>a</sup> Overlapping peaks (additional peaks were not recorded). <sup>b</sup> Several peaks of this phase coincided with peaks of another phase and intensities are not considered reliable.

**X-Ray Results. Single Crystal Data.**—Systematic absences of reflections from the powder patterns indicated that the space group of the orthorhombic silicides was either Imma or Im2a.

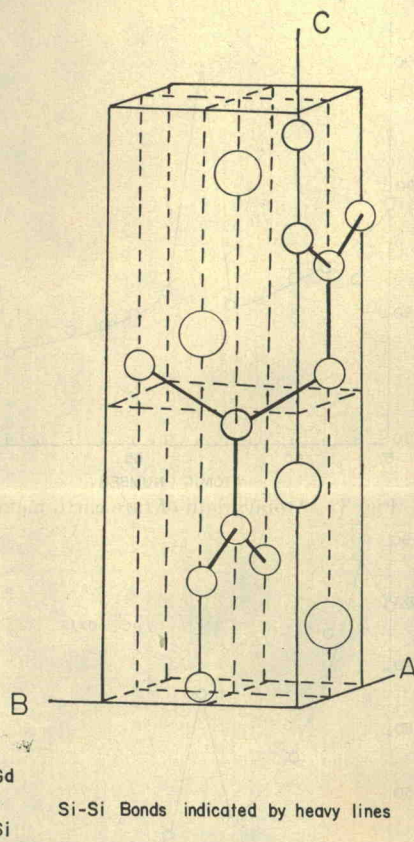
A few small single crystals of GdSi<sub>2</sub> were found in one of the preparations. Two of these were examined by single crystal techniques. The crystals were tiny rhombs having maximum dimensions of less than 0.1 mm. X-Ray photographs taken with the precession camera, using Mo K radiation, confirmed that the space group was either Imma or Im2a and that, within the limits of experimental error,  $I_{hkl} = I_{khl}$ . This also was indicated, for fewer reflections, by the powder diffractometer data. It was therefore felt that Imma, in which the same symmetry elements are associated with both the "a" and "b"-axes, is the more probable space group.

In order to determine the positional parameters in the orthorhombic phase, careful measurements were made of eight observable 00*l* reflections (004, 008, 0012, 0020, 0024, 0028 and 0032). The crystal was mounted along [100] and the intensities of the diffracted beams were recorded with a scintillation counter. Filtered Mo K radiation was used. A voltage and current stabilized source of X-radiation was used. The counter was kept in a fixed position, with the window open, and the diffracted beam was recorded as the crystal was turned slowly through the diffracting position. The window on the scintillation counter covered a range of 4°(2θ) and the crystal was rotated at 1/4°(θ) per min. The diffracted peaks were recorded on a strip chart and their areas were subsequently measured with a planimeter.

The usual Lorentz and polarization corrections were applied in order to convert the measured (integrated) intensities to numbers proportional to |F<sup>2</sup>|. No absorption correction was applied; approximate calculations showed that, for all but the (004) reflection, the absorption factor varied linearly with sin<sup>2</sup>θ/λ<sup>2</sup> and could therefore be absorbed into the usual "temperature factor."

No signs of 00*l* reflections with  $l \neq 4n$  were detected either with the scintillation counter or on highly over-exposed precession photographs.

In the tetragonal unit cell (I4<sub>1</sub>/amd) the metal atom has a fixed value of *z* ( $z_m = 0.375$ ) and the arrangement of the silicon atoms is such that they lie at eight different levels; *i.e.*, if  $z = 0.786$ , then



○ Gd  
○ Si  
Si-Si Bonds indicated by heavy lines

Fig. 1.—Arrangement of atoms in  $MiSi_2$  unit cell.

