

## On the Crystal Structure of Silicon Carbide and its Content of Impurities

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The crystal structure of silicon carbide presents a pronounced peculiarity which has hitherto been observed in only a few other substances. It appears in a number of closely related crystal forms, which do not, however, constitute different modifications. Similar cases are met with in, for example, the tridymite<sup>1</sup>, parisite and coquimbite<sup>2</sup>. We have in silicon carbide the formation of a special series of superstructures. The difference in lattice energy between these structures is definitely very small, and it has not been possible to detect any chemical or physical differences between them indicating that they belong to different modifications or phases.

The most common forms were investigated by Baumhauer<sup>3</sup> when he first studied the morphology of silicon carbide. He named the phenomenon polytypy. The old-established names of the common forms also date from him; he called them types I, II and III in turn, as he investigated them. The so-called amorphous silicon carbide, formerly named type IV, occupies a special position, and Thibault<sup>2</sup> has recently proposed the name  $\beta$ -SiC to distinguish it from all the other types which come under the name  $\alpha$ -SiC.

This  $\beta$ -SiC is formed at a lower temperature than  $\alpha$ -SiC, and has a structure characteristically different from the other types. I may, therefore, be justifiable to distinguish this form as a separate modification. However, as the use of the prefixes  $\alpha$  and  $\beta$  may possibly cause some misunderstanding, since here they are applied in the reverse order from what is customary in phase diagrams, we shall call them here by more explicit names, the cubic («amorphous») silicon carbide being called the *low temperature modification*. All the other types then belong to the *high temperature modification*.

The low temperature modification is normally formed at 1800—1950° C, but under special conditions, it may also be formed at temperatures down to

1200—1300° C<sup>4</sup>. At 1950—2200° C it is monotropically transformed into the high temperature modification, mainly via the gaseous phase.

The low temperature modification crystallizes in a diamond lattice. All the types of the high temperature modification constitute mean-stages between a diamond and a wurtzite lattice, but a pure wurtzite lattice is never formed.

The structures of types I, II and III were established by Ott<sup>5</sup>, who also observed a new type called V, the structure of which has recently been calculated by Zhdanov and Minervina<sup>6</sup> and Ramsdell<sup>7</sup>. Ott, however, assumed that each type represented a separate modification and the long established denotions mod. I, mod. II, etc., are due to him. Later on Thibault<sup>2</sup>, Ramsdell<sup>7</sup> and Zhdanov and Minervina<sup>6</sup> reported the appearance of further types, so that at present the number of closely investigated types is 7 or 8. It is, however, necessary to remember that only types I, II and III (and the low temperature modification) appear normally. The other types have only been observed in unique specimens. For a full account of these types, the reader must be referred to the literature. A complete survey of the range up to 1944 is to be found in Thibault<sup>2</sup>.

In the following discussion we will avoid dividing the structures into cubic, hexagonal and rhombohedral systems as has often been done. Instead, we will describe all the types starting from their hexagonal cells. Then all the types have the same *a*-axis, whereas the length of the *c*-axis varies with the number of layers which characterizes the type in question. Each kind of atom is tetrahedrally coordinated by the other kind. The tetrahedrons may be stacked with successive layers, parallel or anti-parallel to each other.

Until now, very little has been known as to the reason for the development of certain characteristic sequences of alternating cubic and hexagonal closest packing in the silicon carbide structures. It is true that Baumhauer<sup>3</sup> could state that *green* crystals were characteristic of type II, *yellow* crystals of type I and that the *black* crystals were most frequently built up of intimately coalescent domains of types I, II and III. Some investigators have, on the whole, confirmed Baumhauer's observations, but Thibault<sup>2</sup>, who has recently investigated a great number of silicon carbides, has not been able to find such a correlation for the American products. The other types are very rarely observed.

