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Crystal Structure of Sm_5Ge_4*

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A new phase in the samarium–germanium system has been shown by X-ray diffraction techniques to have the stoichiometry Sm_5Ge_4. The crystals are orthorhombic with $a=7{\cdot}75$, $b=14{\cdot}94$, $c=7{\cdot}84$ Å; $D_x=7{\cdot}62$ g.cm^{-3} for four Sm_5Ge_4 units per unit cell. Systematic extinctions are characteristic of the space groups *Pnma* and $Pn2_1a$. The structure is conveniently described in terms of three layers which occur along the *b* axis. Layer *G* contains Ge atoms only; layer *S*, Sm only. Layer *C* is a combination of *G* and *S*, but with the roles of Ge and Sm interchanged. Layer *C* serves as a mirror plane in *Pnma*, but only as a quasi-mirror plane in $Pn2_1a$. Least-squares refinement in *Pnma* gives an *R* index of 9·3%; in $Pn2_1a$, an *R* index of 9·0%. Differences between the two sets of parameters are small, and it is concluded that the structure is adequately described in terms of *Pnma*. The similarity of the layers to those occurring in $CuAl_2$ and U_3Si_2 is noted.

Introduction

In the past year or so, structural data on rare earth–germanium compounds have become more plentiful. Surveys of the structure types found for rare earth monogermanides have been given by Gladyshevskii & Uhryn (1965) and independently by Tharp, Smith & Johnson (1966) and Hohnke & Parthé (1966). The digermanides are described by Gladyshevskii (1964*a*), and the R_5Ge_3 compounds by Gladyshevskii (1964*b*). Two other compounds, apparently unique to the particular earth element involved, are known: Yb_3Ge_5 (Smith, Johnson & Tharp, 1965) and $EuGe_2$ (Gladyshevskii, 1964*c*).

Before learning of the results of Gladyshevskii (1964*b*) on the R_5Ge_3 compounds, we had begun a study at this same composition. In agreement with Gladyshevskii, we found Nd_5Ge_3 and Gd_5Ge_3 to be of the $D8_8$–Mn_5Si_3 type. Powder patterns of a Sm_5Ge_3 preparation, however, contained a considerable number of lines not accountable for in terms of the Mn_5Si_3 structure type. An examination of single crystals from this preparation shows the phase to be orthorhombic of an unknown structure type. The crystal-structure determination herein reported indicates the stoichiometry to be Sm_5Ge_4.

Experimental

The preparation was made by arc-melting amounts of samarium and germanium appropriate to a 5:3 composition in a gettered atmosphere of argon. The fused button was turned over and remelted several times to improve the homogeneity. Single-crystal fragments were obtained by crushing the button.

Oscillation, Weissenberg and precession photographs show the crystals to be orthorhombic with the following lattice constants: $a=7{\cdot}75$, $b=14{\cdot}94$, $c=7{\cdot}84$ Å (accuracy of the order of 0·2–0·3%; λ Cu $K\alpha=1{\cdot}5418$ Å). The systematic extinctions ($0kl$, $k+l=$odd; $hk0$, $h=$odd) are characteristic of the space groups *Pnma* and $Pn2_1a$ (*International Tables for X-ray Crystallography*, 1952).

Intensity measurements were carried out on a General Electric XRD-5 diffractometer equipped with a goniostat, scintillation counter, and pulse-height discrimination circuitry. The crystal specimen was approximately rhombic in shape, measuring 0·21 × 0·15 mm along the diagonals and 0·05 mm thick (along the *b* axis). Zr-filtered Mo $K\alpha$ radiation was employed in conjunction with the stationary-crystal stationary-counter technique (Furnas, 1957). A total of 445 reflections were recorded up to a 2θ-cutoff of 40°. These intensities were corrected for background and a φ-dependent absorption, and were converted to a set of relative $|F|$'s through the application of Lorentz-polarization factors. At a later stage when the stoichiometry became known, the φ-dependent absorption factors were replaced by more sophisticated corrections (Wehe, Busing & Levy, 1962). In this latter calculation, a linear absorption coefficient of 460 cm^{-1} was used; this value was obtained from the calculated density (7·62 g.cm^{-3}) and the mass absorption coefficients (for Mo $K\alpha$) tabulated in *International Tables for X-ray Crystallography* (1962).

