

## Crystal Structure of $\text{Sm}_5\text{Ge}_4$ \*

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A new phase in the samarium-germanium system has been shown by X-ray diffraction techniques to have the stoichiometry  $\text{Sm}_5\text{Ge}_4$ . The crystals are orthorhombic with  $a=7.75$ ,  $b=14.94$ ,  $c=7.84$  Å;  $D_x=7.62$  g.cm<sup>-3</sup> for four  $\text{Sm}_5\text{Ge}_4$  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  $\text{CuAl}_2$  and  $\text{U}_3\text{Si}_2$  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  $\text{R}_5\text{Ge}_3$  compounds by Gladyshevskii (1964*b*). Two other compounds, apparently unique to the particular earth element involved, are known:  $\text{Yb}_3\text{Ge}_5$  (Smith, Johnson & Tharp, 1965) and  $\text{EuGe}_2$  (Gladyshevskii, 1964*c*).

Before learning of the results of Gladyshevskii (1964*b*) on the  $\text{R}_5\text{Ge}_3$  compounds, we had begun a study at this same composition. In agreement with Gladyshevskii, we found  $\text{Nd}_5\text{Ge}_3$  and  $\text{Gd}_5\text{Ge}_3$  to be of the  $D8_8\text{-Mn}_5\text{Si}_3$  type. Powder patterns of a  $\text{Sm}_5\text{Ge}_3$  preparation, however, contained a considerable number of lines not accountable for in terms of the  $\text{Mn}_5\text{Si}_3$  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  $\text{Sm}_5\text{Ge}_4$ .

### 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:  $a=7.75$ ,  $b=14.94$ ,  $c=7.84$  Å (accuracy of the order of 0.2–0.3%;  $\lambda$  Cu  $K\alpha=1.5418$  Å). The systematic extinctions ( $0kl$ ,  $k+l=\text{odd}$ ;  $hk0$ ,  $h=\text{odd}$ ) 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  $0.21 \times 0.15$  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  $2\theta$ -cutoff of  $40^\circ$ . These intensities were corrected for background and a  $\varphi$ -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  $\varphi$ -dependent absorption factors were replaced by more sophisticated corrections (Wehe, Busing & Levy, 1962). In this latter calculation, a linear absorption coefficient of  $460$  cm<sup>-1</sup> was used; this value was obtained from the calculated density ( $7.62$  g.cm<sup>-3</sup>) 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  $\text{R}_5\text{Ge}_3$  composition is 20 Sm and 12 Ge. The unit cell volume ( $908$  Å<sup>3</sup>) is only about 8% larger than the volume ( $841$  Å<sup>3</sup>) required for 20 Sm, 12 Ge in the  $D8_8$ -type  $\text{Sm}_5\text{Ge}_3$  (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<sup>3</sup>) might result from the insertion of addition atoms. The atomic volumes of Sm and Ge being 33.1 and 22.6 Å<sup>3</sup>, 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<sub>1</sub>a*, with all atoms in the 4(*a*) positions (*x, y, z; x̄, ½ + y, z̄; ½ - x, ½ + y, ½ + z; ½ + x, y, ½ - 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<sub>1</sub>a* now being coalesced into single eightfold sets in *Pnma*, the reduction in the number of structural parameters was nontrivial (36 in *Pn2<sub>1</sub>a* 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  $\sum w(F_o - F_c)^2$ . 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<sub>1</sub>a* 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 con-

sidered. With respect to the question of space group, the conventional *R* values were: 9.3% for *Pnma* and 9.0% for *Pn2<sub>1</sub>a*. (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<sub>1</sub>a*, 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<sub>1</sub>a*. 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  $\phi$ ,  $\chi$  and  $2\theta$  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<sub>1</sub>a*. 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

