Short Communications

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Structures of the rare earth germanides at or near equiatomic proportions*.

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The rare earth elements are unique in that, with the exception of europium and ytterbium, their atomic radii decrease uniformly with increasing atomic number; and despite differing electronic configurations their chemical behavior is remarkably similar. The decrease in size makes these elements of especial interest in structural chemistry where the combining element is another metal or a semimetal.

Structural data for rare earth silicides and germanides are relatively meager. The available information, however, is of some interest. Two germanides, Yb_3Ge_5 (Smith, Johnson & Tharp, 1965) and $EuGe_2$ (Gladyshevskii, 1964), crystallize with structures which are comparatively scarce. For the rare earth disilicides, a total of three different structures have been observed (Mayer, Banks & Post, 1962; Tharp, 1962). Other available data are extremely scattered and incomplete.

The present study was undertaken to survey the rare earth germanides formed when the initial composition is equiatomic. During the course of this work we became aware of the work of Parthé & Hohnke (1965; see also Hohnke & Parthé, 1966), which is along somewhat similar lines.

Experimental

Samples were prepared for all of the rare earth elements except lanthanum, praseodymium and promethium by mixing appropriate quantities of metal with germanium and arc-melting the mixture in a gettered atmosphere of argon. In order to improve their homogeneity, the fused buttons were turned over and remelted several times. Many were subsequently annealed for six to eight hours near the melting point of the specimens.

Lattice constants of the CrB-type monogermanide phases were obtained from powder patterns prepared with filtered Cu($K\alpha_1 = 1{\cdot}5405$ Å) or Cr($K\alpha_1 = 2{\cdot}2896$ Å) radiation. The powdered samples were sealed in 0·2-mm-diameter capillaries to prevent oxidation. The lattice constants were subsequently refined by use of the least-squares program of Heaton, Gvildys & Mueller (1964). Lattice constants of the body-centered tetragonal type were obtained from single-crystal oscillation and Weissenberg photographs.

Structural results

Single-crystal and powder studies demonstrated the existence of the CrB (B_f) structure type for NdGe, SmGe, EuGe, GdGe and TbGe. This structure type was previously reported for PrGe (Iandelli, 1959) and for GdGe and DyGe (Baenziger & Moriarty, 1961).

Single crystals obtained from preparations with similar initial compositions but using dysprosium, holmium, erbium, thulium, ytterbium and lutetium were of a recognizably different morphology. Oscillation and Weissenberg photographs showed them to be body-centered tetragonal of an unknown structure type. The diffraction symmetry is $4/mmm$, and there are no systematic extinctions other than $h+k+l=2n+1$. The probable space group is thus $I4/mmm$, or a subgroup thereof. We were also able to obtain a single crystal of this tetragonal phase from the Gd preparation as well as from the Tb preparation, although, as indicated above, the predominant phase in these two preparations is the orthorhombic CrB-type compound.

In a private communication, Professor Parthé informed us that he had observed the CrB structure type as far as erbium. A careful study of our powder patterns indicated a similar behavior. Additional lines belonging to the tetragonal phase first appear on the TbGe photographs and extend with greater intensity to thulium and possibly to ytterbium and lutetium. The presence of this complex set of lines makes it difficult to be absolutely positive concerning the CrB structure type assignment for ErGe. In spite of the obvious presence of the CrB-type structure in preparations using Dy and Ho, single crystals of this phase were never obtained. On the other hand, single crystals of the CrB-type in monogermanide preparations of Tb, Gd, Eu, Sm, and Nd were not difficult to obtain.

Powder patterns of YbGe and LuGe, while somewhat similar in appearance with one another, are not altogether similar to patterns from the earlier members of the series. Nonetheless, as previously mentioned, single crystals of the body-centered tetragonal type were obtained for both ytterbium and lutetium. In addition, a few small needle-like crystals in the LuGe preparation proved to have a rhombohedral unit cell, geometrically similar to the Cr_5Al_8 structure (Bradley & Lu, 1937; see also Pearson, 1958), but with the lower Laue symmetry $\bar{3}$. The unit-cell dimensions from oscillation and Weissenberg photographs are: $a = 9{\cdot}00$ Å, $\alpha = 109{\cdot}5°$ (the corresponding triply primitive hexagonal cell has $a_H = 14{\cdot}70$, $c_H = 8{\cdot}98$ Å); the probable space groups are $R\bar{3}$ or $R3$. Despite several conditions of heat treatment, good quality powder photographs could not be obtained, and thus it is not certain whether either the tetragonal type or the rhombohedral variety constitute major phases in the YbGe and LuGe preparations.