Determination of the structure

The centrosymmetric space group *Pnma* provides eightfold general positions and fourfold special positions; the general positions in $Pn2_1a$ are fourfold. Thus, the simplest number of atoms consistent also with the expected R_5Ge_3 composition is 20 Sm and 12 Ge. The unit cell volume (908 Å^3) is only about 8% larger than the volume (841 Å^3) required for 20 Sm, 12 Ge in the $D8_8$-type Sm_5Ge_3 (Gladyshevskii, 1964*b*), and thus a less-dense 5:3 modification was not unreasonable. It was also recognized that the extra volume

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(67 Å^3) might result from the insertion of addition atoms. The atomic volumes of Sm and Ge being 33·1 and 22·6 Å^3, respectively (Teatum, Gschneidner & Waber, 1959), four additional Ge atoms were considered the more likely.

An essential difference between the space group alternatives is in the symmetry along the *b* axis. For *Pnma*, vector interactions across the mirror plane give rise to Patterson peaks along the line, O,W,O. The observed Patterson map, however, had only one large peak on this line; this peak, however, was not the largest one in the map. We were thus led to try a solution in terms of the non-centrosymmetric space group, $Pn2_1a$, with all atoms in the 4(*a*) positions $(x,y,z;\ \bar{x},\frac{1}{2}+y,\bar{z};\ \frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}+z;\ \frac{1}{2}+x,y,\frac{1}{2}-z)$. A structure model involving 16 Sm atoms in four sets of these positions accounted for the majority of peaks in the Patterson map. With these atoms as phase determining, Fourier syntheses of electron density disclosed another fourfold Sm and four sets of fourfold Ge atoms.

It was then realized that this structure was describable also in terms of *Pnma*, *i.e.* the unit of structure seemed to have a mirror plane of symmetry. (Alternatively, a center of symmetry operation could be applied to the above listed 4(*a*) positions.) With several pairs of what were independent fourfold atoms in $Pn2_1a$ now being coalesced into single eightfold sets in *Pnma*, the reduction in the number of structural parameters was nontrivial (36 in $Pn2_1a$ *vs* 22 in *Pnma*). For comparative purposes, refinement cycles were carried out in both space groups and with both types of absorption corrections. Refinement was *via* the full-matrix, least-squares program of Gantzel, Sparks & Trueblood (ACA Program No. 317, unpublished). The scattering factors were Hartree–Fock–Slater values of Hanson, Herman, Lea & Skillman (1964) for the neutral atoms. The quantity minimized was $\Sigma w(F_o-F_c)^2$. As an approximation to a weighting scheme appropriate for diffractometric data, the following weights were used: $w=F_o^{1/4}$ for $F_o<A$, $w=A^{5/4}F_o^{-1}$ for $F_o>A$. The value of A depended upon which absorption corrections were used, and was adjusted to make refinement cycles directly comparable. On the scale of the structure-factor data in Table 1, A is 368. For the refinement in $Pn2_1a$ the y parameter of Sm(3) was fixed at 0·25.

