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Developments in Silicon Carbide Research*

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An additional five new types of SiC are described, and their unit-cell dimensions and atomic arrangements given. The five types are $8H$ (4 4); $27R$ (2 2 2 3); $51R_{(b)}$ (2 2 2 2 2 2 2 3), differing from the original $51R_{(a)}$, whose sequence is 3 3 3 3 3 2; $75R$ (3 2 3 2 3 2 2 3 2 3); and $84R$ (3 3 3 3 3 3 3 2 3 2).

In order to explain the astounding number of polymorphs of SiC (now 14 fully-described types), it is postulated that in the growth of SiC by sublimation, there are formed certain clusters of atoms (polymers), each characterized by a particular temperature stability range. At a given characteristic temperature, a single type of polymer would produce a 'pure' type, with the sequence consisting of identical pairs, such as 2 2 in $4H$, 3 3 in $6H$, or 3 2 in $15R$. If stability ranges overlap, two polymers might exist simultaneously, resulting in a 'mixed' type. Variations in the proportions of the two polymers present would produce types composed of the same polymers, but in differing proportions, such as

$33R$	3 3 3 2	1:1
$51R_{(a)}$	3 3 3 3 3 2	2:1
$87R$	3 3 3 3 3 3 3 3 3 2	4:1

It would not be possible to have three polymers stable simultaneously, hence no type should be composed of more that two polymers.

No experimental evidence can be advanced to support this idea, but it has served a useful purpose in suggesting possible atomic arrangements for some of the new types.

Introduction

Five new modifications of silicon carbide have been found, and their structures are reported in the first part of this paper. According to the nomenclature of Ramsdell (1947), and in order of increasing unit-cell dimensions, they are $8H$, $27R$, $51R_{(b)}$, $75R$, and $84R$. This brings to 14 the number of SiC polymorphs whose structures have been definitely established. Two additional rhombohedral types have recently been reported, one with about 270 layers, which is a member of a series based on type $15R$ (Zhdanov & Minervina, 1947), and the other with about 594 layers (Honjo, Miyake & Tomita, 1950). Also, Weissenberg photographs of several more types having large rhombohedral unit-cells have been obtained in our laboratory, but their structures have not yet been determined.

If a new polymorph is a member of a series which is based predominately upon a single simple type, its structure determination may be comparatively easy. For example, in the '3---2 rhombohedral series' (Ramsdell, 1947), the larger unit-cells become increasingly like $6H$, and the distribution of the intensity maxima approaches more closely that of $6H$. But if the structure is of a mixed character, with more than one simple type present, choices must be made between possible structures differing by a shift in the positions of only a few atoms. There may be insufficient change in the calculated intensities to make an unequivocal decision. The larger the unit-cell, the greater this difficulty becomes. Only when a large cell has a distribution of intensity maxima such as to clearly identify it with a simple type, is there much hope for an unambiguous solution.

Type 8*H*

The existence of this polymorph and its structure were predicted by Ramsdell (1947). As the symbol indicates, it has an eight-layer hexagonal unit-cell. The space group is $C6_3mc$, as in the $4H$ and $6H$ polymorphs. The unit-cell dimensions are

$$a_0 = 3{\cdot}073, \quad c_0 = 20{\cdot}106_4 \text{ kX.}, \quad \text{and} \quad Z = 8\,.$$

The zigzag sequence is 4 4, resulting in the following coordinates for the Si and C atoms:

$$\begin{aligned} 8\text{Si at } & 0, 0, 0;\ 0, 0, \tfrac{1}{2};\ \tfrac{2}{3}, \tfrac{1}{3}, \tfrac{1}{8};\ \tfrac{2}{3}, \tfrac{1}{3}, \tfrac{3}{8};\ \tfrac{2}{3}, \tfrac{1}{3}, \tfrac{6}{8};\\ & \tfrac{1}{3}, \tfrac{2}{3}, \tfrac{2}{8};\ \tfrac{1}{3}, \tfrac{2}{3}, \tfrac{5}{8};\ \tfrac{1}{3}, \tfrac{2}{3}, \tfrac{7}{8}.\\ 8\text{C at } & 0, 0, \tfrac{3}{32};\ 0, 0, \tfrac{19}{32};\ \tfrac{2}{3}, \tfrac{1}{3}, \tfrac{7}{32};\ \tfrac{2}{3}, \tfrac{1}{3}, \tfrac{15}{32};\\ & \tfrac{2}{3}, \tfrac{1}{3}, \tfrac{27}{32};\ \tfrac{1}{3}, \tfrac{2}{3}, \tfrac{11}{32};\ \tfrac{1}{3}, \tfrac{2}{3}, \tfrac{23}{32};\\ & \tfrac{1}{3}, \tfrac{2}{3}, \tfrac{31}{32}. \end{aligned}$$

Assuming the basic tetrahedral arrangement of silicon and carbon atoms, there are only three possible arrangements of the atoms for the required eight-layer unit-cell. These have the zigzag sequences 2 1 1 1 1 2, 3 1 1 3, and 4 4. The first two of these

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have the symmetry $C3m$, the third $C6_3mc$. Intensity calculations were made for all three structures, and the 4 4 sequence proved to be the correct one. This is in keeping with the apparent limitation of sequences to the numbers 2, 3 and 4, which has been the case for all previously-reported hexagonal and rhombohedral types of SiC.

Most of the crystals described in this paper are intergrowths of two or more types. It is usually impossible to effect a mechanical separation of the types, and composite Weissenberg photographs are obtained. There may be complete coincidence of certain reflections common to both types, or some may be so close together as to cause overlapping, and thus make intensity estimates useless. Likewise, the distributions of the patterns over the film may be variable, with one or the other pattern fading out in certain areas. The observed intensity values given in this paper represent observations of independent observers and were obtained by averaging results from those portions of the films where the pattern was comparatively uniform.

Fig. 1 compares the observed intensities with those calculated for the 4 4 structure. Since the crystal is intergrown with $6H$, the reflection of (10.4) ($8H$) coincides with (10.3) ($6H$) and cannot be used. The $8H$ spacings for (10.0) and (10.8) likewise coincide with (10.0) and (10.6), respectively, for $6H$, but since the latter planes both have missing reflections, the two $8H$ reflections can be used. The graph shows excellent correlation between observed and calculated intensities, and there is no doubt that the sequence 4 4 properly describes the structure.

