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The Crystal Structures of New Forms of Silicon and Germanium

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The structures of new dense forms of silicon and germanium, recovered from high pressure experiments, have been determined from their Debye–Scherrer patterns. For silicon, the space group is $Ia3$ (T_h^7), $a = 6{\cdot}636 \pm 0{\cdot}005$ Å, $Z = 16$, and there is one structural parameter corresponding to occupancy of 16(c) positions, with $x = 0{\cdot}1003 \pm 0{\cdot}0008$. The measured and calculated density is 2·55 g.cm^{-3}. The space group of germanium is $P4_32_12$ (D_4^8) with $a = 5{\cdot}93 \pm 0{\cdot}01$, $c = 6{\cdot}98 \pm 0{\cdot}01$ Å, and $Z = 12$. Two kinds of germanium atom occupy the 4(a), $xx0$, *etc.*, and 8(b) xyz, *etc.*, positions; x for 4(a) is $0{\cdot}0912 \pm 0{\cdot}0060$, and for 8($b$) $x = 0{\cdot}1730 \pm 0{\cdot}0037$, $y = 0{\cdot}3784 \pm 0{\cdot}0051$, $z = 0{\cdot}2486 \pm 0{\cdot}0048$. The measured density is 5·88 g.cm^{-3}, the calculated 5·91 g.cm^{-3}.

The two structures represent two different ways of achieving higher density relative to the diamond structure without change of coordination number and with little effect on interatomic distance. The angular distortions, particularly for germanium, are, however, appreciable.

New dense forms of silicon and germanium, recovered after subjecting the ordinary forms to high pressures, have been reported recently (Bundy & Kasper, 1963; Wentorf & Kasper, 1963). Only a brief account of the approximate crystal structures could be given in these reports and it is the purpose of this article to give the details of the structural investigation and the resulting refined values of structural parameters.

Experimental

Samples of both silicon and germanium in the new forms are always polycrystalline, with an average particle size not greater than 1 micron. Consequently the structure studies have been made with Debye–Scherrer patterns. Preliminary determinations of the approximate structure were done with irregular fragments and visual estimation of intensities. For the more refined determination of structural parameters, cylindrical specimens were used, absorption corrections (*International Tables for X-ray Crystallography*, 1959) were applied and the intensities were measured with a densitometer. The intensity data in Tables 1 and 2 are for the areas of peaks, measured with a planimeter, from the densitometer measurements. The sizes of the cylindrical specimens were: for silicon, 0·016 cm diameter, 0·058 cm length; for germanium, 0·016 cm diameter, 0·053 cm length. Copper $K\alpha$ radiation was used for both cases.

Table 1. *Debye–Scherrer Pattern for the dense form of silicon*

hkl	d_c	d_o	I_c		I_o
200	3·318	3·294	206		224
211	2·709	2·691	1031		836
220	2·346	2·331	14		15
222	1·916		5		< 5
312 132	1·773	1·768	42 715	757	686
400	1·659	1·649	175		184
411	1·564	1·558	67		90
420	1·484	1·479	46		55
332	1·415	1·409	51		54
422	1·355	1·353	3		7
314 134	1·301	1·298	6 95	101	88
512 152	1·212	1·210	118 0	118	116
440	1·173	1·171	75		84
433	1·138	1·133	10		< 5
600 442	1·106	1·106	47 12	59	49
611 532 352	1·076	1·075	22 222 0	244	202
620	1·049	1·047	15		20
514 154	1·024	1·023	29 0	29	27
622	1·000		3		< 5
136 316	0·9784	0·9793	48 3	51	57
444	0·9578	0·9572	22		35
534 354	0·9384	0·9391	67 0	67	83
640	0·9202	0·9191	94		112
712 172 633 552	0·9030	0·9026	6 120 7 0	133	134
642	0·8867	0·8855	—		W

Structure determination

Silicon

Generally, 23 lines could be observed in Debye–Scherrer patterns obtained with Cu $K\alpha$ radiation (Table 1), 21 of which were suitable for densitometer measurements. Only traces of ordinary silicon could be detected in some of the patterns — otherwise all lines could be readily indexed for a body-centered cubic cell with $a = 6{\cdot}636 \pm 0{\cdot}005$ Å. There appeared to be the absence of $hk0$ reflections with h and k odd, although this was definite only for 110 and 310 since the other such reflections overlap with permissible *hkl* reflections. The space group then would appear to be $Ia3$ (T_h^7). From the experimental density of 2·55 g.cm^{-3} (determined by a sink-float method)* exactly 16 atoms per unit cell would be called for. They would be in the 16(*c*) positions *xxx*, *etc.* and with x about 0·1, it was ascertained that good intensity agreement resulted as well as a plausible structure in which each silicon atom has a distorted tetrahedral environment with interatomic distances very close to those for the usual diamond arrangement.