The results from these refinements showed a clear-cut superiority of the absorption corrections calculated by the method of Wehe, Busing & Levy (1962). In subsequent cycles, only these corrections were considered. With respect to the question of space group, the conventional R values were: 9·3% for *Pnma* and 9·0% for $Pn2_1a$. (For both cases, parameter shifts in the last cycle were <0·1 the corresponding e.s.d.'s.) Thus, despite the greater flexibility of model in $Pn2_1a$, the R value was not materially improved. In fact, the positional parameters were very nearly the same for the two refinements series (as might be judged from the similarity in R values obtained). Temperature parameters were well-behaved during the refinement in *Pnma*, and, all told, there is no compelling reason to abandon *Pnma* in favor of $Pn2_1a$. Grosser features of the structure are, of course, unaltered, whichever space group is adopted.*

The relatively large R values obtained in these refinements reflect, we judge, uncertainties in the absorption corrections. These corrections are large, and over the range of φ, χ and 2θ encountered, vary between rather wide limits (minimum value 10; maximum value 99). The dimensions of the crystal were

* In the first version of this manuscript, we had erroneously stated that the refinement in *Pnma* gave an R of 14·8%, and we had concluded that the space group was more likely $Pn2_1a$. This error, later traced to faulty computer input, was called to our attention by the referee, Dr R. E. Marsh. We are greatly indebted to Dr Marsh for his efforts in this matter.

Table 1. *Observed and calculated structure factors*

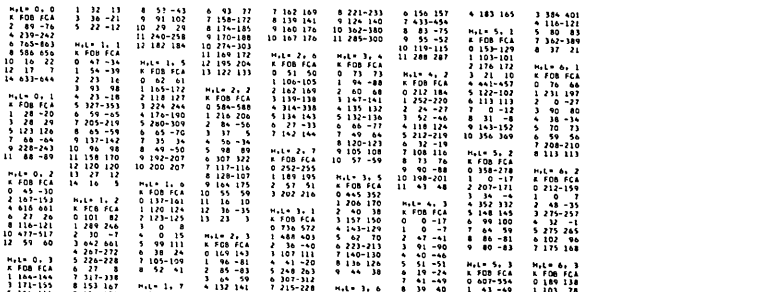

Table 2. *Final parameters in* Sm_5Ge_4

E.S.D.'s are given in parentheses.

Atom	Wyckoff symbol	10^4x	10^4y	10^4z	B
Sm(1)	(*d*)	1205 (5)	1157 (3)	3388 (5)	1·1 ± 0·1 Å^2
Sm(2)	(*d*)	−253 (5)	1004 (3)	−1781 (5)	1·1 ± 0·1
Sm(3)	(*c*)	2880 (8)	2500	24 (8)	1·1 ± 0·1
Ge(1)	(*c*)	−868 (16)	2500	1115 (15)	1·2 ± 0·2
Ge(2)	(*c*)	1761 (15)	2500	−3667 (15)	1·1 ± 0·3
Ge(3)	(*d*)	2206 (11)	−449 (6)	−4688 (11)	1·1 ± 0·2

carefully measured, but its actual shape could be only approximately described. Considerable error in the corrections may have resulted where absorption is large and/or varying rapidly. Such a case of large absorption occurs for low-angle reflections with small values of the Miller index k. There, the observed structure amplitudes are generally larger than the calculated values, as if absorption was overestimated in this region.

Atomic parameters obtained from the refinement in *Pnma* were accepted as final. These are given in Table 2.

Discussion

The structure is conveniently described in terms of three types of network (Fig. 1) which occur along the b axis. Layer G contains Ge atoms only; layer S, Sm atoms only. (There are twice as many atoms per layer in S as in G.) Layer C is a combination of G and S, but with the roles of Ge and Sm interchanged. The stacking sequence for $0 \le y \le \frac{1}{2}$ is *GSCSG* with layer C at $y = \frac{1}{4}$ serving as a mirror plane in *Pnma*. A twofold screw axis passing through the origin operates on these nets to produce the stacking sequence for $\frac{1}{2} \le y \le 1$. Interestingly enough, this arrangement gives a calculated density (7·62 g.cm^{-3}) for Sm_5Ge_4 which is slightly larger than the density (7·54 g.cm^{-3}) in metallic samarium (Daane, Rundle, Smith & Spedding, 1954).