|            |                  |            |              |              |              |            |            |            |
|------------|------------------|------------|--------------|--------------|--------------|------------|------------|------------|
| hkl 0 0 0  | 1 32 13          | 8 57 43    | 6 93 77      | 7 162 160    | 8 221-233    | 6 150 157  | 4 283 165  | 3 356 401  |
| hkl 0 0 1  | 2 89 76          | 5 22 12    | 10 29 29     | 8 136 161    | 9 126 140    | 7 433 456  | 4 116 121  | 4 116 121  |
| hkl 0 0 2  | 4 233 229        | 11 240 258 | 9 170 188    | 9 161 172    | 10 164 180   | 8 83 75    | 7 332 389  | 4 37 21    |
| hkl 0 0 3  | 6 765 103        | 12 182 186 | 11 169 187   | 10 169 187   | 11 285 300   | 9 55 52    | 8 FDB FCA  | 4 101 115  |
| hkl 0 0 4  | 8 556 556        | 13 182 186 | 12 182 186   | 12 182 186   | 13 285 300   | 10 119 115 | 9 151 151  | 8 151 151  |
| hkl 0 0 5  | 10 10 12         | 14 633 633 | 13 122 133   | 12 182 186   | 13 285 300   | 11 288 287 | 10 101 101 | 9 176 176  |
| hkl 0 0 6  | 12 17 17         | 15 56 59   | 14 107 111   | 13 122 133   | 14 51 50     | 10 71 73   | 9 21 10    | 8 FDB FCA  |
| hkl 0 0 7  | 14 633 633       | 16 23 16   | 15 67 61     | 14 107 111   | 15 106 105   | 11 76 68   | 10 FDB FCA | 9 276 276  |
| hkl 0 0 8  | 16 23 16         | 17 93 98   | 16 105 112   | 15 67 61     | 16 102 102   | 12 60 68   | 11 212 184 | 10 271 197 |
| hkl 0 0 9  | 18 108 108       | 18 23 16   | 17 118 127   | 16 105 112   | 17 118 127   | 13 136 136 | 12 252 270 | 11 270 270 |
| hkl 0 0 10 | 20 270 270       | 19 93 98   | 18 224 244   | 17 118 127   | 18 224 244   | 14 135 132 | 13 252 270 | 12 270 270 |
| hkl 0 0 11 | 24 324 324       | 20 23 16   | 19 246 266   | 18 224 244   | 19 246 266   | 15 132 132 | 14 270 270 | 13 270 270 |
| hkl 0 0 12 | 28 396 396       | 21 93 98   | 20 270 290   | 19 246 266   | 20 270 290   | 16 130 130 | 15 270 270 | 14 270 270 |
| hkl 0 0 13 | 34 468 468       | 22 23 16   | 21 306 326   | 20 270 290   | 21 306 326   | 17 128 128 | 16 270 270 | 15 270 270 |
| hkl 0 0 14 | 40 540 540       | 23 93 98   | 22 342 362   | 21 306 326   | 22 342 362   | 18 126 126 | 17 270 270 | 16 270 270 |
| hkl 0 0 15 | 48 648 648       | 24 23 16   | 23 378 398   | 22 342 362   | 23 378 398   | 19 124 124 | 18 270 270 | 17 270 270 |