Zhdanov and Minervina<sup>6</sup> have assumed that the appearance of the different types is caused kinetically or by impurities, but no systematic comparisons between X-ray crystallographic investigations and chemical or spectro-chemical analyses are to be found anywhere in the literature. For a closer understanding of the connection and differences between the structure types it seemed, however, necessary to find if there exists some correlation between the types and the content of impurities in the silicon carbide.

A comprehensive investigation on the chemical and physical properties of silicon carbide has been in progress at the Electrothermal Institute since 1945. In these investigations we have considered it especially important that *all* the samples of silicon carbide obtained should be studied by *all* the methods developed and the results systematically correlated. The results of the correlated series of spectrochemical analyses\* and X-ray crystallographic investigations\*\* are given below. The results of the remaining investigations will soon appear in a technical publication (*Acta Polytechnica*).

### EXPERIMENTS

*The X-ray analyses* were carried out by the powder method with focussing cameras of Bohlin-Phragmén type. Most of the photograms used for identifying the structural types were taken with cameras with dispersion angle  $\Theta = 29^\circ\text{--}57^\circ$ . For precision determination of the cell dimensions only cameras with dispersion angle  $47^\circ\text{--}82^\circ$  were used. The wavelengths of the Cr-radiation used were taken as  $K\alpha_1 = 2.289\ 62\ \text{\AA. U.}$  and  $K\alpha_2 = 2.293\ 52\ \text{\AA. U.}$  The preparations had to be moved during the exposures, otherwise the lines became spotty.

*The spectrochemical analyses* have been made with a continuous d. c. arc between coal electrodes. The spectrograms have been taken in a large Hilger spectrograph with quartz optic. Standard No. 112 Silicon Carbide from the National Bureau of Standards has been used as the standard preparation. All the preparations have been crushed in an agate mortar to approximately the same grain size as the standard. The samples were taken from grains of 0.30—0.25 mm of the preparations, which had been carefully washed in hydrochloric acid.

The greater part of the spectrochemical analysis has comprised only the elements Al, Fe, Mn and Mg. In addition to these elements, the analysis of the standard also included Ti, Zr and Ca. Preparatory qualitative spectrochemical analyses have also shown the presence of V, Cr, Ni, Sn and Pb.

A preliminary investigation showed, however, that only the first-mentioned elements were present in such percentages that it was necessary to determine them in the preparations now studied.

Systematic determinations of the *specific weight* of the different products and *microscopical investigations* have also been carried out in connection with the analyses and X-ray investigations. The microscopical investigation comprised a study of the structure of natural crystals and cut specimens as well as a determination of the relative content of grains of different colours in crushed products of different grain-sizes.

A large number of silicon carbide products of Swedish, Norwegian and American origin have been examined. It has been considered of great importance to extend the investigation to comprise as many qualities and materials with as different an origin, prior

\* The spectrochemical analyses have been performed at the Metallographic Institute by G. Carlsson and P. Spiegelberg to whom the author is much indebted.

\*\* The X-ray photographs have been made at the Institute of Inorganic and Physical Chemistry at the University of Stockholm by S. Sahlquist and H. Larsson to whom many thanks are due.

treatment and content of impurities as possible. In several cases the normal commercial products have been supplemented by specially synthesized preparations. In all, about 200 products have been studied.

In most cases the preparations have been taken from crushed silicon carbide of the same origin and with the same grain-size (0.30—0.25 mm). The analyses obtained have been representative of a large quantity of silicon carbide — well mixed. This procedure has been necessary in view of the connection between these investigations and the others that have been carried on at the same time. By this procedure, however, it has not been possible to find the characteristic variations and their connections with the same accuracy as would have been the case if it had been possible to take only single homogeneous crystals for the X-ray investigations and the spectrochemical analyses. As large and homogeneous crystals, however, only constitute a minor part of the yield of a silicon carbide furnace, this inconvenience has been thought fully compensated by the advantage of a broader survey. In addition, the individual crystals are not usually homogeneous, but contain zones with different crystal types and probably with different content of impurities.