Layers G and S are similar to those found in the tetragonal $CuAl_2$–$C16$ structure type. (Indeed, Sm_5Ge_4 is pseudo-tetragonal in its lattice constants.) The S-type net has also been singled out by Frank & Kasper (1958, 1959) as a frequent structural motif in intermetallic compounds. A network of the C type occurs in U_3Si_2, (Zachariasen, 1949) as does the S type. Thus, in a formal sense, the Sm_5Ge_4 structure is a hybrid of the $CuAl_2$ and U_3Si_2 networks, an appropriate number of layer types being included to give the required composition. However, it should be pointed out that some of the lines which connect atoms in Fig. 1 do not necessarily represent bonds between atoms. For example, in the C layer, the Ge atoms occur actually in pairs, the bond distance being 2·66 Å. In the S layer, distances involving the five neighbors of a given Sm always exceed twice the radius of Sm; some are ~17% in excess of this value. Very similar features are found in U_3Si_2. In particular, the Si atoms occur also in pairs.

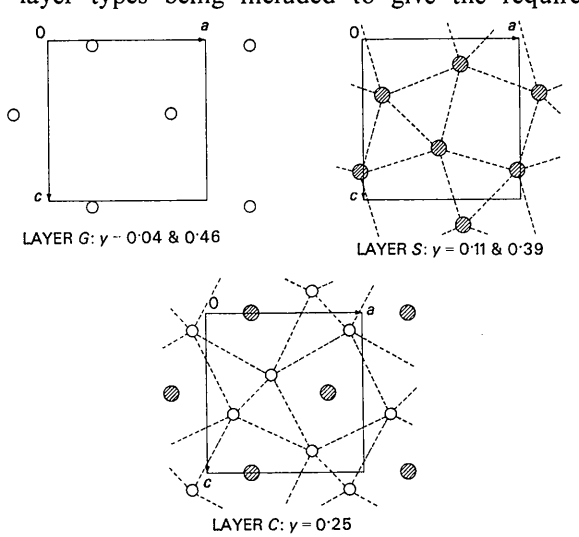

Fig. 1. The three types of network in Sm_5Ge_4 and their elevations along the b axis. Open circles: Ge; shaded circles: Sm.

Coordination polyhedra are most readily visualized for atoms in layer C. Sm(3) is surrounded by a cube of Sm atoms and an octahedron of Ge, thereby attaining a coordination number (C.N.) of 14. Alternatively, the configuration can be regarded as a cuboctahedron +2 Ge. (Several atoms being in general positions, the geometric figures are not in general regular.) The Sm(3)–8Sm distances (Table 3) are in the range 3·50–3·68 Å; the Sm(3)–6 Ge distances, 3·02–3·19 Å. For purposes of comparison, the atomic radii for C.N. = 12 are: Sm = 1·80 Å, Ge = 1·37 Å (Teatum, Gschneidner & Waber, 1959). Ge(1) and Ge(2) are both surrounded by 6 Sm in a trigonal prism arrangement; 2 Sm and a Ge within the C layer complete a ninefold coordination. The Ge–Sm distances are 3·03–3·24 Å; the Ge–Ge distance, also referred to above, is 2·66 Å. These coordination polyhedra have their counterparts in U_3Si_2. The coordination, however, about uranium is that of a cuboctahedron, *i.e.* C.N. = 12.

Interatomic distances involving atoms in the G and S layers are rather more diffuse and the coordination polyhedra less well-defined. The four closest Sm neighbors around both Sm(1) and Sm(2) outline a tetrahedron; however, as previously mentioned, there are additional samarium atoms within the S layer which are at distances not much greater than twice the atomic radius of Sm. The following results for Sm(1) are cited to typify this situation: the four shortest Sm(1)–Sm distances are 3·50, 3·54, 3·56 and 3·83 Å; the five longer distances are 3·96, 4·01, 4·12(twice) and 4·22 Å. The germanium atom coordination around each of the S-layer Sm atoms is roughly octahedral. The extremes in these distances are 2·91 and 3·26 Å. Ge(3) is surrounded by 7 Sm atoms in a configuration loosely describable as pentagonal bipyramidal. The extremes in distances here are also 2·91 and 3·26 Å. Ge(3) does not form bonds with other germanium atoms.