| hkl 0 0 16 | 56 784 784       | 25 93 98   | 24 414 434   | 23 342 362   | 24 414 434   | 20 122 122 | 19 270 270 | 18 270 270 |
| hkl 0 0 17 | 66 936 936       | 26 23 16   | 25 450 470   | 24 414 434   | 25 450 470   | 21 120 120 | 20 270 270 | 19 270 270 |
| hkl 0 0 18 | 78 1116 1116     | 27 93 98   | 26 486 506   | 25 450 470   | 26 486 506   | 22 118 118 | 21 270 270 | 20 270 270 |
| hkl 0 0 19 | 92 1320 1320     | 28 23 16   | 27 522 542   | 26 486 506   | 27 522 542   | 23 116 116 | 22 270 270 | 21 270 270 |
| hkl 0 0 20 | 108 1560 1560    | 29 93 98   | 28 558 578   | 27 522 542   | 28 558 578   | 24 114 114 | 23 270 270 | 22 270 270 |
| hkl 0 0 21 | 126 1824 1824    | 30 23 16   | 29 594 614   | 28 558 578   | 29 594 614   | 25 112 112 | 24 270 270 | 23 270 270 |
| hkl 0 0 22 | 146 2112 2112    | 31 93 98   | 30 630 650   | 29 594 614   | 30 630 650   | 26 110 110 | 25 270 270 | 24 270 270 |
| hkl 0 0 23 | 168 2424 2424    | 32 23 16   | 31 666 686   | 30 630 650   | 31 666 686   | 27 108 108 | 26 270 270 | 25 270 270 |
| hkl 0 0 24 | 192 2760 2760    | 33 93 98   | 32 702 722   | 31 666 686   | 32 702 722   | 28 106 106 | 27 270 270 | 26 270 270 |
| hkl 0 0 25 | 218 3120 3120    | 34 23 16   | 33 738 758   | 32 702 722   | 33 738 758   | 29 104 104 | 28 270 270 | 27 270 270 |
| hkl 0 0 26 | 246 3504 3504    | 35 93 98   | 34 774 794   | 33 738 758   | 34 774 794   | 30 102 102 | 29 270 270 | 28 270 270 |
| hkl 0 0 27 | 276 3912 3912    | 36 23 16   | 35 810 830   | 34 774 794   | 35 810 830   | 31 100 100 | 30 270 270 | 29 270 270 |
| hkl 0 0 28 | 308 4344 4344    | 37 93 98   | 36 846 866   | 35 810 830   | 36 846 866   | 32 98 98   | 31 270 270 | 30 270 270 |
| hkl 0 0 29 | 342 4800 4800    | 38 23 16   | 37 882 902   | 36 846 866   | 37 882 902   | 33 96 96   | 32 270 270 | 31 270 270 |
| hkl 0 0 30 | 378 5280 5280    | 39 93 98   | 38 918 938   | 37 882 902   | 38 918 938   | 34 94 94   | 33 270 270 | 32 270 270 |
| hkl 0 0 31 | 416 5784 5784    | 40 23 16   | 39 954 974   | 38 918 938   | 39 954 974   | 35 92 92   | 34 270 270 | 33 270 270 |
| hkl 0 0 32 | 456 6300 6300    | 41 93 98   | 40 990 1010  | 39 954 974   | 40 990 1010  | 36 90 90   | 35 270 270 | 34 270 270 |
| hkl 0 0 33 | 500 6840 6840    | 42 23 16   | 41 1026 1046 | 40 990 1010  | 41 1026 1046 | 37 88 88   | 36 270 270 | 35 270 270 |
| hkl 0 0 34 | 546 7404 7404    | 43 93 98   | 42 1062 1082 | 41 1026 1046 | 42 1062 1082 | 38 86 86   | 37 270 270 | 36 270 270 |
