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Refinement of the Crystal Structure of SiC Type 6*H*

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The known *c*/*a* ratio of SiC type 6*H* is incompatible with an ideal structure built up from perfect tetrahedra. The present work is an attempt to reveal the fine details of the structure in order to determine if and how the distortions of the tetrahedra are related to the positions which the atoms involved occupy in the stacking sequence *hcchcc* ... of Si–C double-layers in hexagonal (*h*) and cubic (*c*) environment.

From carefully collected three-dimensional X-ray data convincing evidence of space group $P6_3mc$ is obtained. More or less independent refinements by means of least-squares techniques and on the basis of Fourier methods result in weighted *R* indices of 2·1 % and 2·9 % respectively. The refinements include a correction for secondary extinction for which a new formula is given, applicable to the case of equi-inclination geometry.

It is shown that the experimental data contain no information about the exact position of the hexagonally surrounded double layer. The distance between two adjacent *c* double layers, 2·5163 ± 0·0008 Å, is definitely shorter than the average $h-c$ distance of 2·5212 ± 0·0004 Å. The Si–C bonds parallel to the *c* axis are longer than those inclined to it. The bond angles do not deviate significantly from the tetrahedral angle of 109·5°. The results throw some new light on the problem of polytypism.

Introduction

Silicon carbide is known to occur in fifty or more different modifications (types). Although a vast amount of literature is available about polytypism in SiC (*e.g.* Verma & Krishna, 1966), the explanation of this phenomenon is by no means clear. Thermodynamic properties (vibration entropy, internal energy) as well as growth kinetic effects (screw dislocations, intergrowth of crystals) have been put forward to explain the occurrence of this great number of structures, but so far no explanation covers all experimental facts.

The building units of all SiC structures are hexagonal double-layers of Si–C. These are stacked together in such a way that each silicon atom is surrounded tetrahedrally by four carbon atoms and *vice versa*. The SiC types crystallize in the space groups $P3m1$, $R3m$, $P6_3mc$ and $F\bar{4}3m$. They are usually described in a hexagonal lattice. All atoms are located on threefold axes in the (110) plane. There are two limiting structures:

(1) All double layers occur in a hexagonal environment, wurtzite structure, type 2*H*, stacking sequence *ABAB* ... or *hhh* ...

(2) All double layers occur in a cubic environment, sphalerite structure, type 3*C*, stacking sequence *ABCABC* ... or *ccc* ...

All other SiC structures are built up from *h* and *c* double layers which are stacked in some periodic sequence.

If the tetrahedral structure were an ideal one, the *c*/*a* ratio per double layer in the hexagonal unit cell would be $\frac{1}{3}\sqrt{6}=0{\cdot}8165$. Instead, one finds slightly different values for some hexagonal types, *viz.* 0·8179 for 6*H* (Taylor & Jones, 1959; henceforth denoted as T. & J.) and 0·8205 for 2*H* (Adamsky & Merz, 1959). A comparison of the lattice constants (Table 1) shows that the introduction of *h* double layers is accompanied by an elongation of the hexagonal *c* axis and a contraction of the axes perpendicular to it. The internal energy differences probably associated with the distortion of the tetrahedra may play a certain role in the formation of the different types.

Table 1. *Lattice constants of some* SiC *structures*

p is the number of Si–C double layers in the hexagonal unit cell.

Type	*c* (Å)	*c*/*p* (Å)	*a* (Å)	*c*/*pa*	d_x (*g*.cm^{-3})
2*H**	5·048^{0}	2·524	3·076^{3}	0·8205	3·214
6*H*†	15·1173^{8}	2·5196	3·0806^{5}	0·8179	3·211
3*C*†	7·5510	2·5170	3·0827	0·8165	3·210

* Adamsky & Merz (1959).
† Taylor & Jones (1959).

The SiC crystals usually obtained are not free from stacking faults and admixtures of various structure types. Recently, however, the preparation procedure has been refined to such an extent that chemically and structurally pure SiC-6*H* crystals can now be grown (Knippenberg & Gomes de Mesquita, 1965). It was thought worth while to try and determine bond angles and interatomic distances in this structure where hexagonal and cubic double layers are stacked in the order *hcchcc* ... (Fig. 1), and to investigate whether there is a correlation between the distortion of the tetrahedra and the positions of the pertinent atoms in the stacking sequence. In this way some additional insight might be gained into the phenomenon of polytypism, which has been treated up till now as if deviations from the ideal tetrahedral structure were non-existent.

Experimental

From a batch of crystals containing less than 0·0001 at.% of chemical impurities a specimen was selected under the polarizing microscope. It was ground into a spherical shape by means of an apparatus described by Schuyff & Hulscher (1965), in which a boron carbide ring was inserted as abrasive. Particles adhering to the crystal were removed by ultrasonic cleaning after the grinding. The diameter of the sphere, as measured in a great number of directions, was 0·223–0·227 mm.

The crystal was oriented on the diffractometer 'PAILRED' (Philips Automatic Indexing Linear Reciprocal-space Exploring Diffractometer) along the *b* axis to within about one minute of arc. Preliminary intensity measurements revealed no evidence of stacking faults. Difference syntheses made in a later stage of the refinement confirmed the absence of stacking disorder in any measurable amount.

Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å) was chosen in order to minimize the absorption-correction errors and to make high-order reflexions accessible. A flat (20.3) plate of α-quartz ($d = 1{\cdot}3748$ Å) was used to monochromatize the radiation.