The determination of the best value of x was made with a least-squares program, which was a modification of the Busing & Levy (1959) program that allowed consideration of overlapped data and which was prepared by Kennicott (1963). The F^2 values used were from intensities corrected for absorption with a weighting scheme based on the agreement of intensity measurements from three separate films.

Two cycles of refinement of structural parameter and scale factor were done, maintaining a fixed value of the thermal parameter B, after which B was allowed to vary. Three additional cycles were sufficient to achieve convergence. The resulting parameters with their standard deviations were:

$$x = 0{\cdot}1003 \qquad \sigma_x = 0{\cdot}0008$$
$$B = 0{\cdot}89 \qquad \sigma_B = 0.30.$$

The discrepancy index, R (based on F^2 values), was 0·15. The intensity agreement is given in Table 1.

While the value of x is reliable, that for B is not believed to be very significant. Its large magnitude relative to that of ordinary silicon ($\sim$ 0·2) could be due in part to the imperfect nature of the crystallites, but it may also be a rather indeterminate quantity because of the nature of the data. The correlation matrix for parameter interactions was investigated in the manner suggested by Geller (1961) and very strong correlation (0·894) between the scale factor and the temperature factor was indicated.

Thus, although no significance is attached to the B value, the x parameter is considered reliable to the significance indicated. In support of this, some experimentation with the least-squares program with different weighting schemes, with exclusion of some information and even with uncorrected intensities (from irregular fragments) gave little variation in the

Table 2. *Debye-Scherrer pattern for the dense form of germanium*

hkl	d_c	d_o	I_c		I_o
101	4·504	4·502	87		96
110	4·181		0		< 30
111	3·582	3·573	270		221
102	2·996	2·993	706	714	663
200	2·957		8		
201	2·721	2·714	1961	2487	1779
112	2·673	2·666	518		
210	2·644		8		
211	2·472	2·471	309		345
202	2·252		0	23	< 200
103	2·157	2·159	8		
212	2·104		14		
220	2·091	2·094	1		
113	2·026	2·026	97	111	198
221	2·002		14		
301	1·896	1·896	358		577
310	1·870	1·870	217		317
203	1·824	1·825	756	1129	1080
311	1·806		373		
222	1·791	1·791	1187		1344
213	1·743	1·741	126	518	798
004	1·738		392		
302	1·714		10		< 97
104	1·667		0		< 69
312	1·647		13	374	417
320	1·640	1·642	361		
114	1·605		5		< 53
321	1·596		25		27
223	1·552		13		< 17
303	1·501	1·503	172	180	191
204	1·498		8		
322	1·483		40	269	283
400	1·478	1·480	229		
313	1·455	1·456	208	242	239
214	1·452		0		
401	1·446		8		
410	1·443		26		
411	1·413		29	128	103
330	1·394	1·394	99		
331	1·367	1·372	37	126	< 100
402	1·360		0		
105	1·353		3		
323	1·338	1·344	14		
224	1·336		0		
412	1·333		4		
420	1·322	1·325	16		
115	1·319		52		
304	1·303		0	292	280
421	1·299	1·299	234		
332	1·294		58		
314	1·273	1·276	167		168
205	1·258	1·261	254	261	296
403	1·246		7		
422	1·236	1·234	38	101	112
215	1·230		33		
413	1·225		30		
333	1·194	1·199	29	279	260
324	1·193		244		
430	1·183		6		
501	1·166	1·166	3	104	102
431	1·166		72		
510	1·160		22		
225	1·158		7		
423	1·148	1·149	160	331	292
511	1·144		66		
106	1·137		34		
305	1·136		71		
404	1·126	1·129	196	730	672
502	1·120	1·122	252		
432	1·120		67		
116	1·116		77		
315	1·116		103		
414	1·110		35		
512	1·100	1·103	174	182	261
520	1·098		8		
334	1·087	1·087	110	317	279
521	1·085		207		
206	1·079		0		

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* This was done by R. H. Wentorf, Jr.

value of x, while B values were found to change drastically. As an extreme, for corrected intensities and for unit weighting of all reflections, a value of $x=0{\cdot}102$ could be obtained, but with a much larger value of σ.

The simple structural problem with silicon was considered a good test case for the working of the modified least-squares program as a preliminary to the more exacting problem with germanium.