| hkl 0 0 35 | 594 7992 7992    | 44 23 16   | 43 1098 1118 | 42 1062 1082 | 43 1098 1118 | 39 84 84   | 38 270 270 | 37 270 270 |
| hkl 0 0 36 | 644 8604 8604    | 45 93 98   | 44 1134 1154 | 43 1098 1118 | 44 1134 1154 | 40 82 82   | 39 270 270 | 38 270 270 |
| hkl 0 0 37 | 696 9240 9240    | 46 23 16   | 45 1170 1190 | 44 1134 1154 | 45 1170 1190 | 41 80 80   | 40 270 270 | 39 270 270 |
| hkl 0 0 38 | 750 9900 9900    | 47 93 98   | 46 1206 1226 | 45 1170 1190 | 46 1206 1226 | 42 78 78   | 41 270 270 | 40 270 270 |
| hkl 0 0 39 | 806 10584 10584  | 48 23 16   | 47 1242 1262 | 46 1206 1226 | 47 1242 1262 | 43 76 76   | 42 270 270 | 41 270 270 |
| hkl 0 0 40 | 864 11292 11292  | 49 93 98   | 48 1278 1298 | 47 1242 1262 | 48 1278 1298 | 44 74 74   | 43 270 270 | 42 270 270 |
| hkl 0 0 41 | 924 12024 12024  | 50 23 16   | 49 1314 1334 | 48 1278 1298 | 49 1314 1334 | 45 72 72   | 44 270 270 | 43 270 270 |
| hkl 0 0 42 | 986 12780 12780  | 51 93 98   | 50 1350 1370 | 49 1314 1334 | 50 1350 1370 | 46 70 70   | 45 270 270 | 44 270 270 |
| hkl 0 0 43 | 1050 13560 13560 | 52 23 16   | 51 1386 1406 | 50 1350 1370 | 51 1386 1406 | 47 68 68   | 46 270 270 | 45 270 270 |
| hkl 0 0 44 | 1116 14364 14364 | 53 93 98   | 52 1422 1442 | 51 1386 1406 | 52 1422 1442 | 48 66 66   | 47 270 270 | 46 270 270 |
| hkl 0 0 45 | 1184 15184 15184 | 54 23 16   | 53 1458 1478 | 52 1422 1442 | 53 1458 1478 | 49 64 64   | 48 270 270 | 47 270 270 |
| hkl 0 0 46 | 1254 16020 16020 | 55 93 98   | 54 1494 1514 | 53 1458 1478 | 54 1494 1514 | 50 62 62   | 49 270 270 | 48 270 270 |
| hkl 0 0 47 | 1326 16872 16872 | 56 23 16   | 55 1530 1550 | 54 1494 1514 | 55 1530 1550 | 51 60 60   | 50 270 270 | 49 270 270 |
| hkl 0 0 48 | 1400 17740 17740 | 57 93 98   | 56 1566 1586 | 55 1530 1550 | 56 1566 1586 | 52 58 58   | 51 270 270 | 50 270 270 |
| hkl 0 0 49 | 1476 18624 18624 | 58 23 16   | 57 1602 1622 | 56 1566 1586 | 57 1602 1622 | 53 56 56   | 52 270 270 | 51 270 270 |
| hkl 0 0 50 | 1554 19524 19524 | 59 93 98   | 58 1638 1658 | 57 1602 1622 | 58 1638 1658 | 54 54 54   | 53 270 270 | 52 270 270 |
| hkl 0 0 51 | 1634 20440 20440 | 60 23 16   | 59 1674 1694 | 58 1638 1658 | 59 1674 1694 | 55 52 52   | 54 270 270 | 53 270 270 |
| hkl 0 0 52 | 1716 21372 21372 | 61 93 98   | 60 1710 1730 | 59 1674 1694 | 60 1710 1730 | 56 50 50   | 55 270 270 | 54 270 270 |