Because of the high symmetry a sufficiently complete set of three-dimensional data is contained in the levels *h*0*l*, *h*1*l* and *h*2*l*. These were measured up to $\Upsilon = 100°$ utilizing the ω-scan technique and equi-inclination geometry. The ω-scan range was 2·0° for the zero level and 2·4° for the others. In view of the required accuracy the scan speed was taken as slow as 0·5°.min^{-1}. The radiation background was measured during 60 seconds at either side of the scan range with stationary crystal and stationary counter. Each layer-line was remeasured with a slightly incorrect (0·3–0·5°) inclination angle so as to facilitate the detection of double reflexions.

Altogether 929 reflexions were measured in the correct inclination setting, 25 of which were rejected because the two background measurements were incompatible, *i.e.* $|b_1 - b_2| > 6[(b_1 + b_2)/2]^{\frac{1}{2}}$, or because double reflexions were clearly involved. The remaining 904 reflexion intensities were corrected in the usual way for Lorentz, polarization and absorption effects.

In the least-squares refinement weight factors, w, were attributed to the structure factors. The formula used for the stronger reflexions with $I \geq 2\sigma(I)$ was $w^{\frac{1}{2}} = 2I/[F_o\,.\,\sigma(I)]$, where $\sigma(I)/I$ stands for the relative counting-statistical error. A minimum value of 0·02 was set for $\sigma(I)/I$ corresponding to the experimental agreement between strong symmetry-related reflexions. Weaker reflexions were treated in a somewhat different way (J. Hornstra, to be published).

The atomic scattering factors used throughout were those computed by Cromer & Waber (1965). Dispersion corrections were applied to the real part of the scattering factor only; the imaginary part is negligible.

The lattice constants were taken from T & J: $a = 3{\cdot}08065$, $c = 15{\cdot}11738$ Å. The c/a ratio computed from these values is 4·907 in close agreement with the value $c/a = 4{\cdot}908 \pm 0{\cdot}002$ obtained from measurements on the present crystal and significantly larger than the ideal value of $2\sqrt{6} = 4{\cdot}8990$.

The space group

Space group $P6_3mc$ (no. 186) has always been assigned to the structure of SiC type 6*H*. Though there is no particular reason to doubt the assignment, yet a careful check seems desirable in order to establish a firm base for the refinement.

The space group requires the systematic absence of reflexions *hkl* with $h-k=3n$, $l=2n+1$. The experimental data include 167 reflexions of this type, measured at the correct inclination angle. Their observed intensities corrected for background radiation range from $-3\sigma(I)$ to $+9\sigma(I)$. Almost 90% of the data are between $-2\sigma(I)$ and $+2\sigma(I)$, but 16 reflexions have stronger intensities. Each of these was examined individually and proved to be attributable to the Renninger effect. In some cases, where the applied missetting of the inclination angle had been ineffective, this called for additional experimental work. As an example thereof Fig. 2 shows the intensity of the space-group forbidden 00.3 reflexion recorded during a rotation of the crystal about the *c* axis. It demonstrates at the same time how difficult it is to avoid double reflexions altogether.

The above systematic absence already provides rather convincing evidence of space group $P6_3mc$. Nevertheless another check was made which would make it possible to distinguish between this space group and the only reasonable alternative, $P3m1$. In both space groups *hkl* and $\bar{k}\bar{h}l$ are equivalent reflexions and *hkl* and $kh\bar{l}$ likewise if Friedel's law holds. $P6_3mc$ requires in addition that *hkl* and *khl* be equivalent. In order to test the extent to which these conditions are fulfilled experimental agreement indices were calculated using a set of 358 data of reflexions *hkl* with $h-k \neq 3n$:

$$R_1 = \frac{\Sigma\,\big||F_o(hkl)|^2 - |F_o(kh\bar{l})|^2\big|}{\Sigma\,[|F_o(hkl)|^2 + |F_o(kh\bar{l})|^2]} = 1{\cdot}86\%$$

$$R_2 = \frac{\Sigma\,\big||F_o(hkl)|^2 - |F_o(khl)|^2\big|}{\Sigma\,[|F_o(hkl)|^2 + |F_o(khl)|^2]} = 1{\cdot}50\%\,.$$

Since the same data were used to compute both R_1 and R_2, the two denominators are equal; the numerators differ, because the pairs of reflexions were taken in a different way. $P6_3mc$ would correspond to $R_1 = R_2$, $P3m1$ to $R_1 < R_2$. The higher value of R_1 actually found is considered as strong confirmation of space group $P6_3mc$.

The establishment of the space group makes it possible to compute the intensities of the 279 independent reflexions by taking the weighted average of all symmetry-related ones. The excellent agreement between equivalent reflexions is clearly shown by the low values of the above experimental agreement indices, which even refer to measurements at different inclination angles ($h \neq k$).

The structure-factor formulae

Besides the space-group extinctions the ideal model of Fig. 1 entails the systematic absence of reflexions hkl with $h-k=3n$, $l \neq 6n$ and $h-k \neq 3n$, $l=6n$. The experimental data include 83 non-equivalent reflexions of these types whose observed intensities are all smaller than $+3\sigma(I)$. Therefore one would be inclined to conclude that there are no measureable differences between the true structure and the ideal one. It will be shown below that this conclusion is unjustified, because the intensities of the reflexions in question are insensitive to small coordinate shifts. In any case, the situation compels us to examine the structure-factor formula closely in order to establish the amount of information contained in the experimental data.

The expression $F(hkl)=\sum\limits_j f_j \exp[2\pi i(hx_j+ky_j+lz_j)]$ can be simplified considerably assuming that each pair of Si–C atoms has the same scattering factor. This would mean that each atom of the same kind has the same thermal-vibration parameters and that all Si(i)–C(i) bonds ($i=1,2,3$) are equally long. Eventually, the results of the refinement justify these assumptions, but some justification can also be given in advance.