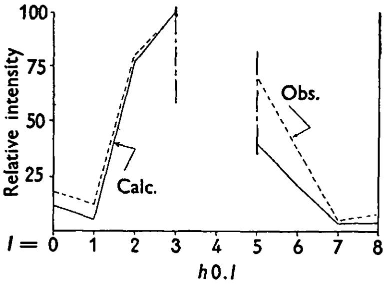

Fig. 1. Comparison of observed intensities with those calculated for 4 4 structure.

Pyramid faces attributable exclusively to $8H$ were found in four adjacent hexagonal bipyramid zones. Goniometric reflections from these faces were poor, the best being rated as 'C'. Table 1 gives the distribution of faces, with the larger basal face arbitrarily chosen as upper. The morphological data are shown in Table 2.

Type 27*R*

This new rhombohedral modification of SiC has the following (hexagonal) cell dimensions:

$$a_0 = 3{\cdot}073, \ c_0 = 67{\cdot}859 \text{ kX.}, \ Z = 27;$$

or, for rhombohedral axes,

$$a_{\text{rh}} = 22{\cdot}68_9 \text{ kX.}, \ \alpha = 7^\circ 46', \ Z = 9 .$$

Chronologically, this was the last of the five types herein described to be discovered. Shortly before it was found, the structure of a new $51R$ type had been determined (see below) and found to be based on a sequence 2 2 2 2 2 2 2 3. This suggested a new series analogous to the '3---2' series proposed by Ramsdell (1947):

Old series 3---2

	$6H$
$15R$	3 2
$33R$	3 3 3 2
$51R_{(a)}$	3 3 3 3 3 2
($69R$)	3 3 3 3 3 3 3 2
$87R$	3 3 3 3 3 3 3 3 3 2

New series 2---3

	$4H$
$15R$	2 3
$27R$	2 2 2 3
($39R$)	2 2 2 2 2 3
$51R_{(b)}$	2 2 2 2 2 2 2 3
($63R$)	2 2 2 2 2 2 2 2 2 3

Each of these sequences must be repeated three times to give the complete unit-cell. Obviously, there is no difference between the sequences 3 2 and 2 3. Thus $15R$ is a member of both series, one converging toward $6H$, the other toward $4H$. The relationship of the two $51R$ types will be discussed later. The forms listed in parentheses remain to be found.

When the $27R$ type was discovered, the sequence 2 2 2 3 was the first to be tested. As a matter of fact, if the sequence numbers are limited to 2, 3 and 4, 2 2 2 3 is the only possible combination which will give a 27-layer rhombohedral cell.

The crystal was intergrown with $6H$, which predominated. Accordingly, the reflections from the $27R$ portion were of comparatively low intensity and in some cases missing. However, sufficient data were obtained from a series of films taken with different orientations to make a satisfactory determination. Fig. 2 compares the calculated intensities with the

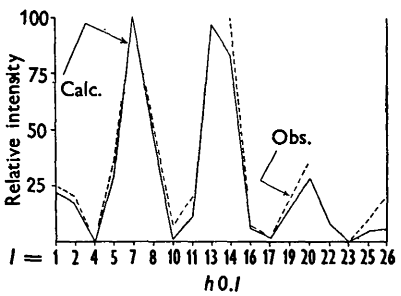

Fig. 2. Comparison of calculated and averaged observed intensities.

Table 1. *Distribution of 8H Faces*

$(1\ 0.l)$	$(0\ 1.l)$	$(\bar{1}\ 1.l)$	$(\bar{1}\ 0.l)$	$(0\ \bar{1}.l)$	$(1\ \bar{1}.l)$
—	—	—	—	—	$(1\ \bar{1}.6)$
—	—	$(\bar{1}\ 1.5)$	—	—	$(1\ \bar{1}.5)$
(1 0.3)	—	—	—	—	—
(1 0.2)	—	—	—	—	—
(1 0.1)	—	—	—	—	—
$(1\ 0.\bar{1})$	—	—	—	—	—
—	$(0\ 1.\bar{5})$	—	—	—	—

Table 2. *Morphological data of* SiC *type 8H.*

	No.		Angle between form and base		
Form	times observed	Quality	Range	Weighted average	Calc.
(0001)	2	*A*			
(1 0.6)	1	*D–E*	51° 34′–51° 40′	51° 38′	51° 33′
(1 0.5)	3	*C–E*	56° 19′–57° 12′	56° 29′	56° 30·5′
(1 0.3)	1	*E*	68° 34′	68° 34′	68° 20·5′
(1 0.2)	1	*E*	75° 01′–75° 13′	75° 09′	75° 10·5′
(1 0.1)	2	*C*	82° 28′–82° 30′	82° 29′	82° 27·5′

Table 3. *Morphological data of* SiC *type 27R.*

	No. times		Angle between form and base		
Form	observed	Quality	Range	Weighted average	Calc.
(0001)	2	*A–E*			
(1 0.13)	1	*E*	63° 03′	63° 03′	62° 59′
(1 0.7)	1	*D–E*	74° 24′–74° 37′	74° 34′	74° 39′
$(1\ 0.\bar{2})$	1	*C–D*	85° 36′–85° 52′	85° 41′	85° 31′
(1 0.1)	1	*C–D*	87° 38′–87° 48′	87° 43′	87° 45′

averaged observed intensities. Intensities for (10.13) and (10.22) are not plotted, for their reflections overlapped those of (10.3) and (10.5), respectively, of 6*H*. The excellent correlation shown by the graph leaves no doubt that the correct structure for 27*R* is described by the sequence 2 2 2 3 (repeated three times).

Just as in the '3---2 series' there results a marked similarity in intensity distribution to 6*H*, so in the '2---3 series' there sould be a corresponding similarity to 4*H*. This is definitely the case for 27*R*, thus giving an additional confirmation of the chosen structure.