| hkl 0 0 53 | 1800 22320 22320 | 62 23 16   | 61 1746 1766 | 60 1710 1730 | 61 1746 1766 | 57 48 48   | 56 270 270 | 55 270 270 |
| hkl 0 0 54 | 1886 23280 23280 | 63 93 98   | 62 1782 1802 | 61 1746 1766 | 62 1782 1802 | 58 46 46   | 57 270 270 | 56 270 270 |
| hkl 0 0 55 | 1974 24252 24252 | 64 23 16   | 63 1818 1838 | 62 1782 1802 | 63 1818 1838 | 59 44 44   | 58 270 270 | 57 270 270 |
| hkl 0 0 56 | 2064 25236 25236 | 65 93 98   | 64 1854 1874 | 63 1818 1838 | 64 1854 1874 | 60 42 42   | 59 270 270 | 58 270 270 |
| hkl 0 0 57 | 2156 26232 26232 | 66 23 16   | 65 1890 1910 | 64 1854 1874 | 65 1890 1910 | 61 40 40   | 60 270 270 | 59 270 270 |
| hkl 0 0 58 | 2250 27240 27240 | 67 93 98   | 66 1926 1946 | 65 1890 1910 | 66 1926 1946 | 62 38 38   | 61 270 270 | 60 270 270 |
| hkl 0 0 59 | 2346 28260 28260 | 68 23 16   | 67 1962 1982 | 66 1926 1946 | 67 1962 1982 | 63 36 36   | 62 270 270 | 61 270 270 |
| hkl 0 0 60 | 2444 29292 29292 | 69 93 98   | 68 1998 2018 | 67 1962 1982 | 68 1998 2018 | 64 34 34   | 63 270 270 | 62 270 270 |
| hkl 0 0 61 | 2544 30336 30336 | 70 23 16   | 69 2034 2054 | 68 1998 2018 | 69 2034 2054 | 65 32 32   | 64 270 270 | 63 270 270 |
| hkl 0 0 62 | 2646 31392 31392 | 71 93 98   | 70 2070 2090 | 69 2034 2054 | 70 2070 2090 | 66 30 30   | 65 270 270 | 64 270 270 |
| hkl 0 0 63 | 2750 32460 32460 | 72 23 16   | 71 2106 2126 | 70 2070 2090 | 71 2106 2126 | 67 28 28   | 66 270 270 | 65 270 270 |
| hkl 0 0 64 | 2856 33540 33540 | 73 93 98   | 72 2142 2162 | 71 2106 2126 | 72 2142 2162 | 68 26 26   | 67 270 270 | 66 270 270 |
| hkl 0 0 65 | 2964 34632 34632 | 74 23 16   | 73 2178 2198 | 72 2142 2162 | 73 2178 2198 | 69 24 24   | 68 270 270 | 67 270 270 |
| hkl 0 0 66 | 3074 35736 35736 | 75 93 98   | 74 2214 2234 | 73 2178 2198 | 74 2214 2234 | 70 22 22   | 69 270 270 | 68 270 270 |
| hkl 0 0 67 | 3186 36852 36852 | 76 23 16   | 75 2250 2270 | 74 2214 2234 | 75 2250 2270 | 71 20 20   | 70 270 270 | 69 270 270 |
| hkl 0 0 68 | 3300 37980 37980 | 77 93 98   | 76 2286 2306 | 75 2250 2270 | 76 2286 2306 | 72 18 18   | 71 270 270 | 70 270 270 |
| hkl 0 0 69 | 3416 39120 39120 | 78 23 16   | 77 2322 2342 | 76 2286 2306 | 77 2322 2342 | 73 16 16   | 72 270 270 | 71 270 270 |
| hkl 0 0 70 | 3534 40272 40272 | 79 93 98   | 78 2358 2378 | 7            |              |            |            |            |