The Debye temperature of SiC is high; the literature values spread from about 1400°K to 1800°K. Therefore the temperature factors must be small and differences between them even smaller. There is some experimental evidence to corroborate this. Reflexions $hk0$ ($h-k \neq 3n$) could have occurred only if like atoms vibrated perpendicular to the c axis with different mean square displacements from their equilibrium positions. Actually, however, none of these reflexions is observed; their intensities range from $-2\sigma(I)$ to $+\sigma(I)$.

The equality of all Si–C bond distances parallel to the c axis cannot be anticipated, but chances are fair that they will turn out to be equal within the limits of accuracy.

With these assumptions the structure-factor formula reads:

$$F(hkl)=[f_{\mathrm{Si}}+f_{\mathrm{C}} \exp 2\pi il(z_{\mathrm{C}}-z_{\mathrm{Si}})] \times \sum_{\mathrm{Si}} \exp 2\pi i(hx_{\mathrm{Si}}+ky_{\mathrm{Si}}+lz_{\mathrm{Si}}) \,.$$

The factor between square brackets is the scattering factor of a Si–C pair and needs no further consideration. The coordinates of the Si atoms can simply be substituted. One Si atom, Si(1) say, is held fixed at $x=y=z=0$ (polar space group); the other Si atoms are located at or near their ideal positions at $\frac{2}{3},\frac{1}{3},\frac{1}{6}+\delta$ and $\frac{1}{3},\frac{2}{3},\frac{1}{3}+\varepsilon$, where δ and ε represent small quantities. This leads to the following expressions for the intensities of various types of reflexions:

$$h-k=3n,\ l=2n: \quad |F|^2 \sim 12+8 \cos 2\pi l(\tfrac{1}{6}+\varepsilon-\delta)+16 \cos \pi l(\tfrac{1}{2}+\varepsilon+\delta) \cos \pi l(\tfrac{1}{6}+\varepsilon-\delta) \quad (\simeq 36 \text{ for } l=6n;\ \simeq 0 \text{ for } l \neq 6n)$$

$$h-k \neq 3n,\ l=2n: \quad |F|^2 \sim 6+2 \cos 2\pi l(\tfrac{1}{6}+\varepsilon-\delta)-\delta \cos \pi l(\tfrac{1}{2}+\varepsilon+\delta) \cos \pi l(\tfrac{1}{6}+\varepsilon-\delta) \quad (\simeq 9 \text{ for } l \neq 6n;\ \simeq 0 \text{ for } l=6n)$$

$$h-k=3n,\ l=2n+1: \quad |F|^2=0$$

$$h-k \neq 3n,\ l=2n+1: \quad |F|^2 \sim 6-6 \cos 2\pi l(\tfrac{1}{6}+\varepsilon-\delta) \quad (\simeq 3 \text{ for } l=6n \pm 1;\ \simeq 12 \text{ for } l=6n+3) \,.$$

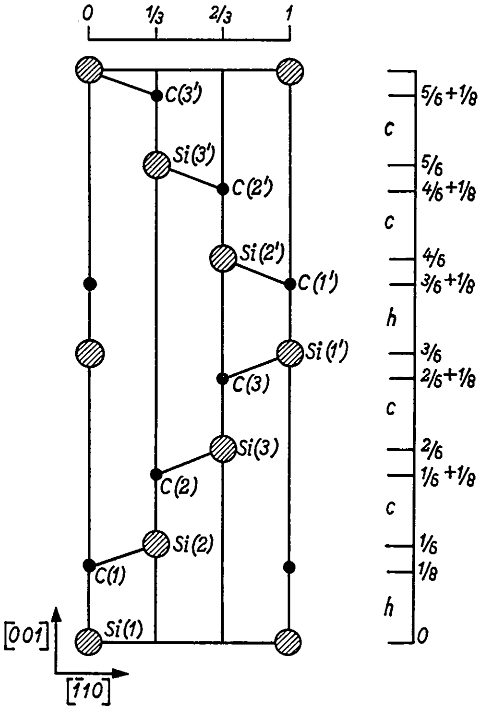

Fig. 1. The structure of SiC type 6*H*. All atoms are located in the (11$\bar{2}$0) plane. The ideal *z* parameters and the layer type are indicated on the right.

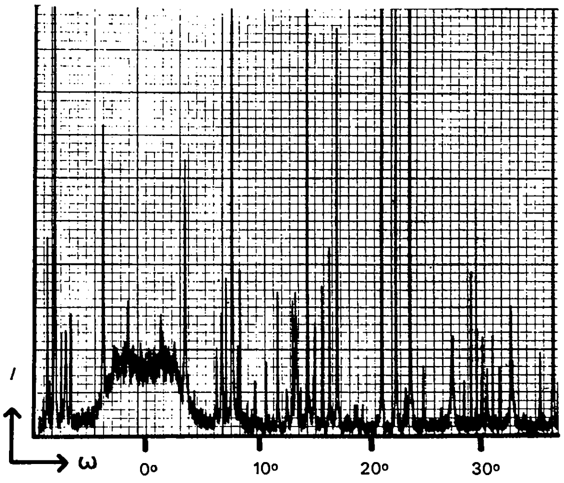

Fig. 2. Evidence of double reflexions. Intensity of the space-group-forbidden 00·3 reflexion registered during a rotation of the crystal about the normal to the reflecting plane (ω axis).