The space group for 27*R* is $R3m$, in keeping with the previously-discovered rhombohedral types. The zigzag sequence 2 2 2 3 results in the following atomic positions:

9Si at $0, 0, 0$; $0, 0, 4z$; $0, 0, 8z$; $0, 0, 10z$; $0, 0, 12z$; $0, 0, 14z$; $0, 0, 16z$; $0, 0, 20z$; $0, 0, 24z$.

9C at $0, 0, p$; $0, 0, 4z+p$; $0, 0, 8z+p$; $0, 0, 10z+p$; $0, 0, 12z+p$; $0, 0, 14z+p$; $0, 0, 16z+p$; $0, 0, 20z+p$; $0, 0, 24z+p$.

9Si and 9C at $\frac{1}{3}, \frac{2}{3}, \frac{2}{3}$ + the above co-ordinates.

9Si and 9C at $\frac{2}{3}, \frac{1}{3}, \frac{1}{3}$ + the above co-ordinates.

$$z = \tfrac{1}{27};\ p = \tfrac{1}{36}.$$

Table 3 gives the morphological data for those 27*R* faces measured on the crystal. These faces were confined to one pyramid zone, where they were found along with faces of the hexagonal modification.

Type 51$R_{(b)}$

Films of this new type were obtained in 1948. They were set aside for further study because they showed, in addition to the presence of both 6*H* and 4*H*, indications of a fairly large rhombohedral structure. The films have now been interpreted, but in the meantime the crystal has been lost. The structure proved to be a 51-layer type, but with an intensity distribution differing completely from the previously-described type 51*R*. The authors are at a loss to know how to name these types. For the present they are designated merely as 51$R_{(a)}$ and 51$R_{(b)}$. These two have the same symmetry and identical cell constants:

$$a_0 = 3{\cdot}073,\ c_0 = 128{\cdot}17_8\ \text{kX.},\ Z = 51;$$

or, for rhombohedral axes,

$$a_{\text{rh}} = 42{\cdot}76_3\ \text{kX.},\ \alpha = 4°\ 07',\ Z = 17$$

(Ramsdell, 1947).

The reflections shown on Weissenberg photographs have an intensity distribution very similar to 4*H*, which suggests that it belongs to a series based on 4*H*. Actually, in addition to the 51$R_{(a)}$ sequence, 3 3 3 3 3 2, there is only one other combination of any pair of the numbers 2, 3 and 4 which will give a 51-layer rhombohedral unit-cell when repeated three times. Intensity calculations show this (2 2 2 2 2 2 2 3) to be the correct structure. Because of the presence of three different structures on the X-ray photographs and the incomplete nature of the rhombohedral series, it was not immediately evident whether the structure was 48*R*, $51R_{(b)}$ or 54*R*. For 48*R*, the only combination of two and three which results in a 48-layer rhombohedral unit-cell when repeated three times is 3 3 3 2 3 2. The only sequence fulfilling the same requirements for 54*R* is 2 2 2 2 2 3 2 3. No combination of three and four exists for either 48*R* or 54*R*. Accordingly, intensities for both these structures were calculated. The 48*R* arrangement did not check at all with the observed intensity data. The 54*R* structure, because of its limited similarity to 4*H*, showed some correlation, but there were sufficient intensity reversals to discard the structure.

Thus we have a situation in which one and the same compound has been found to crystallize so as to give two forms, each with a unit-cell of the same dimensions and symmetry but with completely different atomic positions. To the knowledge of the authors, this is a phenomenon unique in inorganic crystal chemistry.

Type $51R_{(b)}$ falls in the second series given above (p. 216) and suggests that 39*R*, a more simple type of this same series, will very probably be discovered in future research on the subject. It is interesting to note that a 39*R* structure can also be obtained by repeating the sequence 3 3 3 4 three times. The latter structure falls in the '3---4 series (rhombohedral types)' predicted by Ramsdell (1947) and follows type 21*R*, a form which has already been found. Both these 39*R* modifications are high on the list of probable future discoveries, and if such is the case, a situation analogous to that of 51*R* will be recorded, with different structures having identical symmetry and cell dimensions. It is information of this type which should throw substantial light on the problem of the entire silicon carbide series. Some theoretical aspects of this problem are discussed elsewhere in this article as the 'polymer theory'.

The space group of type $51R_{(b)}$ is $R3m$, as in the other known rhombohedral polymorphs. The sequence 2 2 2 2 2 2 2 2 3 results in the following atomic positions:

17 Si at $0, 0, 0;\ 0, 0, 3z;\ 0, 0, 7z;\ 0, 0, 11z;\ 0, 0, 15z;\ 0, 0, 19z;\ 0, 0, 21z;\ 0, 0, 23z;\ 0, 0, 25z;\ 0, 0, 27z;\ 0, 0, 29z;\ 0, 0, 31z;\ 0, 0, 33z;\ 0, 0, 35z;\ 0, 0, 39z;\ 0, 0, 43z;\ 0, 0, 47z.$

17 C at $0, 0, p;\ 0, 0, 3z+p;\ 0, 0, 7z+p;\ 0, 0, 11z+p;\ 0, 0, 15z+p;\ 0, 0, 19z+p;\ 0, 0, 21z+p;\ 0, 0, 23z+p;\ 0, 0, 25z+p;\ 0, 0, 27z+p;\ 0, 0, 29z+p;\ 0, 0, 31z+p;\ 0, 0, 33z+p;\ 0, 0, 35z+p;\ 0, 0, 39z+p;\ 0, 0, 43z+p;\ 0, 0, 47z+p.$

17 Si and 17 C at $\frac{1}{3}, \frac{2}{3}, \frac{2}{3}$ + the above co-ordinates.

17 Si and 17 C at $\frac{2}{3}, \frac{1}{3}, \frac{1}{3}$ + the above co-ordinates.

$$z = \frac{1}{51};\ p = \frac{1}{68}.$$

No goniometric measurements were made on the crystal before it was lost, so that no comparison is possible with calculated pyramid angles. The two *a*-axis, zero-level Weissenberg photographs, however, show that the more common types 6*H* and 4*H* occur together with the new form in the crystal. The series of reflections on the photographs are very irregular, but from different portions of the two films fairly adequate intensity data can be obtained. Table 4 compares those sufficiently separate and distinct rhombohedral reflections with the corresponding calculated intensities. The correlation is such as to leave little doubt that the correct structure for type $51R_{(b)}$ is described by the sequence 2 2 2 2 2 2 2 2 3 (repeated three times).