## RESULTS

The common structure types, normally called types I, II and III, have appeared regularly in the X-ray photograms. No certain observations have been made of the types VI, V, IV, etc. which are reported in the literature in unique specimens. Usually the low-temperature modification does not appear in the commercial products. In most photographs, however, *extra reflexions* have appeared. The positions of these extra reflexions have varied from preparation to preparation. Only a few of them have reappeared in more than two different photograms. It has not been possible to identify the lines with any of the reflexions that might be expected to originate from the different conceivable impurities. A reasonable explanation is, therefore, that we are dealing here with effects of the same phenomenon that give rise to the appearance of the types I, II, III, etc. We have found many new types out of the great number of varieties that may be assumed to appear. In several cases it has been possible to calculate the probable axis lengths of these types. As the well-mixed material may always contain several new types at the same time, no special regard has been given to the calculations, which have been founded on only a few reflexions from each special photogram, and which are, therefore, quite uncertain.

## Connection between the structure types and the colours of the crystals

Even at an early stage it was possible to confirm that a connection existed between the different colours of the grains and the structure types appearing in them. Preliminary indications in this direction were also in fact observed

during an investigation made in 1943—44 by N. Schrewelius\*, who assumed the type II to be characteristic of white crystals. The relative content of the common types I, II and III in differently coloured preparations is listed in Table 1. The values given are means of three sets of preparations that have been separated from two different Swedish and one American product. The contents are estimated visually from the powder photographs.

*Table 1. Relative content of structure types I, II and III in differently coloured fractions of silicon carbide products. Means of three sets of preparations.*

Type	White light green	Green dark green	Yellow yellow-green	Blue-grey blue-green	Black half-opaque	Opaque
II	100	70	10	45	30	20
I	0	25	85	40	40	10
III	0	5	5	15	30	70

It was thus possible to state that type II seemed to be characteristic of pure white and green silicon carbide (free or nearly free from observable impurities). Type I seemed to appear most rich in yellow and yellow-green crystals, (in a moderately impure material) and type III seemed above all to characterize a more highly impure black product. This product has been called opaque-black, on account of its colour and appearance in the microscope, as compared with the half-opaque products which are more translucent in thin laminae and where the black colour seems largely to originate from a content of small particles of graphite. (See further below.)

### The lattice dimensions

For a clear understanding of the causes of the appearance of the different types, it seemed of special importance to establish as accurately as possible the appearance of any characteristic variations in the lattice constants. No such variations are stated in the literature, but earlier comparisons have mainly dealt with possible variations in the *c*-axis in the same type, or have been carried out with cameras with a limited resolving power.

To get an elucidating comparison between the different types, it is necessary to investigate the relations between the smallest fundamental distance

\* Private communication.

along the *c*-axis of the different types, *i. e.* the distance between the silicon layers.

To achieve the best possible precision in this respect, two preparations were exposed in the same camera and on the same film one after the other. The one preparation was of a very pure silicon carbide (Al and Fe less than 0.01 %) which contained exclusively type II, but for a few weak extra lines. The other preparation was of a very impure silicon carbide (Al 0.30 %, Fe 0.07 %) which contained only type III and a little of type I.

The lattice dimensions were:

Type II	<i>a</i>	=	3.0800 ± 0.0002 Å. U.	
	<i>c</i>	=	15.098 ± 0.001 Å. U.	
	<i>c</i> /6	=	2.5164 ± 0.0002 Å. U.	
	Si-C	=	1.8861 Å. U.	
	$\sigma_{\text{calc.}}$	=	3.213	$\sigma_{\text{obs.}} = 3.209 + 0.001$
Type III	<i>a</i>	=	3.0800 ± 0.0002 Å. U.	
	<i>c</i>	=	10.081 ± 0.001 Å. U.	
	<i>c</i> /4	=	2.5202 ± 0.0002 Å. U.	
	$\sigma_{\text{calc.}}$	=	3.208	$\sigma_{\text{obs.}} = 3.201 + 0.005$
Type I	<i>a</i>	=	3.0800 Å. U.	
	<i>c</i>	=	37.817 Å. U.	
	<i>c</i> /15	=	2.521 (± 0.001) Å. U.	