Germanium

A complex Debye–Scherrer pattern of 51 lines (for Cu $K\alpha$ radiation) was given by germanium specimens in the new form. This pattern was indexed by consideration of differences of $\sin^2\theta$ values for a tetragonal cell with $a=5{\cdot}93\pm0{\cdot}01$, $c=6{\cdot}98\pm0{\cdot}01$ Å (See Table 2). Although there is considerable overlap of reflections, at least the low index reflections indicate the absence of $00l$ reflections unless $l=4n$, and the absence of $h00$ reflections when h is odd. Hence the probable space group is $P4_32_12$ (D_4^8) (or its enantiomorph $P4_12_12$, D_4^4). The approximate density called for 12 atoms in the unit cell suggesting the choice of $4(a)$ $x\,x\,0$, *etc.* and $8(b)$ $x\,y\,z$, *etc.* positions. It was found by trial and error that with x of $4(a)=0{\cdot}075$, and with $x=\frac{1}{6}$, $y=\frac{3}{8}$, $z=\frac{1}{4}$ in $8(b)$ there resulted both good intensity agreement and a plausible structure. Although quite different from the structure of silicon, the germanium structure also has the general feature of distorted tetrahedral arrangements with interatomic distances close to those in the normal form.

The choice of 12 atoms per unit cell gives a calculated density of 5·91 g.cm^{-3}. This is in excellent agreement with the experimental values obtained by Simons (1963) of $5{\cdot}86\pm0{\cdot}12$ and $5{\cdot}90\pm0{\cdot}12$ g.cm^{-3}. The density is clearly substantially higher than that of normal germanium (5·32 g.cm^{-3}).

The refinement of structure was done by means of the least-squares analysis for intensities measured with the densitometer for a cylindrical specimen and with absorption corrections. Here the weighting was made inversely proportional to the F_o^2 values. After three cycles with fixed temperature factors, four more cycles gave convergence with the following parameter values:

$$\begin{array}{lll}
\text{Ge(1) }(4a) & x = 0{\cdot}0912, & \sigma_x = 0{\cdot}0060 \\
 & B = 4{\cdot}51, & \sigma_B = 1{\cdot}14 \\
\text{Ge(2) }(8b) & x = 0{\cdot}1730, & \sigma_x = 0{\cdot}0037 \\
 & y = 0{\cdot}3784, & \sigma_y = 0{\cdot}0051 \\
 & z = 0{\cdot}2486, & \sigma_z = 0{\cdot}0048 \\
 & B = 1{\cdot}15, & \sigma_B = 0{\cdot}45
\end{array}$$

The value of R (F^2 basis) was 0·187. Intensity agreement is shown in Table 2, which extends in range to the point where useful densitometer measurements could be made. Beyond this point, the overlap is quite severe although 18 more lines could be measured and these are useful for indexing and identification.

Some strong correlations were noted in the matrix, the strongest of which was between the B of atom (1) and the scale factor. Again, no significance is attached to the B values but the structural parameters are taken to be significant to the indicated amounts. Unfortunately, the standard deviations even on the structural parameters are rather large, but it is felt that this reflects a limitation imposed by the complexity of the problem.

Discussion of the structures

The two structures, shown in projection in Figs. 1 and 2, represent two different arrangements of distorted tetrahedra whereby greater density is achieved relative to the diamond structure without large changes in interatomic separations but with substantial angular distortion and loss of symmetry.

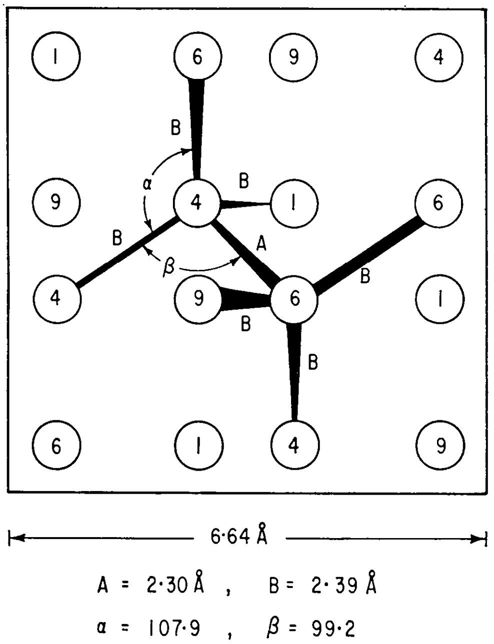

Fig. 1. Projection of the structure of dense silicon on (001). Elevations (in $\frac{1}{10}c$) are given by the numbers inside the circles.

Actually, in silicon the angular distortions are not too severe, with three angles of 108° and 3 of 99° for the six tetrahedral angles. The bond distances seem to be definitely different—the one distance ($2{\cdot}30\pm0{\cdot}01$ Å) along a trigonal axis being significantly shorter than the three others at $2{\cdot}39\pm0{\cdot}01$ Å. They bracket the normal tetrahedral distance of 2·35 Å. The increase in density over the diamond arrangement is reflected in the occurrence of a next nearest neighbor distance of 3·45 Å (along the triad axes), which has no counterpart in the diamond arrangement and is shorter than the next nearest neighbor distances (3·84 Å) in ordinary silicon. There does not appear to be any simple mechanism of transforming the diamond structure into the new structure, for example by simple shearing.