Table 4. *Comparison of observed and calculated intensities for some of the reflections of type* $51R_{(b)}$.

(1 0.*l*)	I_c	I_o
(1 0.1)	24	*s*
4	0·8	*vvw*
7	0·1	*a*
10	0·1	*a*
13	102	*vvs*
16	1·7	*vw*
19	1·3	*vw*
22	2·7	*w*
25	107	*vvs*
28	4·7	*mw*
31	1·6	*w*
37	15	*ms*
40	7·6	*mw*
43	1·5	*vw*
46	1·2	*vw*
49	3·4	*w*
(1 0.$\bar{2}$)	12	*ms*
$\bar{5}$	4·3	*mw*
$\bar{8}$	5·5	*m*
$\overline{11}$	28	*s*
$\overline{14}$	51	*vs*
$\overline{17}$	5·5	*mw*
$\overline{20}$	3·3	*vw*
$\overline{23}$	6·8	*w*
$\overline{26}$	100	*vvs*

Type 75*R*

The existence of type 75*R* was predicted by Ramsdell (1947). It was included as a member of the '3---4 series (rhombohedral types)', of which only 21*R*, with the zigzag sequence 3 4 (repeated three times), has been found. The structure predicted for 75*R* was 3 3 3 3 3 3 3 3 4. However, when calculations were made for this atomic arrangement, they showed no correlation at all with the intensities observed on the Weissenberg photographs. Since no clues as to the probable correct structure for 75*R* were available at the time, the crystal, originally discovered in May of 1948, remained untouched for quite some time.

Geometrically speaking, there are an enormous number of possibilities for the arrangement of 75 silicon (or carbon) atoms in a unit-cell having the dimensions and symmetry indicated by the Weissenberg photographs of type 75*R*. If the empirical limitation of the sequences to the numbers 3 and 2 or 3 and 4 is imposed, the possible arrangements are reduced to 17. The calculation of 17 structures for a unit-cell of the magnitude of 75*R* would be an arduous and time-consuming task. An additional limitation which would further reduce the number of possible arrangements was sought. The only sequence of the numbers 3 and 4 giving a 75-layer rhombohedral unit-cell when repeated three times is 3 3 3 3 3 3 3 4. This, however, is the sequence which proved incorrect when tested by calculations. A combination of one 3 and eleven 2's (2 2 2 2 2 2 2 2 2 2 2 3) results in the required unit-cell, but this would necessitate an intensity maxima distribution very close to that of 4*H*. Such a distribution was not indicated by the X-ray photographs, and the structure was eliminated. The remaining possibilities result from a combination of five 3's and five 2's. The number of such sequences fulfilling the requirements of 75*R* is 15, still a formidable calculation task. A further restriction, based on considerations mentioned later in this article was imposed. It was postulated that the 75*R* structure was made up entirely of 3 2 (and 2 3) units, i.e., of units having the zigzag sequence 3 2 (and 2 3). This effectively reduced the number of possible arrangements to two. These structures are given by the sequences 3 2 3 2 2 3 3 2 2 3 and 3 2 3 2 3 2 2 3 2 3. The latter structure was set up and the intensities calculated. The results showed an excellent correlation with the intensities observed on the Weissenberg photographs and left no doubt that the correct structure for 75*R* had been found. Sufficient calculations were made on the arrangement having the sequence 3 2 3 2 2 3 3 2 2 3 to show that it was not the correct structure. Table 5 compares the calculated intensities for the sequence 3 2 3 2 3 2 2 3 2 3 with those observed on the films.

The fact that the correct atomic arrangement for 75*R* was deduced by assuming that the structure was made up entirely of 3 2 (and 2 3) units does not by any means prove the 'polymer theory' of silicon carbide growth, but if additional structures can be solved in a similar manner, strong evidence in favor of the theory will have been recorded. Type 15*R*, with the sequence 3 2 (repeated three times), and type 10*H*, having the sequence 3 2 2 3 (Ramsdell & Kohn, 1951), are also to be included in the list of silicon carbide structures made up entirely of 3 2 (and/or 2 3) units.

The symmetry of type 75*R* is *R*3*m*. The cell constants are as follows:

hexagonal unit,

$$a_0 = 3{\cdot}073,\ c_0 = 188{\cdot}49_7\ \text{kX.},\ Z = 75;$$

rhombohedral unit,

$$a_{\text{rh}} = 62{\cdot}85_7\ \text{kX.},\ \alpha = 2^\circ\,48',\ Z = 25\ .$$

The sequence 3 2 3 2 3 2 2 3 2 3 results in the following atomic positions:

25Si at $0, 0, 0$; $0, 0, 3z$; $0, 0, 7z$; $0, 0, 9z$; $0, 0, 11z$; $0, 0, 15z$; $0, 0, 19z$; $0, 0, 21z$; $0, 0, 23z$; $0, 0, 27z$; $0, 0, 29z$; $0, 0, 31z$; $0, 0, 35z$; $0, 0, 38z$; $0, 0, 42z$; $0, 0, 45z$; $0, 0, 49z$; $0, 0, 51z$; $0, 0, 55z$; $0, 0, 58z$; $0, 0, 62z$; $0, 0, 64z$; $0, 0, 66z$; $0, 0, 68z$; $0, 0, 72z$.

25C at $0, 0, p$; $0, 0, 3z+p$; $0, 0, 7z+p$; $0, 0, 9z+p$; $0, 0, 11z+p$; $0, 0, 15z+p$; $0, 0, 19z+p$; $0, 0, 21z+p$; $0, 0, 23z+p$; $0, 0, 27z+p$; $0, 0, 29z+p$; $0, 0, 31z+p$; $0, 0, 35z+p$; $0, 0, 38z+p$; $0, 0, 42z+p$; $0, 0, 45z+p$; $0, 0, 49z+p$; $0, 0, 51z+p$; $0, 0, 55z+p$; $0, 0, 58z+p$; $0, 0, 62z+p$; $0, 0, 64z+p$; $0, 0, 66z+p$; $0, 0, 68z+p$; $0, 0, 72z+p$.