Refined lattice constants for those rare earth monogermanides with the CrB structure are given in Table 1. Those of other workers are included for the sake of comparison. The space group for this structure is *Cmcm*. Four Ge atoms

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Table 1. *Rare earth monogermanides with* CrB*-type structure*

	a (Å)	σ(*a*) (Å)	*b* (Å)	σ(*b*) (Å)	*c* (Å)	σ(*c*) (Å)	Vol. (Å³)	Reference
PrGe	4·474		11·098		4·064			(1)
NdGe	4·456	0·004	11·027	0·01	4·035	0·004	198·3	This work
SmGe	4·387	0·004	10·890	0·01	3·993	0·004	190·8	This work
EuGe	4·730	0·004	11·194	0·01	4·105	0·004	217·4	This work
GdGe	4·339	0·004	10·788	0·01	3·973	0·004	186·0	This work
	4·175 ± 0·002		10·61 ± 0·01		3·96 ± 0·003			(2)
	4·327		10·77		3·954			(3)
TbGe	4·300	0·004	10·717	0·01	3·950	0·004	182·0	This work
DyGe	4·272	0·004	10·678	0·01	3·931	0·004	179·3	This work
	4·112 ± 0·002		10·81 ± 0·02		3·924 ± 0·006			(2)
	4·263		10·675		3·924			(3)
HoGe	4·247	0·005	10·63	0·02	3·919	0·005	176·9	This work
	4·234		10·61		3·911			(3)
ErGe	4·20		10·58		3·92		174·2	This work (only 5 lines)

(1) Iandelli (1959).
(2) Baenziger & Moriarty (1961).
(3) Parthé, Hohnke, Jeitschko & Schob (1965).

Note: The order of axes in the present results conforms to the space group *Cmcm*. There is some confusion in the literature concerning the order of axes. Baenziger & Moriarty appear to have interchanged *b* and *c*. Iandelli gives no space group so that it is not possible to tell definitely whether $a > c$ or not. (The positional parameters as given correspond also to an *anti*-CrB structure, *i.e.* chains of Pr atoms.) These literature values have here been arranged to correspond with our order.

occupy 4(*c*) positions, $\pm(0, y, \frac{1}{4}; \frac{1}{2}, \frac{1}{2}+y, \frac{1}{4})$ with $y \sim 0{\cdot}42$, and four rare earth atoms occupy another set of 4(*c*) positions with $y \sim 0{\cdot}14$. Using these parameters and scattering factors from *International Tables for X-Ray Crystallography* (1962), the powder pattern for GdGe was calculated with the program of Smith (1963). These results are listed in Table 2.

Table 2. *Crystallographic data for orthorhombic* GdGe

Cu radiation ($K\alpha_1 = 1{\cdot}54050$ Å)

h k l	$\sin^2\theta$* (obs.)	$\sin^2\theta$ (calc.)	*I** (obs.)	*I* (calc.)
0 2 0	—	0·0204	—	1
1 1 0	—	0·0367	—	5
0 2 1	0·0577	0·0581	*w*	20
1 1 1	0·0741	0·0743	*s*	85
1 3 0	0·0774	0·0775	*m*	33
0 4 0	0·0816	0·0817	*m*+	24
1 3 1	0·1150	0·1152	*m*+	40
0 4 1	0·1195	0·1193	*m*	13
2 0 0	0·1266	0·1263	*m*	21
2 2 0	—	0·1467	—	<1
0 0 2	0·1508	0·1506	*m*	16
1 5 0	—	0·1592	—	<1
0 2 2	—	0·1710	—	<1
0 6 0	—	0·1838	—	<1
2 2 1	0·1843	0·1843	*w*	7
1 1 2	—	0·1873	—	1
1 5 1	0·1966	0·1969	*w*+	8
2 4 0	0·2082	0·2080	*w*+	10
0 6 1	0·2216	0·2215	*w*+	6
1 3 2	0·2284	0·2281	*w*+	11
0 4 2	0·2321	0·2323	*w*+	9
2 4 1	0·2455	0·2456	*w*	7
2 0 2	0·2769	0·2769	*m*−	10
1 7 0	0·2821	0·2818	*m*−	9
3 1 0	—	0·2892	—	<1
2 2 2	—	0·2973	—	<1
1 5 2	—	0·3098	—	<1
2 6 0	—	0·3101	—	<1
1 7 1	—	0·3194	—	1

* Dashes indicate unobserved reflexions

$a = 4{\cdot}339$ Å $\quad y_{Gd} = 0{\cdot}14$
$b = 10{\cdot}788$ $\quad y_{Ge} = 0{\cdot}42$
$c = 3{\cdot}973$

Cell constants for the phases with the body-centered tetragonal unit cell are given in Table 3. These values were obtained from single-crystal photographs, and are thus somewhat less accurate than those in Table 2. Crystals of this type are currently under investigation to determine their structure.

Table 3. *Lattice constants* of rare earth monogermanides, body-centered tetragonal type*

	a	*c*	Volume
GdGe	10·93 Å	16·67 Å	1991 Å³
TbGe	10·89	16·49	1956
DyGe	10·81	16·29	1904
HoGe	10·79	16·23	1890
ErGe	10·76	16·09	1863
TmGe	10·72	16·01	1840
YbGe	10·67	16·58	1888
LuGe	10·63	15·78	17·83

* Accuracy is of the order of 0·5 %.