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  $0 \leq y \leq \frac{1}{2}$  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  $\frac{1}{2} \leq y \leq 1$ . Interestingly enough, this arrangement gives a calculated density ( $7.62 \text{ g.cm}^{-3}$ ) for  $\text{Sm}_5\text{Ge}_4$  which is slightly larger than the density ( $7.54 \text{ g.cm}^{-3}$ ) in metallic samarium (Daane, Rundle, Smith & Spedding, 1954).

Layers  $G$  and  $S$  are similar to those found in the tetragonal  $\text{CuAl}_2$ - $C16$  structure type. (Indeed,  $\text{Sm}_5\text{Ge}_4$  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  $\text{U}_3\text{Si}_2$ , (Zachariasen, 1949) as does the  $S$  type. Thus, in a formal sense, the  $\text{Sm}_5\text{Ge}_4$  structure is a hybrid of the  $\text{CuAl}_2$  and  $\text{U}_3\text{Si}_2$  networks, an appropriate number of layer types being included to give the required

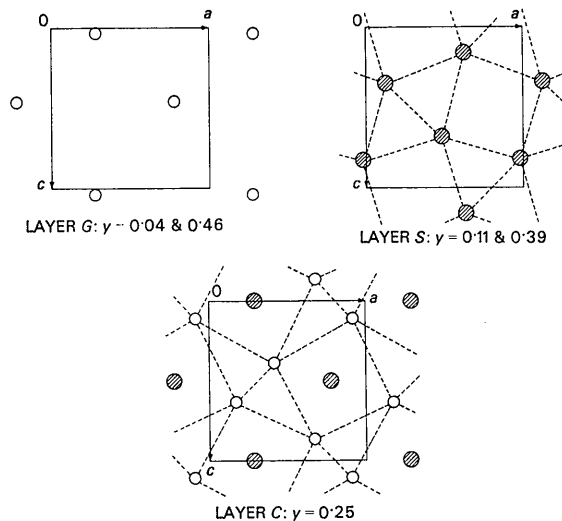


Fig. 1. The three types of network in  $\text{Sm}_5\text{Ge}_4$  and their elevations along the  $b$  axis. Open circles: Ge; shaded circles: Sm.

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  $2.66 \text{ \AA}$ . In the  $S$  layer, distances involving the five neighbors of a given Sm always exceed twice the radius of Sm; some are  $\sim 17\%$  in excess of this value. Very similar features are found in  $\text{U}_3\text{Si}_2$ . In particular, the Si atoms occur also in pairs.

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  $3.50$ - $3.68 \text{ \AA}$ ; the Sm(3)-6 Ge distances,  $3.02$ - $3.19 \text{ \AA}$ . For purposes of comparison, the atomic radii for C.N. = 12 are: Sm =  $1.80 \text{ \AA}$ , Ge =  $1.37 \text{ \AA}$  (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  $3.03$ - $3.24 \text{ \AA}$ ; the Ge-Ge distance, also referred to above, is  $2.66 \text{ \AA}$ . These coordination polyhedra have their counterparts in  $\text{U}_3\text{Si}_2$ . 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  $3.83 \text{ \AA}$ ; the five longer distances are  $3.96$ ,  $4.01$ ,  $4.12$  (twice) and  $4.22 \text{ \AA}$ . The germanium atom coordination around each of the  $S$ -layer Sm atoms is roughly octahedral. The extremes in these distances are  $2.91$  and  $3.26 \text{ \AA}$ . 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  $3.26 \text{ \AA}$ . 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  $\text{Sm}_5\text{Ge}_4$* The  $\sigma$ 's include only uncertainties in positional parameters.