25Si and 25C at $\frac{1}{3}, \frac{2}{3}, \frac{2}{3}$ + the above co-ordinates.

25Si and 25C at $\frac{2}{3}, \frac{1}{3}, \frac{1}{3}$ + the above co-ordinates.

$$z = \tfrac{1}{75};\ p = \tfrac{1}{100}.$$

Table 5. *Comparison of observed and calculated intensities for some of the reflections of type* 75*R*.

$(1\,0.l)$	I_c	I_o
(1 0.1)	1·1	*vvw*
4	9·1	*w*
7	16	*mw*
10	16	*mw*
13	17	*mw*
16	5·9	*w*
19	72	*s*
22	91	*vs*
25	20	*m*
28	9·1	*w*
31	3·4	*vw*
34	59	*ms*
37	100	*vvs*
$(1\,0.\bar{2})$	4·0	*w*
$\bar{5}$	4·6	*w*
$\bar{8}$	29	*ms*
$\overline{11}$	37	*ms*
$\overline{14}$	5·0	*w*
$\overline{17}$	18	*m*
$\overline{20}$	40	*ms*
$\overline{23}$	79	*s*
$\overline{26}$	30	*ms*
$\overline{29}$	2·7	*vw*
$\overline{32}$	15	*mw*
$\overline{35}$	35	*ms*

The first *a*-axis, zero-level Weissenberg photograph showed that the crystal was composed of type 6*H* together with the new form. The 6*H* reflections, however, were slightly displaced from the 75*R* lattice lines. After a first-level exposure was taken, an appendage was broken off the original crystal and photographed separately. The appendage structure proved to be entirely 6*H*. Additional photographs of the original crystal showed that the structure was now entirely 75*R*.

Six trigonal pyramids were identified, with one more probable and several others doubtful. Table 6 gives the distribution of faces, with the morphological data shown in Table 7.

Table 6. *Distribution of* 75*R faces*

$(1\ 0.l)$	$(0\ 1.l)$	$(\bar{1}\ 1.l)$	$(\bar{1}\ 0.l)$	$(0\ \bar{1}.l)$	$(1\ \bar{1}.l)$
—	—	$(\bar{1}\ 1.\overline{53})$	—	—	—
—	$(0\ 1.\overline{52})$	—	—	—	—
—	—	$(\bar{1}\ 1.\overline{38})$	—	—	—
—	$(0\ 1.\overline{37})$	—	—	—	$(1\ \bar{1}.\overline{37})$
—	—	—	$(\bar{1}\ 0.\overline{22})$	—	$(1\ \bar{1}.\overline{22})$
—	—	—	—	$(0\ \bar{1}.\bar{8})$	—
—	—	$(\bar{1}\ 1.16)$	—	—	—
—	—	$(\bar{1}\ 1.22)$	—	—	—
—	—	$(\bar{1}\ 1.37)$	—	—	—

Table 7. *Morphological data of* SiC *type* 75*R*

Form	No. times observed	Quality	Angle between form and base		
			Range	Weighted average	Calc.
(0001)	2	*A–C*			
$(1\ 0.\overline{53})$	1	*C*	53° 07′–53° 21′	53° 13′	53° 10′
(1 0.52)	1	*C*	53° 52′–54° 00′	53° 56′	53° 45′
$(1\ 0.\overline{38})$	1	*B–C*	61° 37′–61° 43′	61° 40′	61° 48′
(1 0.37)	3	*B–E*	62° 20′–62° 52′	62° 35′	62° 26′
(1 0.22)	3	*B–E*	72° 44′–73° 30′	72° 52′	72° 45′
(1 0.16)?	1	*E*	74° 14′	77° 14′	77° 16′
$(1\ 0.\bar{8})$	1	*D*	83° 12′–83° 34′	83° 23′	83° 34′

Type 84*R*

The fifth and last new form to be described is one with an 84-layer rhombohedral unit-cell. The original Weissenberg *a*-axis, zero-level photograph showed a spacing of reflections approximately the same as that found in 87*R*. However, careful measurement indicated a form either midway between 75*R* and 87*R* or closer to the latter structure. Thus the new rhombohedral polymorph was either 81*R* or 84*R*. The presence of the more common type 6*H* was also indicated by the X-ray photographs. An attempt was made to distinguish between the two rhombohedral possibilities by comparing the distribution of reflections with those of the hexagonal structure. However, because of the lack of sufficient resolution, results from various parts of the films studied were anomalous, and the distinction could not be made on this basis. Accordingly, a Laue photograph was taken of the crystal, with a crystal-to-film distance of 6·5 cm. This gave sufficient resolution for a unit-cell determination. The distribution of reflections, upon comparison with those of 6*H*, demonstrated clearly that the rhombohedral structure in question was 84*R*.

Upon imposing the empirical limitation that the sequences be limited to the numbers 2 and 3 or 4 and 3, the number of possible atomic arrangements resulting in a rhombohedral unit-cell having the proper dimensions and symmetry reduce to 17. Two of the sequences are made up of four 3's and four 4's. One of these (3 4 4 3 4 3 4 3) would require an intensity maxima distribution similar to type 21*R*, and the films showed no such similarity. The other structure (3 3 3 4 3 4 4 4) is eliminated because of the fact that three different polymers (3 3, 4 4, and 3 4) would be needed for its formation (see p. 222). An additional 13 sequences are derived from a combination of eight 2's and four 3's. Here again, three different polymers are required for the formation of the structures, and the latter are eliminated on this basis. Thus the number of sequences reduce to only two possibilities, these being made up of eight 3's and two 2's. The arrangement 3 3 3 3 3 3 3 2 3 2 was calculated first and showed an excellent correlation with observed intensity data (Table 8). The remaining sequence, 3 3 3 3 3 2 3 3 3 2, as might be expected, showed somewhat similar intensities, but there were sufficient pronounced reversals to eliminate that structure. It is postulated, then, that the 84*R* structure is made up

Table 8. *Comparison of observed and calculated intensities for some of the reflections of type* 84*R*.