At the transition from type II to type III (I), the silicon layers thus increase their distance from 2.5164 to 2.5202 Å. U. or 0.15 %. The observed specific weight of type II agrees well with the theoretical value, whereas the observed specific weights of the black opaque silicon carbides, rich in type III, show slightly greater deviations owing to their content of foreign matter. It is of importance to note that the reflexions in most cases have been very sharp. No general broadening of the lines is observed. Reflexions common to all types are, however, split up in a number of closely spaced fine lines when more than one type is present.

### The spectrochemical analyses

For the spectrochemical analyses 60 preparations were selected from the total of about 200 preparations investigated by X-rays. The analyses showed great variations in the content of Al, smaller variations in the Fe content and very small in Mg and Mn. Systematic comparisons between the analyses and the structure types of the samples showed clearly a close connection between

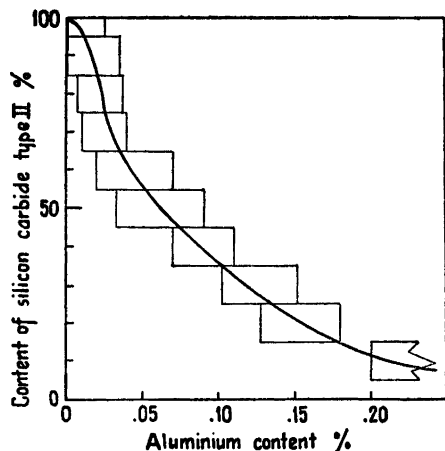


Figure 1. Correlation between the aluminium content of silicon carbide and its relative content of type II as estimated visually from the powder photograms. The relative uncertainty of the values is indicated by the rectangles.

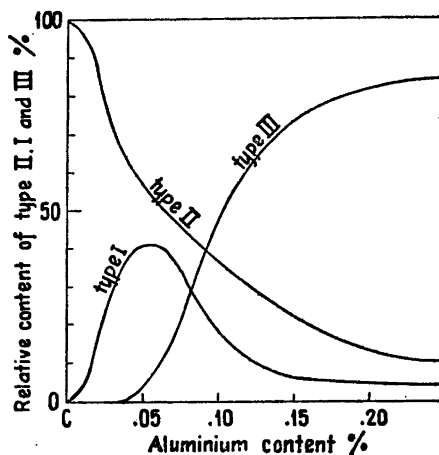


Figure 2. Correlation between the aluminium content and the relative content of the three main types of silicon carbide.

the Al content and the relative content of structure types III and I. This is illustrated in Fig. 1, where the Al content is plotted against the relative content of type II as estimated visually from the powder photograms. The relative uncertainty of the measurements is indicated by the size of the rectangles. In Fig. 2 the connection between the Al content and the relative content of all the three main types is drawn in an idealized form.

No such correlation could be observed between the structure types and the content of Fe, Mg or Mn. It must, however, be pointed out that the Al content in all the samples, with only a few exceptions, was larger than the content of any other impurity. In a few cases the Fe content was considerably higher than the Al content, but not even in these cases was it possible to find any transition of the structure types to type III with increasing Fe content.

Thus, silicon carbide when free from impurities, crystallizes in type II. With increasing content of impurities, above all of aluminium, there appears a transition to type I, the relative content of which has a maximum at about 0.05–0.06 % Al. At still increasing percentage of Al the transition proceeds to type III which begins to dominate at about 0.10 % Al. Samples with more than 0.20 % Al have 70–90 % of type III.

Even at very high contents of Al, however, the preparations still have appreciable percentages of type II (and I). If we want to explain the type

transition by the Al-atoms entering and causing the periodic re-arranging of the lattice, some difficulties arise at first as to how to explain why a lattice which is evidently saturated with Al does not crystallize exclusively in type III.