| Atom 1 | Atom 2 | Distance (Å) | $\sigma$ (Å) | Atom 1 | Atom 2 | Distance (Å) | $\sigma$ (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   | Ge 2   | 2.658        | 0.017        |       |
|        | Ge 1   | 3.128        | 0.010        |        | Sm 3   | 3.029        | 0.014        |       |
|        | Sm 3   | 3.496        | 0.007        |        | 2 Sm 1 | 3.054        | 0.010        |       |
|        | Sm 2   | 3.544        | 0.006        |        | 2 Sm 1 | 3.128        | 0.010        |       |
|        | Sm 3   | 3.560        | 0.007        |        | Sm 3   | 3.180        | 0.014        |       |
|        | Sm 2   | 3.830        | 0.006        |        | 2 Sm 2 | 3.222        | 0.010        |       |
|        | Sm 2   | 3.960        | 0.006        |        | 2 Ge 3 | 4.224        | 0.012        |       |
|        | Sm 1   | 4.012        | 0.008        |        | Ge 2   | 4.268        | 0.017        |       |
|        | 2 Sm 1 | 4.119        | 0.003        |        | 2 Ge 3 | 4.280        | 0.012        |       |
|        | Sm 2   | 4.215        | 0.006        |        | Ge 2   | Ge 1         | 2.658        | 0.017 |
|        | Sm 2   | Ge 3         | 2.994        | 0.010  |        | Sm 3         | 3.021        | 0.014 |
| Ge 2   |        | 3.012        | 0.009        | 2 Sm 1 |        | 3.089        | 0.010        |       |
| Ge 3   |        | 3.150        | 0.010        | 2 Sm 2 |        | 3.102        | 0.009        |       |
| Ge 1   |        | 3.222        | 0.010        | Sm 3   |        | 3.192        | 0.013        |       |
| Ge 2   |        | 3.237        | 0.009        | 2 Sm 2 |        | 3.237        | 0.009        |       |
| Ge 3   |        | 3.262        | 0.009        | Ge 1   |        | 4.268        | 0.017        |       |
| Sm 1   |        | 3.544        | 0.006        | 2 Ge 2 |        | 4.287        | 0.010        |       |
| Sm 3   |        | 3.592        | 0.007        | Ge 3   |        | Sm 1         | 2.908        | 0.009 |
| Ge 3   |        | 3.680        | 0.010        |        |        | Sm 1         | 2.939        | 0.010 |
| Sm 3   |        | 3.682        | 0.007        |        | Sm 2   | 2.994        | 0.010        |       |
| Sm 1   |        | 3.830        | 0.006        |        | Sm 1   | 3.025        | 0.010        |       |
| Sm 1   |        | 3.960        | 0.006        |        | Sm 3   | 3.073        | 0.009        |       |
| 2 Sm 2 |        | 4.037        | 0.002        |        | Sm 2   | 3.150        | 0.010        |       |
| Sm 2   |        | 4.118        | 0.008        |        | Sm 2   | 3.262        | 0.009        |       |
| Sm 1   |        | 4.215        | 0.006        |        | Sm 2   | 3.680        | 0.010        |       |
| Sm 3   | Ge 2   | 3.021        | 0.014        |        | Ge 3   | 3.706        | 0.018        |       |
|        | Ge 1   | 3.029        | 0.014        |        | 2 Ge 3 | 4.169        | 0.006        |       |
|        | 2 Ge 3 | 3.073        | 0.009        | Ge 1   | 4.224  | 0.012        |              |       |
|        | Ge 1   | 3.180        | 0.014        | 2 Ge 1 | 4.280  | 0.012        |              |       |
|        | Ge 2   | 3.192        | 0.013        |        |        |              |              |       |

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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#### References

- DAANE, A. H., RUNDLE, R. E., SMITH, H. G. & SPEDDING, F. H. (1954). *Acta Cryst.* **7**, 532.
- FRANK, F. C. & KASPER, J. S. (1958). *Acta Cryst.* **11**, 184.
- FRANK, F. C. & KASPER, J. S. (1959). *Acta Cryst.* **12**, 483.
- FURNAS, T. C. (1957). *Single Crystal Orienter Instruction Manual*. Milwaukee: General Electric Company.
- GLADYSHEVSKII, E. I. (1964a). *Zh. Strukturnoi Khim.* **5**, 568.
- GLADYSHEVSKII, E. I. (1964b). *Zh. Strukturnoi Khim.* **5**, 919.
- GLADYSHEVSKII, E. I. (1964c). *Dopovidi Akad. Nauk Ukr. RSR*, p. 209.
- GLADYSHEVSKII, E. I. & UHRYN, N. S. (1965). *Dopovidi Akad. Nauk Ukr. RSR*, p. 1326.
- HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040.
- HOHNKE, D. & PARTHÉ, E. (1966). *Acta Cryst.* **20**, 572.
- International Tables for X-ray Crystallography* (1952). Vol. I. Birmingham: Kynoch Press.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- SMITH, G. S., JOHNSON, Q. & THARP, A. G. (1965). *Acta Cryst.* **18**, 1085.
- TEATUM, E., GSCHNEIDNER, K. & WABER, J. (1959). Los Alamos Scientific Laboratory Report, LA-2345.
- THARP, A. G., SMITH, G. S. & JOHNSON, Q. (1966). *Acta Cryst.* **20**, 583.
- WEHE, D. J., BUSING, W. R. and LEVY, H. A. (1962). Oak Ridge National Laboratory Report, ORNL-TM-229.
- ZACHARIASEN, W. H. (1949). *Acta Cryst.* **2**, 94.