$(1\ 0.l)$	I_c	I_o
(1 0.1)	0·1	*a*
4	0·1	*a*
7	0·8	*vvw*
16	5·0	*mw*
19	0·03	*a*
22	1·9	*vvw*
25	0·5	*vvw*
31	0·5	*vvw*
34	0·1	*vvw*
37	0·03	*a*
$(1\ 0.\bar{2})$	0·8	*vvw*
$\bar{5}$	1·9	*w*
$\bar{8}$	3·6	*w*
$\overline{11}$	2·6	*w*
$\overline{17}$	11	*mw*
$\overline{20}$	14	*m*
$\overline{23}$	22	*ms*
$\overline{26}$	56	*s*
$\overline{29}$	34	*ms*
$\overline{32}$	1·0	*w*
$\overline{35}$	4·8	*mw*

Table 9. *Distribution of* 84*R* *faces*

$(1\,0.l)$	$(1\,0.l)$	$(\bar{1}\,1.l)$	$(\bar{1}\,0.l)$	$(0\,\bar{1}.l)$	$(1\,\bar{1}.l)$
—	—	—	—	$(0\,\bar{1}.58)$?	—
$(1\,0.43)$	—	—	—	—	—
—	—	—	—	—	$(1\,\bar{1}.41)$
—	—	—	$(\bar{1}\,0.29)$	—	—
—	$(0\,1.2)$	—	$(\bar{1}\,0.2)$	—	—
—	—	—	—	$(0\,\bar{1}.\overline{41})$	—

Table 10. *Morphological data of* SiC *type* 84*R*.

	No. times		Angle between form and base		
Form	observed	Quality	Range	Weighted average	Calc.
(0001)	2	*A–C*			
$(1\,0.58)$?	1	*E*	53° 58′	53° 58′	53° 50′
$(1\,0.43)$	1	*B–C*	61° 25′–61° 44′	61° 33′	61° 32′
$(1\,0.\overline{41})$	2	*C*	62° 35′–62° 42′	62° 39′	62° 40′
$(1\,0.\overline{29})$	1	*D–E*	70° 00′–70° 16′	70° 03′	69° 55′
$(1\,0.\bar{2})$	2	*C–E*	88° 14′–88° 40′	88° 29′	88° 29′

of two polymers, these having the sequences 3 3 and 3 2.

The space group of type 84*R* is *R*3*m*, and the unit-cell dimensions are as follows:

hexagonal unit,

$$a_0 = 3{\cdot}073,\ c_0 = 211{\cdot}11_7\ \text{kX.},\ Z = 84;$$

rhombohedral unit,

$$a_{\text{rh}} = 70{\cdot}39_5\ \text{kX.},\ \alpha = 2^\circ\ 30',\ Z = 28\ .$$

The zigzag sequence 3 3 3 3 3 3 3 2 3 2 results in the following atomic positions:

28Si at 0, 0, 0; 0, 0, 3; 0, 0, 6*z*; 0, 0, 9*z*; 0, 0, 12*z*; 0, 0, 15*z*; 0, 0, 18*z*; 0, 0, 21*z*; 0, 0, 25*z*; 0, 0, 27*z*; 0, 0, 29*z*; 0, 0, 33*z*; 0, 0, 35*z*; 0, 0, 39*z*; 0, 0, 41*z*; 0, 0, 45*z*; 0, 0, 47*z*; 0, 0, 51*z*; 0, 0, 54*z*; 0, 0, 58*z*; 0, 0, 60*z*; 0, 0, 64*z*; 0, 0, 66*z*; 0, 0, 70*z*; 0, 0, 72*z*; 0, 0, 76*z*; 0, 0, 78*z*; 0, 0, 80*z*.

28C at 0, 0, *p*; 0, 0, $3z+p$; 0, 0, $6z+p$; 0, 0, $9z+p$; 0, 0, $12z+p$; 0, 0, $15z+p$; 0, 0, $18z+p$; 0, 0, $21z+p$; 0, 0, $25z+p$; 0, 0, $27z+p$; 0, 0, $29z+p$; 0, 0, $33z+p$; 0, 0, $35z+p$; 0, 0, $39z+p$; 0, 0, $41z+p$; 0, 0, $45z+p$; 0, 0, $47z+p$; 0, 0, $51z+p$; 0, 0, $54z+p$; 0, 0, $58z+p$; 0, 0, $60z+p$; 0, 0, $64z+p$; 0, 0, $66z+p$; 0, 0, $70z+p$; 0, 0, $72z+p$; 0, 0, $76z+p$; 0, 0, $78z+p$; 0, 0, $80z+p$.

28Si and 28C at $\frac{1}{3}, \frac{2}{3}, \frac{2}{3}$ + the above co-ordinates.

28Si and 28C at $\frac{2}{3}, \frac{1}{3}, \frac{1}{3}$ + the above co-ordinates.

$$z = \tfrac{1}{84}\,;\ p = \tfrac{1}{112}.$$

The Weissenberg photographs show excellent positive and negative series of the rhombohedral form. The intensity maxima distribution is somewhat intermediate between those of 6*H* and 15*R*, a condition to be expected from the zigzag sequence. Four trigonal pyramid faces have been identified, with one more probable. Table 9 gives the distribution of the faces in the various pyramid zones, while the morphological data are shown in Table 10.

Silicon carbide growth

Since Thibault (1944) organized and clarified the literature on silicon carbide, the number of known modifications of the compound has steadily grown. At present, the structures of 14 such polymorphs have been definitely established. These are listed in Table 11, along with the stacking sequence for each type. This ever-growing list of known SiC structures has attracted a great deal of interest in the processes involved in SiC growth. Why does SiC crystallize in so many modifications?

After the discovery of type 87*R*, there seemed to be evidence of a definite series of structures. The great bulk of commercial SiC consists of type 6*H*, and most of the new types seemed to be closely related to 6*H*, as shown by the following sequences: 6*H* (3 3's only); 87*R* (3 3 3 3 3 3 3 3 3 2); $51R_{(a)}$ (3 3 3 3 3 2); and 33*R* (3 3 3 2). In our original attempts to explain such a series, we thought of them as resulting from an attempt to crystallize as normal 6*H*, but with a 'mistake' occurring with the introduction of a two-layer unit, and with this 'mistake' being propagated periodically in the subsequent crystallization. Zhdanov & Minervina (1947) have indicated a similar point of view. This interpretation gives no explanation of the reversal of the stacking sequence, which occurs even in the normal 6*H*. Likewise, it provides no mechanism by which a 'mistake' can be repeated at regular intervals, which may be measured in hundreds of Ångström units.