A plot of the cell constants *versus* atomic number for the CrB structure type is given in Fig. 1. All three lattice parameters exhibit well-behaved lanthanide contractions, even to the 'abnormally' high values at europium. A lanthanide contraction is also seen (Fig. 2) in the lattice constants of the body-centered tetragonal cell. It is interesting to note that the anomalous behavior expected at ytterbium is reflected only in the *c*-axis repeat distance.

Summary of results

The present investigation, together with the results now available in the literature, furnishes a fairly complete survey of the rare earth germanium compounds at or near equiatomic proportions.

Hohnke & Parthé (1966) report LaGe and CeGe to crystallize in the FeB structure type, and PrGe to be di-

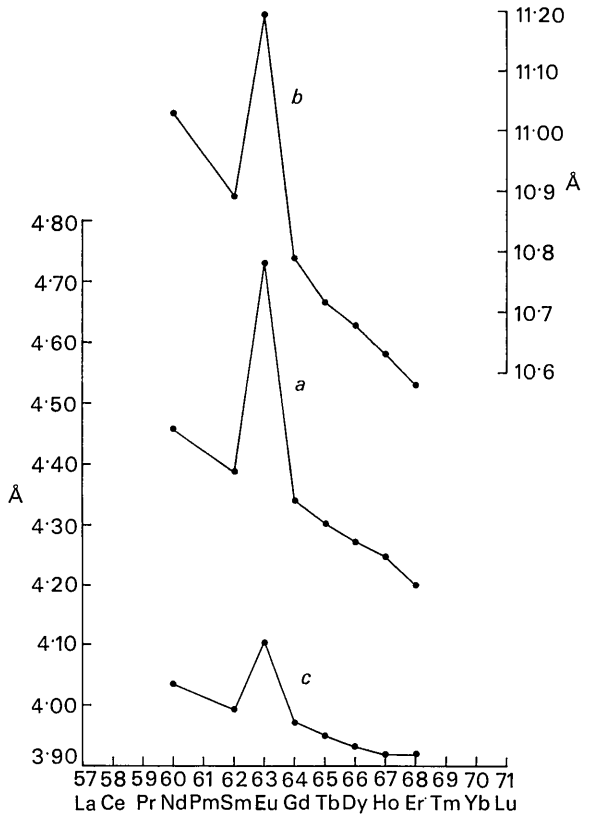

Fig. 1. Variation of the *a*-, *b*-, and *c*-axis lattice constants for the CrB type rare earth monogermanides.

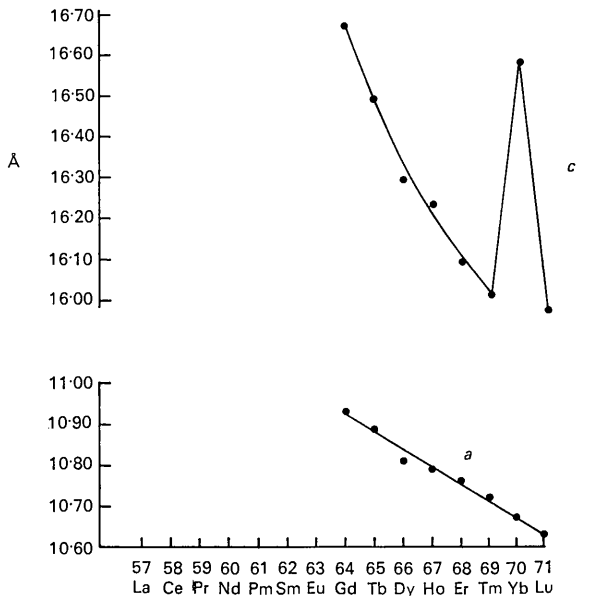

Fig. 2. Variation of the lattice constants for the body-centered tetragonal compounds.

morphous (both FeB and CrB forms). We have confirmed this result for CeGe. The lattice constants obtained, $a = 8{\cdot}356 \pm 0{\cdot}005$; $b = 4{\cdot}084 \pm 0{\cdot}003$; $c = 6{\cdot}041 \pm 0{\cdot}004$ Å ($\lambda = 1{\cdot}54178$ Å), are in good agreement with those of Hohnke & Parthé (1966).

The CrB structure type begins at PrGe (Iandelli, 1959), and our results show that this phase extends to holmium and probably to erbium. Lattice constants for this phase agree excellently with those of Hohnke & Parthé (1966).

About midway through the series, there appears a complex body-centered tetragonal phase. Crystals of this material have been obtained from gadolinium through lutetium. As noted above, Gd, Tb, Dy, Ho, and probably Er also display a CrB-type monogermanide phase. While there is as yet no direct evidence to support formulation of the tetragonal compound as a monogermanide, this material has been consistently obtained when the initial composition of the preparation was equiatomic. A structure analysis is underway (on the holmium compound) to determine the stoichiometry of the crystals.

We wish to thank Prof. E. Parthé for furnishing details of his investigation in advance of publication. We thank also Mr V. Silveira for powder photography.

Note added 16 *September* 1965. – The body-centered tetragonal phase has been found in the yttrium–germanium system. Lattice constants obtained from single-crystal photographs are: $a = 10{\cdot}86$, $c = 16{\cdot}38$ Å.

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