Obviously, the actual parameters are $(\varepsilon+\delta)$ and $(\varepsilon-\delta)$. The former of these occurs only in the expression $\cos \pi l(\frac{1}{2}+\varepsilon+\delta)$ and since this is equal to $\cos \pi l(\frac{1}{2}-\varepsilon-\delta)$, the sign of $(\varepsilon+\delta)$ is undetermined. In terms of the structure this means that if the distances between the h double-layer and its two neighbours are unequal, it is impossible to determine which distance is the longer. Besides this, however, one cannot even decide whether the two distances are equal or not, for the absolute value of $(\varepsilon+\delta)$ hardly enters into the expressions. The expected magnitude of $(\varepsilon+\delta)$ is of the order of 10^{-3}–10^{-4} and even for the highest order reflexions $0{\cdot}995 < |\cos \pi l(\frac{1}{2}+\varepsilon+\delta)| \leq 1{\cdot}000$. The errors inherent in this experiment will certainly obscure such a small effect.

The situation is much more favourable for the determination of the other parameter, $\varepsilon-\delta$. The computed values of $\partial|F|^2/\partial(\varepsilon-\delta)$ given in Table 2 show that relevant information about $\varepsilon-\delta$ is contained in the intensities of the reflexions hkl with $h-k\neq 3n$, $l\neq 3n$. This means that the distance between the two double-layers in cubic environment is a refinable parameter. That no use can be made of the systematically weak reflexions ($h-k=3n$, $l\neq 6n$; $h-k\neq 3n$, $l=6n$) is immediately clear upon inspection of the table: their derivatives are zero or approximately so.

Table 2. *Approximate values of* $\partial|F|^2/\partial(\varepsilon-\delta)$ *for various types of reflexions*

$l=6n+$	1	2	3	4	5	6
$h-k=3n$	0	0	0	0	0	0
$h-k\neq 3n$	$-ql$	$+ql$	0	$-ql$	$+ql$	0

$$q=6\pi\sqrt{3}[f_{\mathrm{Si}}{}^2+f_{\mathrm{C}}{}^2+2f_{\mathrm{C}}f_{\mathrm{Si}}\cos 2\pi l\{z(\mathrm{C})-z(\mathrm{Si})\}]\,.$$

Refinement

Least-squares method

In view of the peculiar nature of the problem it is not surprising that considerable difficulties were encountered in attempts to refine the structure by least-squares methods. A full-matrix treatment was found to be utterly impossible, because the correlation matrix contains several off-diagonal elements whose value is 1·00. Therefore the block-diagonal approximation was applied, minimizing $\Sigma w(|F_o|-|F_c|)^2$ and including as usual only the first derivatives of the structure factors with respect to the parameters to be determined. Coupling was assumed between the scaling factor and an overall temperature factor and also between the (two) elements of the anisotropic thermal-vibration tensor of each atom, which occur in the expression

$$f=f_0 \exp[-b_{11}(h^2+k^2+hk)-b_{33}l^2]\,.$$

There are 19 parameters to be refined: 5 z coordinates, 12 thermal-vibration parameters, 1 scaling factor and 1 secondary extinction parameter. In order to determine this last parameter, C, Zachariasen's extinction-correction formulae (Zachariasen, 1963, formulae 14 and 15*a*) were modified for application to equi-inclination geometry:

$$F_{\mathrm{corr.}} \sim KF_{\mathrm{obs}}[1+\beta'(2\theta)\,.\,C\,.\,F^2_{\mathrm{obs}}]$$

$$\beta'(2\theta)=\frac{A^{*\prime}(2\theta)}{A^*(2\theta)}\cdot\frac{1}{\sin 2\theta}\cdot\frac{a+b\cos^4 2\theta}{a+b\cos^2 2\theta}\,,$$

$$a=\tan^2\theta-\tan^2\nu+\cos^2 2\theta_0\,.\,\tan^2\nu$$

$$b=\tan^2\nu+\cos^2 2\theta_0\,(\tan^2\theta-\tan^2\nu)$$

$$\nu=\text{inclination angle};$$

all other symbols have their usual meaning.

The refinement using all observations was started from the ideal parameters. It converged very slowly towards a minimum, but diverged again afterwards. In the minimum, corresponding to a weighted R index $R_w=\Sigma w||F_o|-|F_c||/\Sigma w|F_o|=2{\cdot}1\%$, the calculated coordinate shifts are still of the order of 10^{-4}–10^{-5} times the unit-cell edge. The best parameters obtained in this way are presented in Table 3, the interlayer and interatomic distances in Table 4.

Fourier methods

Although the least-squares refinement results in a low value of R_w, in fact in fails, because there is no real convergence and because it does not allow residual errors to be found and estimated. As correctly pointed

Table 4. *Bond lengths and interlayer distances resulting from least-squares* (*L*) *and Fourier* (*F*) *refinements*

Bond	L	F
Si(1)–C(1)	1·896 Å	1·894 Å
C(1)–Si(2)	1·885	1·886
Si(2)–C(2)	1·892	1·891
C(2)–Si(3)	1·885	1·885
Si(3)–C(3)	1·893	1·894
C(3)–Si(1′)	1·887	1·886
Δz		
Si(1)–Si(2)	2·5205	2·5212
Si(2)–Si(3)	2·5161	2·5163
Si(3)–Si(1′)	2·5220	2·5212