The industrial growth of SiC crystals obviously is a sublimation process. There is no difficulty involved in understanding the lateral growth of the crystals, which is merely the extension of the fixed sheet structure. The difficulty lies in finding a mechanism capable of controlling the order in which the identical sheets are stacked. The only apparent difference between types is in the stacking sequences. There must be energy differences, but from the geometrical standpoint these must be very slight. All atoms have identical first co-ordination spheres. No matter whether a silicon or a carbon atom lies on a layer where the stacking order is reversed, or on one where no change occurs, each is surrounded tetrahedrally by four atoms of the opposite kind. Differences appear only in the second or higher spheres of co-ordination. In the second sphere, a silicon or a carbon atom has twelve neighbors of the same kind. Regardless of the location of the layer, nine of these are unchanged, and for the remaining three (in the case of a stacking reversal) there is merely a 60° rotation without noticeable change in distance.

If crystal growth proceeded by the addition of single SiC layers, some mechanism would have to be available to cause periodic reversal of the stacking sequence. A single periodicity would give rise to a simple sequence, such as 1 1, 2 2, etc., while a double periodicity would be required for a 'mixed' type, such as 3 3 3 3 3 2. The absence of any 1 1 type of SiC (zincite structure), and the difficulty of explaining a stacking reversal on this basis as anything other than an accidental and random occurrence, do not lend any support to the idea of growth by addition of single SiC layers.

If the above idea is untenable, then an alternative would be growth by the addition of multiple SiC layers. In such a case, it might be assumed that growth occurred by the accretion of clusters of atoms, or polymers of SiC. These polymers might have a stacking reversal inherent in their own structure, or the reversal might result from the fitting together of two successive polymer layers. The existence of such polymers is entirely hypothetical. In the further discussion we will use such expressions as '3 3 polymer' and '3 2 polymer' without any implication as to how the reversal might occur.

A seemingly attractive theory would be that in a given temperature range a certain polymer would be stable, and this would form a certain 'pure' type. Let the following polymers be postulated: 3 3, 3 2, 2 2, 3 4, and 4 4. Growth of SiC by the accretion of each of these 'crystallization units' would result in 'pure' types *6H*, *15R*, *4H*, *21R* and *8H*, respectively. The '3 2 polymer', because of its asymmetry, can be obtained with two different atomic arrangements, as shown in Fig. 3. Let these two be differentiated by '3 2 polymer' and '2 3 polymer'. The same situation would hold for the '3 4 crystallization unit'. Thus the full list of polymers needed to account for all the known hexagonal and rhombohedral forms of SiC is 3 3, 3 2, 2 3, 2 2, 3 4, 4 3 and 4 4—seven in all.

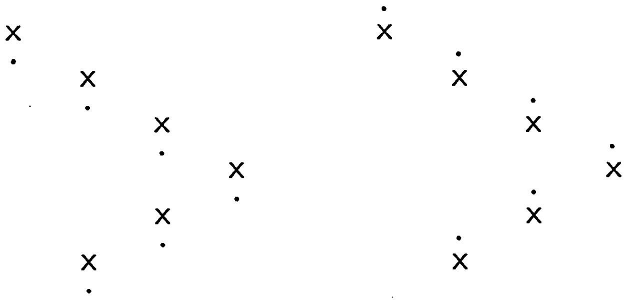

Fig. 3. The different arrangements for the 3 2 sequence.
X = Si • = C

At a temperature between two stability ranges, two polymers might coexist, giving rise to 'mixed' types, as opposed to the 'pure' types mentioned above. It would be impossible for three polymers to exist simultaneously, hence no structure could involve three (or more) different pairs of sequences, such as 2 2, 2 3 and 3 4. This does not mean that an individual crystal may not be a combination of three or more types—such is frequently the case. It merely refers to the type which is crystallizing at a certain time.

If two polymers were present in equal amounts, a structure involving equal proportions, such as 3 3 3 2, or 3 3 3 4, would result. Unequal proportions could give rise to varying structures. Thus, if polymers of the 3 3 and 3 2 types were present in the proportion 4:1, type *87R* (3 3 3 3 3 3 3 3 3 2) would form, with four sets of 3 3 alternating with one of 3 2. Sufficient 3 2 polymers to complete a 3 2 layer would be required at one time, and then further 3 2's would be rejected while four 3 3 layers were being added. This situation would be analogous to certain types of superlattices, where a multiple unit-cell is necessitated by the periodicity of the distribution of some constituent present in a minor amount. These polymers would provide the mechanism for change in the stacking sequence, and the periodicity would be a function of the relative proportions of the two polymers present.

This suggested theory is summarized in Table 12. Those modifications, both known and expected, which result from simple ratios of the polymer pairs 3 3—3 2, 3 2—2 3 and 2 2—2 3 are shown. The forms in parentheses are unreported but very probable. Brackets indicate those undiscovered types whose unit-cells are complete without a tripling of the sequence, and which are hence referred to hexagonal units. The 'crystallization units' in Table 12 are arranged from top to bottom in their *assumed* order of decreasing stability temperature. It is interesting to note that the eight known 'mixed' types are derived from polymer pairs made up of units adjacent to each other in the table. In other words, the known 'mixed' types are derived from polymers which grade into each other in terms of assumed stability temperatures. Forms made up of the polymer pair 3 3—2 2, for example, have not been reported and would not be expected. The fact that no modifications involving the polymer pairs 3 3—3 4, 3 4—4 3 and 4 4—4 3 have been found could be indicative of either a comparatively narrow range of stability overlap or no temperature at which both units of the pair can exist simultaneously. According to the theory, as expressed in Table 12, it is impossible for all

Table 11. *The* 14 *known* SiC *structures*

Type	Sequence	Type	Sequence
Cubic	∞	$15R$	3 2
$4H$	2 2	$21R$	3 4
$6H$	3 3	$27R$	2 2 2 3
$8H$	4 4	$33R$	3 3 3 2
$10H$	3 2 2 3	$51R_{(a)}$	3 3 3 3 3 2
		$51R_{(b)}$	2 2 2 2 2 2 2 3
		$75R$	3 2 3 2 3 2 2 3 2 3
		$84R$	3 3 3 3 3 3 3 2 3 2
		$87R$	3 3 3 3 3 3 3 3 3 2

three of the numbers 2, 3 and 4 to occur in a given sequence.