As mentioned above, however, the samples investigated were not homogeneous. They were prepared as representative samples from large quantities of crushed silicon carbide. Certainly in most cases the primary product came from the same silicon carbide furnace, and frequently from a very narrow range in this furnace. The average analysis should thus be highly characteristic of the silicon carbide in question. Accidental local variations in the concentration of the impurities in the raw material, as well as variations in the running of the furnace, will, however, cause small variations in the content of impurities from point to point in the product. Even large single crystals often show an irregular distribution of their impurities, resulting in differently coloured zones. Consequently, slightly impure material will always appear even in a mass of highly impure silicon carbide. At many points there will also be an excess of impurities and then other phases will appear. Analyses of differently coloured preparations, which have been separated from the same sample (under the microscope), have also shown that the impurities are unevenly distributed in the material.

#### Microscopic observations

The almost colourless or green crystals (which are of type II) when observed in the microscope show very little inclusions, and the very few inclusions observed are evidently carbon particles that have not reacted completely (Fig. 3). The yellow, yellow-green and black crystals, on the other hand, show considerable contents of inclusions. In the yellow (yellow-green) crystals, these inclusions are very finely dispersed (Fig. 4).

In black, half-opaque crystals, which have a higher but still relatively low content of impurities (Al = 0.10—0.15 %), the concentration of inclusions is very high, but the particles are small and the largest of them have the appearance of graphite laminae. When studying such a crystal with increasing amplification, an ever increasing number of smaller and smaller particles is observed (Fig. 5). Most suitable for this study is a thin rough plane crystal. At the same time the colour of the crystal becomes blue and increasingly lighter. Thus the black colour is evidently caused by the great number of more or less finely dispersed foreign particles in the crystal.

In black opaque silicon carbides with still higher Al contents (more than 0.20 %), and with high Fe contents, greater particles appear, the forms of

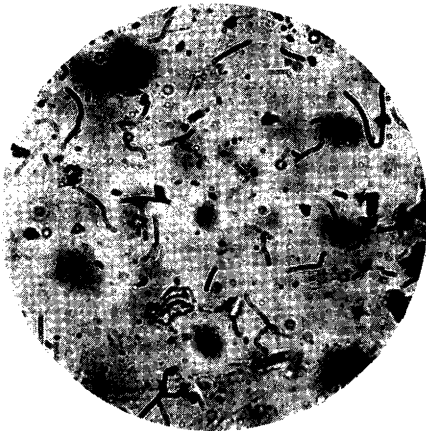




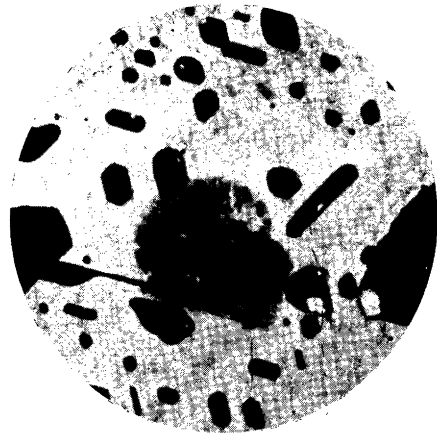
*Figure 3. Green silicon carbide ( $\times 150$ ). Plane rough crystal. Only a few inclusions are observed. The limits of the crystal layers are observed as black streaks.*



*Figure 4. Yellow silicon carbide ( $\times 150$ ). Plane rough crystal. Slightly more opaque than green silicon carbide and containing more inclusions.*



*Figure 5. Black, half-opaque silicon carbide ( $\times 150$ ). Thin plane rough crystal. The number of small inclusions is large.*



*Figure 6. Black, opaque silicon carbide ( $\times 150$ ). Ground specimen. Two phases appear. The black, often pseudo-hexagonal, particles evidently are carbides, silicides or ternary compounds of iron and aluminium. Notice the cloud at the centre of the figure.*