Table 3. *Final parameters obtained by least-squares* (*L*) *and Fourier* (*F*) *methods*

	x	y	z_L	$b_{11}\times 10^4$	$b_{33}\times 10^5$	z_F	$b_{11}\times 10^4$*	$b_{33}\times 10^5$*
Si(1)	0	0	0	101	28	0	62	16
Si(2)	$\frac{2}{3}$	$\frac{1}{3}$	0·16673	94	31	0·16678	62	16
Si(3)	$\frac{1}{3}$	$\frac{2}{3}$	0·33317	89	20	0·33323	62	16
C(1)	0	0	0·12539	89	33	0·12527	111	29
C(2)	$\frac{2}{3}$	$\frac{1}{3}$	0·29186	145	31	0·29188	111	29
C(3)	$\frac{1}{3}$	$\frac{2}{3}$	0·45837	119	27	0·45850	111	29

* Not individually refined.

out to the author by Dr H.D. Megaw (Cambridge University), Fourier methods are superior under such circumstances. Electron-density and difference maps may not only be used to overcome the above difficulties to some extent, but they may also indicate possible errors in the structure which manifest themselves in the occurrence of oddly shaped peaks or maxima and minima away from the atomic centres.

Prior to the application of Fourier methods a least-squares refinement was undertaken. In order not to obscure interesting details of the structure only 4 parameters were included: the scaling factor, the secondary-extinction parameter and one isotropic temperature factor for each of the atomic species. The atoms were held in their ideal position. This refinement converged and led to $R_w = 4{\cdot}0\%$.

At this stage the electron density in the (110) plane was computed from the complete set of 3-D data. The Fourier map shows serious series-termination errors, but near the atomic centres the peaks are well-shaped and like atoms have equal peak heights and curvatures to within 1% and 3% respectively. All peaks are slightly elliptical; their short axis coincides with the *c* axis. This effect, exactly opposed to what would be expected in the case of ill-defined atomic *z* coordinates, is indicative of anisotropic thermal vibrations.

The electron-density map is in general agreement with the structure, but, as expected, it does not yield information about very small coordinate shifts, presumably of the order of 10^{-2}–10^{-3} Å. Therefore the refinement was continued by means of difference syntheses, which are much more sensitive in this respect. All reflexions having small weight factors, *i.e.* the very weak (unreliable phase determination) and the very strong ones (residual extinction and non-linearity errors), were omitted from the calculations. The following reflexions remained:

Reflexion type	Number of reflexions
$h-k=3n,\ l=6n$	12
$h-k\neq 3n,\ l=6n\pm 1$	49
$h-k\neq 3n,\ l=6n\pm 2$	61
$h-k\neq 3n,\ l=6n\pm 3$	31
	153

They contain information about $\varepsilon-\delta$ ($h-k\neq 3n$, $l\neq 3n$), as well as in principle about $\varepsilon+\delta$ ($l=2n$).

The first difference map clearly indicates anisotropic thermal vibrations, in qualitative agreement with the electron-density map. Moreover, there is convincing evidence that the distance between the two cubic double layers is smaller than *c*/6.

As a next step the number of thermal-vibration parameters was increased to 4, two (b_{11} and b_{33}) for each kind of atom. These parameters were refined by least-squares methods; the refinement converged rapidly.

The second difference map shows that the coordinates and the temperature factors can be refined independently: the slopes at the atomic centres are not influenced significantly by the change of the thermal-vibration parameters. Therefore no more attempts were made to adjust these last parameters any further, although there is some evidence of individual differences between like atoms.

Five more difference syntheses were computed, all based on slight variations of the interatomic distances. From the empirical correlation between the applied coordinate shifts and the resulting effect on the difference map the following conclusions have been drawn:

(1) The distance between the two cubic double layers, defined as $z[\mathrm{Si}(3)]-z[\mathrm{Si}(2)]$, is $2{\cdot}5163 \pm 0{\cdot}0008$ Å, distinctly smaller than $c/6 = 2{\cdot}5196$ Å. The same result is obtained from the least-squares refinement. The magnitude of the estimated standard deviation is taken equal to that coordinate shift which results in a slope at the atomic centre equal to the r.m.s. slope of the difference map (due to random fluctuations) far away from any atomic site.

(2) To some extent the position of the *h* double layer is undetermined. It can be taken at *c*/6 from either of the adjacent double-layers, or, alternatively, equidistant from both. The corresponding difference maps are essentially identical, though the two positions of the double-layer are 0·0024 Å apart. Subsequent calculations of bond distances and bond angles are based on the arbitrary assumption that the *h* double-layer is equidistant from its two nearest neighbours.

(3) The Si(*i*)–C(*i*) bond distances are determined to within about 0·002 Å. The bonds involving C(2) are somewhat shorter than those involving the other C atoms.

The adjustment of the coordinates suggested by the various difference maps results in $R_w = 2{\cdot}86\%$. The final difference map is practically 'clean' with highest maxima of the order of 0·1 e.Å^{-3} (*i.e.* about 1% of a carbon maximum in the electron-density map) and zero slope at the atomic positions. The parameters so obtained are given in Table 3, the interatomic distances in Table 4 and Fig. 3. The bond angles are not specifically listed; they are all computed between 109·4 and 109·5°. The structure factors will be found in Table 5.

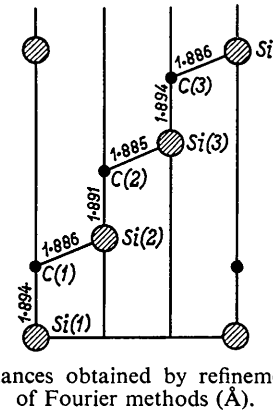

Fig. 3. Bond distances obtained by refinement on the basis of Fourier methods (Å).