There is nothing in the structural results which would seem particular to Sm alone among the rare earth metals. It is therefore not surprising that this phase has now been found for all of the other lanthanide elements thus far examined (Nd, Gd, Tb, Er and Y). The *a priori* case for similar compounds with silicon is harder to assess. On the one hand, the trigonal prism+3-coordination around Ge(1) and Ge(2) is also a persistent grouping in silicides. It is not, however, certain whether the coordination-type exhibited by

Table 3. *Interatomic distances less than* 4·3 Å *in* Sm_5Ge_4

The σ's include only uncertainties in positional parameters.

Atom 1	Atom 2	Distance (Å)	σ (Å)	Atom 1	Atom 2	Distance (Å)	σ (Å)
Sm 1	Ge 3	2·908	0·009	Sm 3	2 Sm 1	3·496	0·007
	Ge 3	2·939	0·010		2 Sm 1	3·560	0·007
	Ge 3	3·025	0·010		2 Sm 2	3·592	0·007
	Ge 1	3·054	0·010		2 Sm 2	3·682	0·007
	Ge 2	3·089	0·010				
	Ge 1	3·128	0·010	Ge 1	Ge 2	2·658	0·017
	Sm 3	3·496	0·007		Sm 3	3·029	0·014
	Sm 2	3·544	0·006		2 Sm 1	3·054	0·010
	Sm 3	3·560	0·007		2 Sm 1	3·128	0·010
	Sm 2	3·830	0·006		Sm 3	3·180	0·014
	Sm 2	3·960	0·006		2 Sm 2	3·222	0·010
	Sm 1	4·012	0·008		2 Ge 3	4·224	0·012
	2 Sm 1	4·119	0·003		Ge 2	4·268	0·017
	Sm 2	4·215	0·006		2 Ge 3	4·280	0·012
Sm 2	Ge 3	2·994	0·010	Ge 2	Ge 1	2·658	0·017
	Ge 2	3·012	0·009		Sm 3	3·021	0·014
	Ge 3	3·150	0·010		2 Sm 1	3·089	0·010
	Ge 1	3·222	0·010		2 Sm 2	3·102	0·009
	Ge 2	3·237	0·009		Sm 3	3·192	0·013
	Ge 3	3·262	0·009		2 Sm 2	3·237	0·009
	Sm 1	3·544	0·006		Ge 1	4·268	0·017
	Sm 3	3·592	0·007		2 Ge 2	4·287	0·010
	Ge 3	3·680	0·010				
	Sm 3	3·682	0·007	Ge 3	Sm 1	2·908	0·009
	Sm 1	3·830	0·006		Sm 1	2·939	0·010
	Sm 1	3·960	0·006		Sm 2	2·994	0·010
	2 Sm 2	4·037	0·002		Sm 1	3·025	0·010
	Sm 2	4·118	0·008		Sm 3	3·073	0·009
	Sm 1	4·215	0·006		Sm 2	3·150	0·010
					Sm 2	3·262	0·009
Sm 3	Ge 2	3·021	0·014		Sm 2	3·680	0·010
	Ge 1	3·029	0·014		Ge 3	3·706	0·018
	2 Ge 3	3·073	0·009		2 Ge 3	4·169	0·006
	Ge 1	3·180	0·014		Ge 1	4·224	0·012
	Ge 2	3·192	0·013		2 Ge 1	4·280	0·012

Ge(3) will be retained when Si with a 4% smaller radius (Teatum, Gschneidner & Waber, 1959) replaces Ge. Work is currently in progress to investigate the occurrence of this phase in rare earth germanium and silicon systems.

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