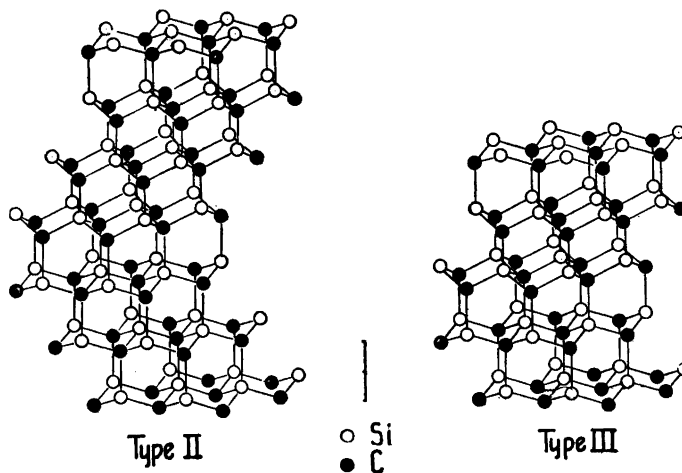


Figure 7. Structures of silicon carbide types II and III according to H. Ott.

which indicate that they were in a molten state when the crystals were formed, and that they were enclosed in cavities with hexagonal faces, thus obviously forming hexagonal crystals (Fig. 5). A direct comparison between a green and a black opaque rough crystal also indicates that the microscopical structure of the black crystal is strongly disturbed even at points where no foreign particles can be observed directly.

These observations, like the results from the X-ray investigation, indicate that the solubility of foreign atoms (*e. g.* Al) in the lattice of SiC is very small. It may be that the solubility is slightly greater at the elevated temperatures where the silicon carbide is formed, and that the Al-rich phase that appears on cooling causes strong strains in the crystal.

#### DISCUSSION OF THE RESULTS

We have found that type II is characteristic of pure silicon carbide and that type III is characteristic of silicon carbide saturated with aluminium, type I of the high-temperature modification evidently forming a mean-stage. For a clear understanding of the connection between all the types appearing, we must consider their crystal structures. Fig. 7 gives the structures for silicon carbide types II and III, according to Ott.

It is possible to describe the similarity, as well as the differences, between the types in a number of ways, all of which show more or less clearly the system according to which the variations appear. It seems most suitable to regard the

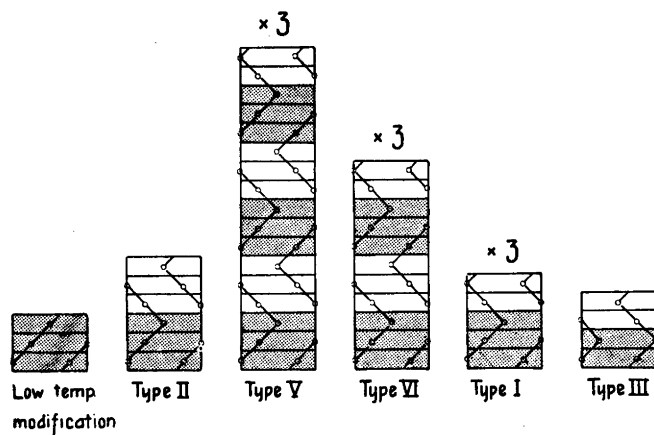


Figure 8. Schematic representation of silicon carbide types.

structure as a close-packed lattice of silicon atoms which is expanded a little by the carbon atoms, but we could also describe it as a close-packed lattice of carbon atoms expanded by the silicon atoms, or as a close-packed lattice of the Si-C-tetrahedrons.

In the low temperature modification the silicon atoms form a cubic closest packing. If we start from this as the fundamental type, we will come to all the realized and conceivable types by permitting a silicon layer to move with regular intervals on to a position above the two preceding layers which belongs to a hexagonal closest packing. In a way we could, therefore, regard all the types of the high temperature modification as super-structures of the low temperature modification.