Discussion

The results of the present structure refinement make it possible to localize the distortion of the tetrahedra which the value of c/a had already shown to exist. Whereas all bond angles are equal to those of a perfect tetrahedron within experimental error, the bond distances are not. Those along the c axis are longer than those inclined to it; the average lengths are 1·893 Å and 1·886 Å respectively.

In general one would hesitate to consider this small difference of 0·007 Å as being significant. In this case, however, confirmative evidence is obtained from spectroscopic investigations. Carefully measured infrared absorption and reflexion spectra of SiC type 6*H* (Spitzer, Kleinman, Frosch & Walsh, 1959) allow the frequency of the fundamental lattice vibration to be determined for the ordinary and the extraordinary wave as $\omega_o = 2{\cdot}380 \times 10^{13}\ \mathrm{sec}^{-1}$ and $\omega_e = 2{\cdot}356 \times 10^{13}\ \mathrm{sec}^{-1}$ respectively. The frequency difference of 1·0% can be interpreted in terms of the above difference in bond length. In order to do so use is made of the Mie–Grüneisen theory (T & J), which actually relates an all-sided compression or expansion of the crystal to the resulting frequency shift. The relevant formulae are:

$$\frac{d\omega}{\omega} = -\gamma \frac{dV}{V}$$

$$\gamma = \frac{\alpha V}{\chi C_v}$$

where

γ = Grüneisen constant
α = coefficient of thermal expansion
V = molar volume
χ = compressibility
C_v = specific heat at constant volume

All physical quantities involved are known with sufficient accuracy to determine the value of γ. $V = 12{\cdot}5$ cm^3.mole^{-1}; $\alpha = 8{\cdot}4 \times 10^{-6}$ deg^{-1} (T & J); $\chi = (4{\cdot}4 \pm 0{\cdot}1) \times 10^{-13}$ cm^2.dyne^{-1} (Arlt & Schodder, private communication); $C_v = 5{\cdot}61 \pm 0{\cdot}87$ cal.mole^{-1} deg^{-1}.* Substitution of these values yields $\gamma = 1{\cdot}0 \pm 0{\cdot}2$.

The relationship $d\omega/\omega = -\gamma dV/V$ is more conveniently expressed as $d\omega/\omega = -3\gamma dl/l$, where l stands for a linear dimension of the lattice. The next step consists in applying this relationship to the present case. First of all we note that ω_e refers to vibrations parallel to the c axis and ω_o to vibrations perpendicular to it. This implies that the bonds parallel to the c axis do not contribute to ω_o. Suppose now that the average length of these last bonds is $r + \Delta r$, whereas the average length of the other bonds is r. If all bonds were of equal length r, the average frequency would be $\bar{\omega} = \omega_o$. In the present situation the average bond length is $r + \frac{1}{4}\Delta r$ and the average frequency is $\frac{1}{3}(\omega_e + 2\omega_o)$. Thus a frequency shift $\Delta\bar{\omega} = \frac{1}{3}(\omega_e + 2\omega_o) - \omega_o = \frac{1}{3}(\omega_e - \omega_o)$ corresponds to a difference of the bond lengths of $\frac{1}{4}\Delta r$. In terms of the formula $d\omega/\omega = -3\gamma dl/l$ this means

$$\frac{\omega_e - \omega_o}{3\bar{\omega}} = -\tfrac{3}{4}\gamma \frac{\Delta r}{r}.$$

Substitution of the appropriate numerical values yields $\Delta r = 0{\cdot}008 \pm 0{\cdot}002$ Å, in quantitative agreement with the X-ray results.

The fact that $\Delta r > 0$ deserves some attention. Careful investigations (Jeffrey, Parry & Mozzi, 1959; Burley,

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* The greatest uncertainty concerns the value of C_v. A Debye temperature of 1430°K (T. & J.) corresponds to $C_v = 4{\cdot}74$ cal.mole^{-1}deg^{-1}, but on the other hand, $C_p \simeq C_v$ and $C_p = 6{\cdot}48$ cal.mole^{-1}deg^{-1} (*Handbook of Physics and Chemistry*, 1963). The mean value, 5·61 cal.mole^{-1}deg^{-1}, is at least of the correct order of magnitude.

Table 5. *Observed and calculated structure factors*

Within each group the columns, reading from left to right, contain the values of l, F_o (corrected for secondary extinction) and $k|F_c|$ (obtained by Fourier methods).