While the silicon structure seems to be novel for an element, it does have a resemblance to the distorted tetrahedral structures found for ZnSb and CdSb (Almin, 1948) which are actually orthorhombic with still more severe distortions and, of course, involving different tetrahedra about the two kinds of atom.

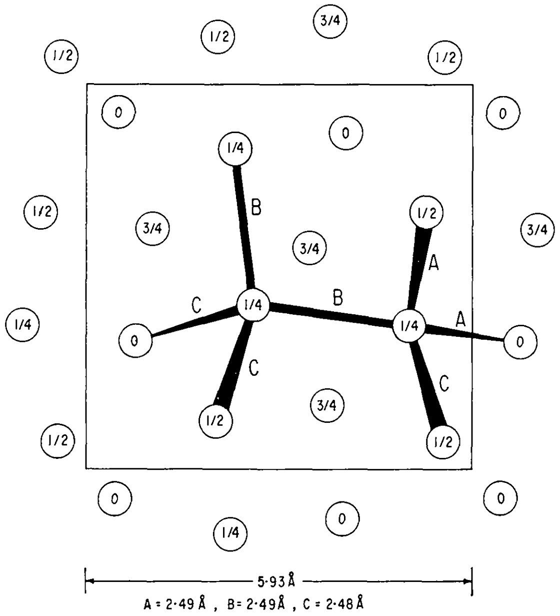

Fig. 2. A projection of the structure of the new dense form of germanium onto (001). The elevations along *c* (in fractions of the cell length) are given by the numbers inside the circles.

The germanium structure can be viewed (Fig. 2) as consisting of fourfold spirals whose axes are parallel to [001] and located at the centers of the *a* and *b* edges. The Ge(1) atoms in 4(*a*) then form tetrahedra with those in the spirals, each Ge(1) forming one bond to an atom of each of the four spirals. The angular distortions from a regular tetrahedron (Fig. 3) are much larger than for silicon, yet the three separate interatomic distances of 2·48 ± 0·04, 2·49 ± 0·04 and 2·49 ± 0·05 Å are essentially equal and somewhat greater, though probably not significantly greater, than the value of 2·45 Å for ordinary germanium. The shortest next nearest neighbor distance, between Ge(1) atoms, is 3·81 Å, compared with 4·00 Å in cubic germanium.

Upon completion of the germanium structure we have become aware of a correspondence between it and two other dense tetrahedral structures, those of keatite, SiO_2 (Shropshire, Keat & Vaughan, 1959), and of ice III, a high pressure form (Kamb & Datta, 1960). In keatite, the silicon sites have the same kind of arrangement as our germanium structure, even to agreement of structural parameters within 0·001 to 0·003. The *c*/*a* for keatite is 1·154 compared with 1·177 for germanium. The refined structure of ice III has not been reported yet, but the indicated arrangement of oxygen atoms is similar to the germanium structure. The *c*/*a* here is only 1·005 and the structural parameters are not nearly as close to those of germanium as for keatite.

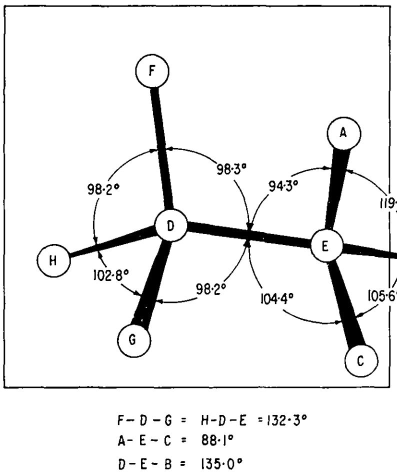

Fig. 3. The various bond angles in the dense form of germanium.

It appears, then, that the germanium structure may be a favored high pressure tetrahedral structure for achieving density increases of about 10% by introducing distortions without affecting coordination number or interatomic distance, not only for an element normally in the diamond arrangement but also for compounds AB_2 with the tetrahedral coordination about A, as in SiO_2 and H_2O. The new silicon structure represents about the same density increase also, and it is not possible to say why corresponding structures have not been found for SiO_2 and H_2O, unless they remain to be discovered.

We are indebted to F. P. Bundy and R. H. Wentorf, Jr., for providing specimens of the new materials which they were the first to make with their high pressure techniques. We are especially grateful to R. H. Wentorf, Jr. for preparing the cylindrical specimens needed for more accurate intensity measurement. Also, we appreciate greatly the aid in various phases of this study given by H. Brandhorst.

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