Now the low temperature modification crystallizes in a diamond lattice, whereas the layers of all the types of the high temperature modification may be grouped together in «diamond»-lamellae. These lamellae are stacked along the  $c$ -axis and each of them is rotated  $180^\circ$  about the  $c$ -axis relatively to the preceding layer. It seems further to be a rule that the number of layers in each lamella is generally only 2 or 3. The only known exception is type IV where the numbers are 3 and 4. In Fig. 8 some of the silicon carbide types are shown schematically. The open rectangles represent the layers in a diamond lamella with all the Si-C-tetrahedrons orientated the same way, while the tetrahedrons in the layers represented by the dashed rectangles are antiparallel to the first set. The zigzag lines indicate the positions of the corresponding atoms in the different layers. (Compare Fig. 7.)

It is possible that the diamond lattice of the low temperature modification of silicon carbide is connected with the lowest free lattice energy. When the temperature rises and the thermal movements of the lattice increase, however, the growth of the diamond lattice is checked after every third layer, giving rise to type II. When the lattice is saturated with aluminium as in type III, the diamond lamellae will only be developed to 2 layers. At intermediate aluminium contents, there will now and then appear the regular alternation of 2 and 3 layer lamellae, which will give rise to the more rare types (IV, V, etc.). The probability of the formation of type I is evidently rather large under these circumstances.

Zhdanov and Minervina<sup>6</sup>, who have discussed some of the silicon carbide structures in a similar manner, have chosen to represent the structures by numerical symbols only, in accordance with a system developed by Belov<sup>8</sup>. If we adopt their system, slightly modifying it by applying a dash above each other number to symbolise the different orientation of neighbouring lamellae, we obtain a very condensed representation of the types (Table 2). A similar system has also been developed by Ramsdell<sup>7</sup>.

Table 2. Numerical symbols of the different types of silicon carbide.

Modification	Type	Hexagonal c-axis	Symbol
Low temp.		7.55 Å.U.	$\infty 3$
High temp.	II	15.098	$3.\bar{3}$
» »	V	128.3	$(3.\bar{3}.3.\bar{3}.3.\bar{2}) \times 3$
» »	VI	82.94	$(3.\bar{3}.3.\bar{2}) \times 3$
» »	IV	52.78	$(4.\bar{3}) \times 3$
» »	I	37.817	$(3.\bar{2}) \times 3$
» »	III	10.081	$2.\bar{2}$

Naturally a number of more complicated sequences will be possible, but the probability of their formation will be small. It is evident that type I, and the other more rare types of the same modification (IV, V, VI), may be looked upon as mean-stages between types II and III, or as coalescences of them — or fractions of them — along the *c*-axis with a fortuitous, but in the special case, strictly regular sequence. In this connection we may remind the reader of the fact that the black crystals most often contain all three types intimately coalescing along the *c*-axis.

In a way, the phenomenon offers an analogy to the conditions of pure cobalt, which have been investigated by Lipson and Edwards<sup>9</sup> and Wilson<sup>10</sup>.

In cobalt, however, there appears a *statistical* alternation of the cubic and hexagonal closest packed lattices of the two modifications of cobalt, while in silicon carbide the alternation is evidently not statistical, but strictly systematic over sufficiently long periods, as we have observed no broadening of the X-ray reflexions.

As has been shown above, Al is the only one of the impurities hitherto studied that has been observed to give a type transition and a perceivable expansion of the lattice. It is interesting to connect this fact with the great resemblance between the structures of SiC and that of the aluminium carbide  $\text{Al}_4\text{C}_3$ .