0 0 L		
4	9	1
6	1421	1417
8	8	4
10	14	4
12	752	727
14	12	4
18	747	735
20	16	5
22	37	6
24	642	642
26	19	5
28	15	4
30	350	357
32	16	4
1 0 L		
0	10	0
1	500	454
2	674	708
3	578	638
4	413	454
5	299	286
6	14	0
7	421	403
8	715	709
9	740	738
10	529	521
11	244	237
12	15	1
13	222	211
14	456	440
15	570	557
16	491	478
17	263	254
18	17	1
19	151	146
20	212	212
21	267	266
22	277	277
23	188	183
24	20	1
25	156	154
26	217	216
27	174	173
28	114	114
29	81	81
30	11	1
31	108	110
32	191	199
2 0 L		
0	8	0
1	352	353
2	512	523
3	490	480
4	376	361
5	242	235
6	14	0
7	325	318
8	573	567
9	610	601
10	446	431
11	208	197
12	13	1
13	181	176
14	379	372
15	482	475
16	418	411
17	225	219
18	20	1
19	123	124
20	176	179
21	226	228
22	241	243
23	163	162
24	17	1
25	133	138
26	192	193
27	149	154
28	99	101
29	68	74
30	17	1
31	91	101
3 0 L		
0	902	951
2	14	1
4	15	1
6	720	732
8	12	2
10	14	2
12	417	416
14	26	3
16	16	3
18	474	478
20	34	3
22	13	4
24	456	462
26	14	4
28	17	3
4 0 L		
0	24	0
1	190	186
2	272	271
3	245	240
4	175	174
5	115	118
6	17	0
7	175	174
8	326	315
9	336	335
10	237	236
11	103	103
12	13	0
13	92	94
14	216	215
15	287	285
16	250	251
17	139	134
18	20	0
19	79	73
20	102	103
21	139	141
22	159	159
23	108	109
5 0 L		
0	16	0
1	137	131
2	188	188
3	168	161
4	110	113
5	79	80
6	12	0
7	128	124
8	233	227
9	244	241
10	178	169
11	76	72
12	11	0
13	71	68
14	164	158
15	227	213
16	195	190
1 1 L		
0	1128	1410
2	19	1
4	9	2
6	960	1050
8	24	3
10	13	3
12	614	607
14	16	4
16	19	5
18	622	629
20	24	4
22	14	5
24	561	571
26	12	4
28	13	4
30	318	326
2 1 L		
0	16	0
1	303	291
2	442	433
3	408	400
4	309	302
5	202	196
6	16	0
7	274	266
8	486	478
9	511	508
10	367	364
11	166	165
12	10	1
13	148	148
14	322	318
15	414	411
16	363	358
17	194	191
18	23	1
19	113	106
20	149	152
21	197	199
22	211	215
23	142	145
24	20	0
25	126	124
26	172	174
27	136	139
28	86	92
29	66	67
3 1 L		
0	13	0
1	215	213
2	309	312
3	283	281
4	206	207
5	135	138
6	10	0
7	196	198
8	357	358
9	373	381
10	267	270
11	116	119
12	26	0
13	112	108
14	242	242
15	319	319
16	279	280
17	150	150
18	21	0
19	82	82
20	110	116
21	152	156
22	167	174
23	112	119
24	19	0
25	103	104
4 1 L		
0	531	557
2	24	0
4	18	1
6	410	423
8	17	1
10	25	1
12	219	228
14	19	2
16	13	2
18	309	312
20	18	2
5 1 L		
0	19	0
1	107	108
2	153	155
3	122	132
5	64	66
6	20	0
7	95	104
8	180	190
9	205	202
2 2 L		
0	764	817
2	20	1
4	14	1
6	608	627
8	12	2
10	37	2
12	347	351
14	17	2
16	12	3
18	413	423
20	16	3
22	27	3
24	413	421
26	15	3
3 2 L		
0	19	0
1	168	164
2	236	237
3	208	208
4	148	149
5	104	103
6	14	0
7	162	154
8	282	280
9	299	298
10	213	210
11	94	90
12	14	0
13	87	83
14	189	192
15	254	256
16	226	227
17	116	122
18	20	0
19	66	66
20	89	94
21	122	129
22	142	146
4 2 L		
0	27	0
1	124	118
2	167	170
3	145	145
4	98	101
5	69	72
6	16	0
7	111	113
8	214	206
9	210	220
10	146	154
11	66	66
12	18	0
13	80	62
14	159	146

1963) of wurtzite type structures with $c/a < 1\cdot633$ have shown that Δr is related to c/a and empirical formulae have been proposed to express this relationship. These expressions imply that $\Delta r > 0$ if $c/a < 1\cdot633$ in agreement with the experimental results. Extrapolation would lead to $\Delta r < 0$ if $c/a > 1\cdot633$. Although strictly speaking the present results do not refer to a wurtzite type structure, yet they strongly suggest that such an extrapolation is unallowable and that the formulae are of limited validity only.

The distance between the two double-layers in cubic environment is $2\cdot5163 \pm 0\cdot0008$ Å, which leaves for the average $h-c$ distance $2\cdot5212 \pm 0\cdot0004$ Å. Thus the $c-c$ and $h-c$ distances are significantly different, as are the interlayer distances in the sphalerite (*B*3) and wurtzite (*B*4) type structures themselves (2·517 Å and 2·524 Å respectively). This indicates that the bond energy of silicon carbide depends markedly on the number of *h* and *c* double layers in the crystal structure. Therefore at least some modifications of SiC, particularly those with short repeat distances along the *c* axis, might correspond to free-energy minima under certain conditions of growth.

Experimental evidence to support this point of view is provided by Knippenberg (1963) who observed that the relative abundance of the various SiC types depends on the growth temperature. According to this author the *B*4 structure built up entirely from hexagonally surrounded double-layers is the stable modification at 1300–1600°C. With increasing growth temperatures the number of *h* double-layers in the structure decreases and the types 4*H* (50%*h*), 15*R* (40%*h*), 6*H* (33%*h*) and 8*H* (25%*h*) are found successively. The *B*3 structure (0%*h*) is metastable at all temperatures. It is noteworthy that the X-ray density decreases in the same order (Table 1).

It would be tempting to extend the above argument to all SiC types and to ascribe the occurrence of the numerous polytypic structures to a very subtle thermodynamic equilibrium which shifts with temperature. Schneer (1955) follows this line of thought in his theory of polytypism. Ultimately, however, this leads to the assumption of ordering forces which act over distances as long as 500 Å (SiC type 594*R*); such forces are not only unknown, but also hard to conceive. Besides this, Knippenberg's experiments do not yet allow the inclusion of any but the above-mentioned types of SiC in a thermodynamic theory of polytypism. Finally, there is other experimental evidence (Knippenberg & Gomes de Mesquita, 1965) to suggest that the formation of long-period SiC structures is not determined by thermodynamic equilibrium conditions, but results from intergrowth of (probably much simpler) structure types. This agrees well with the fact that almost all long-period structures known to date can be described in terms of the types 4*H*, 15*R*, 6*H* and 8*H* in which periodic stacking faults occur. These 'basic' types have at most 5 double layers in the asymmetric unit.