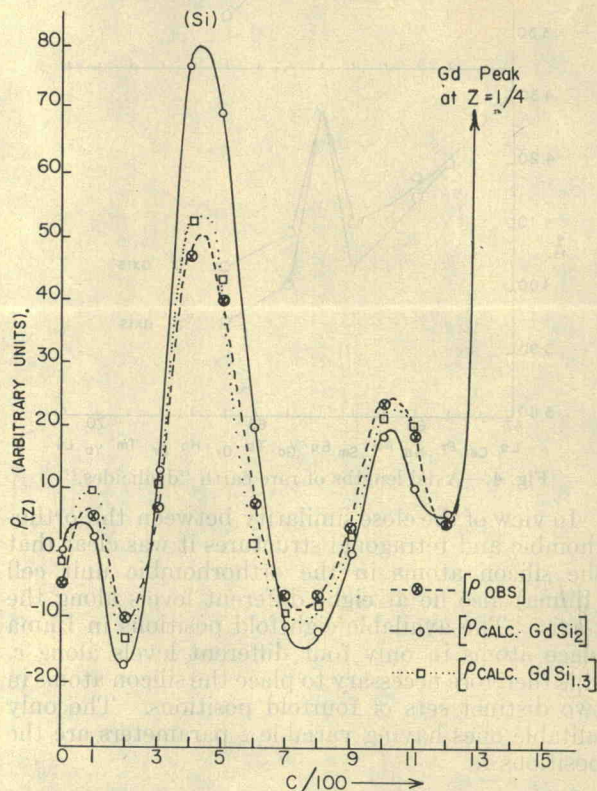


Fig. 2.—(z) calcd. and obsd.

there are silicon atoms at  $z = 0.786, 0.214, 0.036, 0.964, 0.286, 0.714, 0.536, 0.464$ .



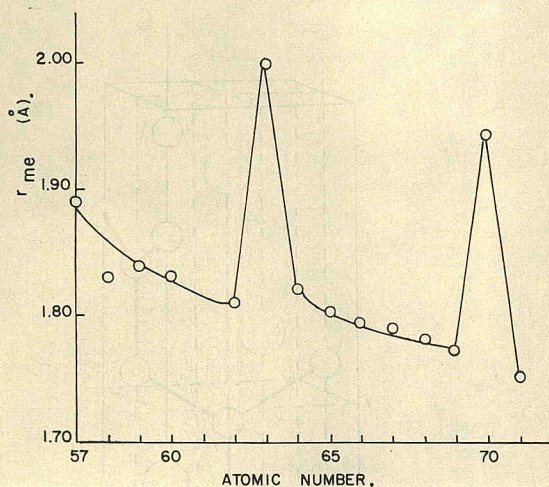
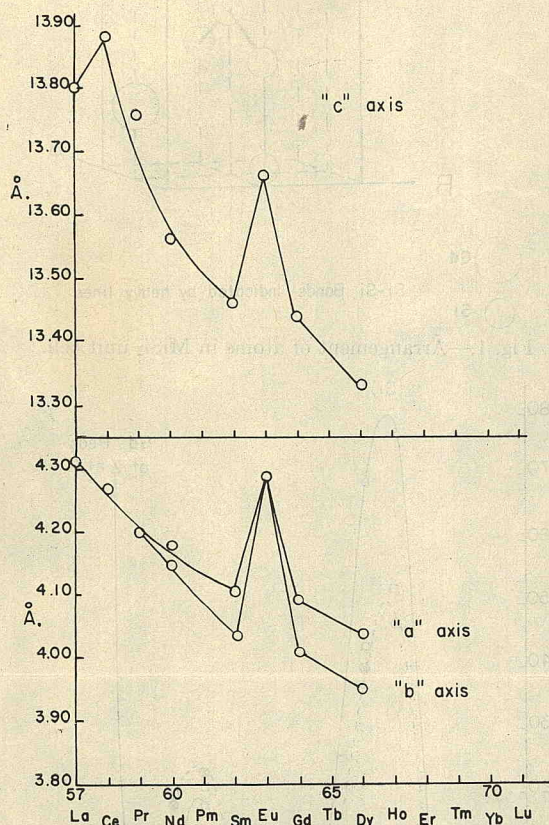
Fig. 3.—Atomic radii of rare earth metals.<sup>3</sup>

Fig. 4.—Axial lengths of rare earth "disilicides."

In view of the close similarity between the orthorhombic and tetragonal structures it was clear that the silicon atoms in the orthorhombic unit cell (*Imma*) also lie at eight different levels along the *c*-axis. The available eightfold positions in *Imma* place atoms in only four different levels along *c*. It is therefore necessary to place the silicon atoms in two distinct sets of fourfold positions. The only suitable ones having variable *z* parameters are the positions  $4c$

$$0, \frac{1}{4}, z, \quad 0, \frac{3}{4}, \bar{z}$$

$$\frac{1}{2}, \frac{3}{4}, \frac{1}{2} + z, \frac{1}{2}, \frac{1}{4}, \frac{1}{2} - z$$

In the tetragonal cell the metal atoms must be in special positions, *i.e.*, at  $z = \frac{3}{8}$  when the origin

is at a center of symmetry. No such restrictions are imposed on the *z* parameters of either the Si or the Gd in the orthorhombic unit cell. However, a study of the diffracted intensities indicates that restrictions are present even though not required by the space group.