According to Stackelberg and Schnorrenberg<sup>11</sup>, who established the latter structure, it is however more convenient to look upon it as a close-packed lattice of  $\text{C}^{4-}$  ions which is rather strongly deformed by  $\text{Al}^{3+}$  ions. The bonds in  $\text{Al}_4\text{C}_3$  have clearly a more ionic character than the pure homopolar bond of SiC. It is thus highly conceivable that an Al-atom (ion) may be substituted for a Si-atom in SiC, but that it will at the same time introduce a strain and a tendency to deform the silicon carbide lattice. A local excess of Al must in turn result in the formation of another phase, *e. g.*  $\text{Al}_4\text{C}_3$ , possibly with some Si substituted for Al.

The pure SiC is a non-conductor of electricity. As Al has one valence electron less than Si, every Al-atom substituted for a Si-atom will give rise to a disturbing centre in the lattice, which will make the crystal a semi-conductor of the electron defect type. (A compensating subtraction of C-atoms would no doubt complicate the case.). Now the black silicon carbides (with their high aluminium contents) really *are* electron defect semi-conductors, and Busch and Labhart<sup>12</sup> have shown by measurements of the Halleffect that the concentration of disturbing centres is rather high. (Their highest values approximately correspond to an Al-concentration of 0.10 %.)

In many silicon carbide products the iron content seems to play an important rôle. Evidently the iron can cause no type transitions, but in most cases it seems to be the Fe content that confers on the green silicon carbide its colour. The green crystals, which have an iron content equal to or even higher than the aluminium content, are semi-conductors of mainly excess electron type. Busch and Labhart have found the maximum concentration of disturbing centres in green SiC to be about a tenth of that of the black types. Probably the iron is still less soluble in the SiC lattice than aluminium, on account of the metallic character of the bonds in the iron carbide. Even with relatively low iron contents, the main part of the iron may be in colloidal dispersion. With increasing Fe content the main part is separated as discrete, molten particles

of iron carbides, silicides or ternary compounds, inside or on the surface of the crystal.

Naturally it is highly conceivable that a lot of other impurities could enter the silicon carbide lattice and disturb it more or less. In the first place this would be true of the other members of the fourth and third groups of the periodic system. It has been observed that boron is rather soluble in the lattice, but in this case it may be a question of an addition compound or of a substitution for the C-atoms.

Hitherto it has not been possible to investigate systematically the different possibilities in this respect on account of the difficulties of making in a laboratory reliable syntheses which would give products formed under almost the same conditions as in a large furnace, but with a better specified composition. Experiments in this direction are, however, planned.

Finally, we must remember that some silicon carbide products may also contain material with a deficit of Si or C in the lattice, which would also cause both lattice defects and semi-conducting power. It would, however, be very difficult to establish such defects.

#### SUMMARY

In connection with a general investigation on the properties of silicon carbide, extensive X-ray studies and spectrochemical analyses have been carried out. The material has also been studied by densitometric and microscopical methods.

It is suggested that, to avoid confusion, the cubic, »amorphous», silicon carbide (the  $\beta$  SiC of Thibault) be called the low temperature modification and that all the other types (the  $\alpha$ -SiC of Thibault) be called the high temperature modification.

It is confirmed that different coloured silicon carbides are characterized by different structure types, only the common types I, II and III being considered.

A great number of extra reflexions with varying positions have been observed in the X-ray powder photographs, indicating the appearance of a great number of hitherto unknown types.

Lattice dimensions are given. The lattice is observed to expand along the *c*-axis by 0.15 % at the transition from type II to type III.

The spectrochemical analyses show that there is an obvious connection between the aluminium content and the structural types. Type II is characteristic of the pure SiC, type I of a SiC with moderate amounts of aluminium and type III of a SiC saturated with aluminium. No such connection is found

for other elements studied, *viz.* Mg, Mn, Fe. The percentages of other common impurities have been very low in the samples studied.

The results of the X-ray investigation and of the spectrochemical analyses are supported by the densitometric and microscopical investigations.

The bearing of the results is further discussed with reference to the close resemblance between the structure of SiC and  $Al_4C_3$  and to the semi-conducting power of SiC.

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