It seems now that any explanation of polytypism in SiC requires:

(1) an understanding of the stability of the basic types,

(2) a suitable mechanism responsible for the periodic mistakes in these basic types leading to the formation of long-period structures.

The present work bears only upon the first item. In this respect it must be noted that it is impossible at present to compute the lattice energies of the basic types, or even of the *B*3 and *B*4 structures only. For II–VI and III–V compounds such calculations based on three-ion interactions were performed with remarkable success (Lombardi & Jansen, 1965) and it was shown that the relative stabilities largely depend on the interatomic distances. In most of the investigated cases *B*3 is stabler than *B*4, but above a certain critical value of the bond distance, *R*, *B*4 is stabler than *B*3. Repulsion between like ions at a distance $R\sqrt{8}$ is the decisive factor. Since the vectors between these ions make an angle of at most 28° with the $a-b$ plane, it is understandable that the c/a ratio of the *B*4 structures concerned (BeO, AlN, MgTe) is somewhat smaller than the ideal value 1·633; this contributes to the stability of the structure. Perhaps for the same reason most other *B*4 structures have $c/a < 1\cdot633$ (Donnay & Nowacki, 1954). Actually, this seems to be a rule with only three exceptions, *viz.* AgI ($c/a = 1\cdot635$), ZnS ($c/a = 1\cdot636$) and SiC ($c/a = 1\cdot641$). For AgI the deviation from the ideal value is not significant (Burley, 1963). It is remarkable that the two remaining compounds offer the most striking examples of polytypism. However, their low-temperature structures are different: *B*3 for ZnS, *B*4 for SiC. Clearly, much work has to be done before all this is satisfactorily explained.

Implicitly or explicitly all theories of polytypism developed so far assume that at least a certain number of polytypic structures are formed under conditions of thermodynamic equilibrium. However, there is no consensus of opinion as to the relative importance of the energy and entropy contributions involved. The present work shows that besides the electron-energy effects (Knippenberg, 1963) the bond-energy effects cannot *a priori* be neglected.

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The Crystal Structure at 220 °C of Orthorhombic High Tridymite from the Steinbach Meteorite

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Tridymite from the Steinbach meteorite has been examined at 220°C and found to be orthorhombic, space group $C222_1$ with $a=8{\cdot}74$, $b=5{\cdot}04$, $c=8{\cdot}24$ Å. The crystal structure has been determined and refined, using single-crystal counter-diffractometer data, to $R=8{\cdot}6\%$. The resulting structure, though similarly connected, is distorted in comparison with the ideal high-tridymite structure. The tetrahedra remain nearly regular but are rotated from the ideal positions. The oxygen atoms show strong disorder which is interpreted as thermal in origin. The magnitudes of the thermal displacements, especially of the oxygen atoms normal to their bonds with silicon atoms, are unusually large, amounting to 0·4 Å.

Introduction

Tridymite, a polymorph of SiO_2, is known from numerous sources (meteorites, refractory silica brick, natural terrestrial occurrences with widely different temperatures of formation, and from numerous diverse syntheses). The variation in diffraction effects observed with crystals from different sources suggests the existence of several different types of tridymite. The (only) three meteoritic and (only) two silica brick tridymites examined to date using single-crystal methods (Dollase & Buerger, 1966) give identical results and constitute the tridymite type considered here. On the basis of an existing chemical analysis the Steinbach meteoritic tridymite was chosen for further structural studies of this tridymite type.

Tridymite from the Steinbach meteorite was found, from film and single-crystal diffractometer observations, to exist in three well defined structural states between room temperature and 250°C. Each of the phases is characterized by a different cell and symmetry (Dollase & Buerger, 1966; Hoffman, 1967). The room-temperature phase is monoclinic, Cc or $C2/c$, with $a=18{\cdot}54$, $b=5{\cdot}00$, $c=23{\cdot}83$ Å, $\beta=105{\cdot}7°$. Above about 107°C this phase transforms reversibly to a phase which shows a cell dimensionally similar to that reported for high tridymite (see below). Photographs taken above this temperature, however, reveal that the reciprocal-lattice points corresponding to this small cell are accompanied by satellites in the pseudohexagonal **a*** direction which are faint, though sharp, and whose spacing indicates a true periodicity that apparently varies continuously from about 105 Å at 107°C to about 65 Å at 180°C; at this temperature the satellites fade into the background. The origin of the satellites is tentatively assigned to strongly correlated thermal motion of the type postulated to account for similar observations in $NaNO_2$ (Tanisaki, 1963).

The polymorph existing from about 180°C to beyond the 250° limit of the investigated temperature range, is here termed orthorhombic high tridymite since it shows the same small cell (though different symmetry) that has been reported for high tridymite (Gibbs, 1927). This paper reports the results of a study of its crystal structure at 220°C.

Previous structural studies of high tridymite

The first structural study of tridymite was that of high tridymite made by R. E. Gibbs in 1927. The source of the tridymite was not given. The unit-cell parameters were measured from Laue and oscillation photographs taken at an undetermined temperature 'well above the transition point'. Gibbs concluded that at this temperature the Laue symmetry was $6mmm$, and that the reflections of the type $hh.l$, $l=2n+1$ were absent. By requiring the structure to be composed of regular SiO_4

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