In *Imma*,  $F_{00l} = \sum_i f_i \cos 2\pi lz_i$ . If a Gd atom is at  $z = \frac{3}{8}$ , it will contribute only to reflections having  $l = 4n$ . If it is shifted to  $\frac{3}{8} + \epsilon$  its contribution to  $00l$  reflections is  $f_{\text{Gd}} \cos 2\pi l(\frac{3}{8} + \epsilon)$ ; this is equivalent to  $f_{\text{Gd}} (\cos 2\pi l \frac{3}{8} \cos 2\pi l \epsilon - \sin 2\pi l \frac{3}{8} \sin 2\pi l \epsilon)$ . For  $l$  even, but not equal to  $4n$ , this gives  $-f_{\text{Gd}} \sin 2\pi l \epsilon$ . On the basis of the observed intensities of high order reflections, it has been estimated that if  $\epsilon \geq 0.001$ , reflections of the type (0026) and (0030) should have been readily detectable. No such reflections were observed. We may conclude that in the orthorhombic cell the value of  $z_{\text{Gd}}$  lies within the range  $z = 0.375 \pm 0.001$ . Similar arguments may be used to limit the extent to which the distance from a gadolinium atom to a silicon atom "above" it differs from that to a silicon atom "below" it; the difference, if it exists, cannot exceed 0.02 Å.

Electron density maps were computed to determine  $\rho(z)$ . These are shown in Fig. 2. "Observed" values of  $F_{00l}$  were used as coefficients for one summation; for the other summations shown, calculated values of  $F_{00l}$  were used as coefficients of the Fourier series. It was assumed that a gadolinium atom was located at  $z = 0.375$  and that silicon atoms were at  $0.375 \pm 0.411$ .

It will be noted that peaks not attributable to either the silicon or gadolinium atoms appear on both maps (at  $z = 0.008$  and  $z = 0.087$ ). Since only gadolinium and silicon atoms were included in the  $F_{\text{calcd}}$  summation it is clear that these are spurious peaks resulting from the use of a small number of terms in the Fourier summations.

In the electron density summations, intensities of (00*l*) reflections other than those having  $l = 4n$  were taken to be equal to zero. It is probable that these do not exactly equal zero, but were merely below the level of detection. However, as a result of taking (00*l*)  $l \neq 4n$  reflections equal to zero, the gadolinium atoms must be found at  $z = \frac{1}{8}, \frac{3}{8}, \frac{5}{8}, \frac{7}{8}$  and the silicon atoms at  $Z_{\text{Gd}} \pm \alpha$ .

The parameters of the silicon atoms as derived from the electron density map shown in Fig. 2, after application of the "back-shift" correction, are  $z = 0.3750 \pm 0.4112$ . As noted previously, the possibility that the distances of the two silicon atoms from the metal atom between them differ slightly cannot be ruled out.

A calculation of the discrepancy factor

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_c|}$$

where  $F_{\text{calcd}}$  was based on  $Z_{\text{Si}} = Z_{\text{Gd}} \pm 0.4112$ , with two silicon atoms per metal atom, led to a value of  $R = 8.3\%$ . It was evident that no adjustment of  $z$  could greatly improve the agreement between  $F_{\text{obsd}}$  and  $F_{\text{calcd}}$ . Slight shifts in either direction improved some values of  $F_{\text{calcd}}$  and made others worse. It was then assumed that the silicon to metal atom ratio was not exactly two, and  $R$  was



computed for  $\text{GdSi}$ ,  $\text{GdSi}_{1.25}$ ,  $\text{GdSi}_{1.50}$  and  $\text{GdSi}_{2.00}$ . For all the calculations  $z_{\text{Gd}} = 0.3750$  and  $z_{\text{Si}} = z_{\text{Gd}} = 0.4112$ . The calculation for  $\text{GdSi}$ , for example, implied that half the available Si positions were randomly unoccupied. A minimum in  $R$  occurs near  $\text{GdSi}_{1.3}$  where  $R$  is somewhat less than 2.7% (Table III). It was felt that there would be little point in attempting to refine this value further.

TABLE III

VALUES OF "R" FOR VARIOUS Si/Gd RATIOS

| Si/Gd | R, % |
|-------|------|
| 1.00  | 4.8  |
| 1.25  | 2.7  |
| 1.50  | 4.3  |
| 2.00  | 8.3  |

It should also be noted that the calculated silicon peaks computed on the basis of a Si/Gd ratio of two are considerably higher than those on the  $F_{\text{obsd}}$  summation. A summation computed on the basis of a Si/Gd ratio of 1.3 is also shown in Fig. 2. The height of the silicon atom peak on this map is in far better agreement with that on the  $F_{\text{obsd}}$  map.

Pycnometric measurements of the density of powdered "GdSi<sub>2</sub>" gave a value of 5.94 g./cc.; the density calculated for GdSi<sub>2</sub> is 6.43 g./cc.; for GdSi<sub>1.4</sub> it is 5.92 g./cc. A chemical analysis indicated a Si/Gd atom ratio of 1.47, in good agreement with X-ray and density measurements. It is clear that the composition of "GdSi<sub>2</sub>" is actually close to GdSi<sub>1.4</sub>. It was not possible to establish whether a range of homogeneity exists for this compound.

**Europium Disilicide.**—The ionic radii of the trivalent rare earth ions decrease regularly as we proceed from La<sup>+++</sup>(1.06 Å.) to Lu<sup>+++</sup>(0.85 Å.).<sup>3</sup> The atomic radii of the elementary metals also decrease with increasing atomic number, with the conspicuous exceptions of Eu and Yb, whose atomic radii are about 10% greater than those of neighboring elements (Fig. 3).<sup>4</sup> This anomaly is associated with the abnormal valencies of these atoms; most of the rare earth metals are essentially trivalent, but Eu and Yb show a large amount of divalent character which usually is attributed to the withdrawal of one electron from the outermost orbit (5d<sup>1</sup>) to fill a gap in an inner one (4f<sup>6</sup>). This leads also to an increase in the effective sizes of these atoms.

(3) D. H. Templeton and C. H. Dauben, *J. Am. Chem. Soc.*, **76**, 5327 (1954).

(4) F. H. Spedding, D. H. Daane and K. W. Herrmann, *Acta Cryst.*, **9**, 559 (1956).

It was felt that the anomaly mentioned above might affect the size of the metal atom in europium disilicide. It has been seen (Table I) that, as we proceed from LaSi<sub>2</sub> to the silicides of metals of higher atomic numbers (and smaller effective sizes) the unit cell decreases progressively in size and the symmetry changes from tetragonal to orthorhombic. In the case of EuSi<sub>2</sub> the size anomaly could lead to crystallization in the tetragonal system.

This proved to be the case. Europium disilicide, prepared by heating Eu<sub>2</sub>O<sub>3</sub> and silicon under vacuum, is tetragonal with  $a = 4.29$  Å.,  $c = 13.66$  Å. Powder diffraction data for this compound are shown in Table IV. Both "a" and "c" are substantially larger than the corresponding axes in either SmSi<sub>2</sub> or GdSi<sub>2</sub>. Figure 4 also shows the "a," "b" and "c" axial lengths of the compounds described above.

TABLE IV

PARTIAL POWDER PATTERN OF EuSi<sub>2</sub> TETRAGONAL

| $hkl$ | $d$ , Å. | $I$                         |
|-------|----------|-----------------------------|
| 101   | 4.09     | 50                          |
| 004   | 3.41     | 38                          |
| 103   | 3.12     | Coincides with Si(111) peak |
| 112   | 2.75     | 100                         |
| 105   | 2.305    | 44                          |
| 200   | 2.147    | 28                          |
| 211   | 1.901    | 31                          |
| 116   | 1.819    | 25                          |
| 108   | 1.779    | 38                          |
| 213   | 1.773    | 38                          |
| 008   | 1.708    | 13                          |
| 215   | 1.523    | 31                          |
| 220   | 1.518    | 19                          |

It is considered very probable that ytterbium disilicide, when prepared, will be found to crystallize in the tetragonal system.

Similar behavior is manifested by the cubic hexaborides of the rare earth metals. These show decreases in unit cell sizes with increasing atomic number of metal atom except for europium and ytterbium hexaborides.<sup>5</sup>

**Acknowledgment.**—The authors wish to thank the American Electro Metal Division of the Firth Sterling Company, Yonkers, New York, for preparing the silicide samples used in this investigation and for valuable technical assistance rendered in the course of the work.

(5) B. Post, D. Moscovitz and F. W. Glaser, *J. Am. Chem. Soc.*, **78**, 1800 (1956).