According to this hypothesis, two polymers can be present in varying proportions, and thus form types with corresponding varying sequences. It might be expected that fluctuating conditions in the furnace could change the proportions of the two polymers, and thus result in a corresponding change in periodicity of the minor polymer. This could result in the beginning of a new type, in parallel position with the old, a very common occurrence, or it could result in variable periodicity. Such evidence of randomness in stacking is found. Some Weissenberg photographs show more or less continuous blackening along the rows of reflections such as (10.*l*), which indicates some degree of randomness. A high degree of randomness would probably be overlooked, for such crystals should have poor development of pyramidal or rhombohedral faces, and would be automatically rejected for single-crystal photographs. The method of selection has been to first examine a group of SiC crystals under the binocular microscope. Those showing good development of pyramidal or rhombohedral faces are selected and angular measurements are made on the two-circle goniometer. If such measurements indicate faces belonging to forms other than the more normal types, a zero-level, *a* axis Weissenberg photograph is taken.

No attempt has been made in this theory to account for the cubic modification of SiC. It is known that this polymorph is the low-temperature form, since it is usually found toward the edge of the crystallization zone of the pig. It has no stacking reversals in its sequence (see Table 11) and therefore cannot be derived directly from any of the polymers considered above.

It is possible that the stability of a given polymer might not be dependent upon temperature alone. At attempt has been made to correlate the various types of SiC with traces of impurities present (Lundqvist, 1948). Analyses of commercial SiC show insufficient amounts of impurities to have a foreign ion present in every polymer unit of the crystal. It might be conceivable that a foreign ion, stabilizing a particular polymer, is rejected at the instant of actual attachment to the growing crystal surface, and thus is available for successive stabilizations of additional polymers. It would seem, however, that this effect could not be limited to a single layer at a time. Hence such a mechanism would account only for 'pure' types, and not for 'mixed' types.

It must be stressed that very little experimental evidence on the growth of SiC crystals is available at present. It is known that type $6H$ is the most abundant form in commercial SiC and that the remaining 'pure' types, arranged in order of decreasing frequency, are $15R$, $4H$, $21R$ and $8H$. It is also known that the cubic modification is found toward the edge of the pig and is, therefore, the low-temperature form. There is, at present, no experimental evidence to prove or disprove the 'crystallization unit'–temperature theory set forth above. The theory is suggested, on purely theoretical grounds, as a possible explanation for the astounding ability of SiC to crystallize in so many structural modifications. To be sure, it has proved convenient in the solution of several SiC structures, but this by no means 'proves' the theory. Experimental evidence is badly needed. If samples, for X-ray analysis, could be taken at definite radial positions in a pig, and a relationship established between structural type and temperature distribution in the

Table 12. *Crystallization units of* SiC

	Units		Ratio								
			1:1	2:1	3:1	4:1	1:2	1:3	1:4	2:3	3:2
	2 2	$4H$									
	2 2—2 3		$27R$	$(39R)$	$51R_{(b)}$	$(63R)$	$(42R)$	$[19H]$	$(72R)$	$[23H]$	$(66R)$
	2 3	$15R$									
↑ Temperature	3 2—2 3		$10H$	$(45R)$	$(60R)$	$[25H]$	$(45R)$	$(60R)$	$[25H]$	$75R$	$75R$
	3 3—3 2		$33R$	$51R_{(a)}$	$(69R)$	$87R$	$(48R)$	$[21H]$	$(78R)$	$[27H]$	$84R$
	3 3	$6H$									
	3 3—3 4		Narrow or non-existent overlap region.								
	3 4	$21R$									
	3 4—4 3		Narrow or non-existent overlap region.								
	4 3—4 4		Narrow or non-existent overlap region.								
	4 4	$8H$									

furnace, strong evidence would be obtained in favor of the temperature hypothesis. In other words, a point has been reached in the study of SiC growth where experimentation is necessary before further theoretical work seems likely to be beneficial.

Note added in proof, 27 *February* 1952. For each of the five types of SiC described above cell dimensions are given in kX. units to agree with earlier published data which, although reported as Ångström units, were really in kX. units.

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The Crystal Structure of the Urea–Hydrocarbon Complexes*

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The structure of the urea–normal hydrocarbon complex has been determined. The unit cell is hexagonal, $a_0 = 8{\cdot}230$, $c_0 = 11{\cdot}005$ Å, space group $C6_12\text{–}D_6^2$, six urea molecules per unit cell. The general features of the structure and the nitrogen positions of the urea were obtained directly from an implication diagram or Patterson–Harker section $P(x, y, \frac{1}{6})$ which, for this space group, is essentially equivalent to an electron-density projection along the c axis. The urea molecules form a hollow channel structure in which the n-hydrocarbon molecules are enclosed. The hydrocarbons are in an extended planar zigzag configuration with their long axis parallel to the c axis. The electron-density projection and the implication diagram indicate that the time average of the positions of the plane of the hydrocarbon molecule are randomly disposed over positions perpendicular to the a axis and at multiples of 60° to this position. Diffuse bands observed in most of the complexes are attributed to the hydrocarbon molecules which behave as a system of linear gratings regularly arrayed in the $x\,y$ plane but with random z coordinates.

Introduction

The formation of crystalline complexes of urea with normal hydrocarbons, fatty acids and other straight-chain molecules was first reported by Bengen. In view of the weak interactions normally expected between hydrocarbons and urea, the formation of stable crystalline complexes of urea and n-hydrocarbons at first appeared somewhat surprising. A general investigation of the field of urea complexes was carried out at these and associated laboratories (Fetterly; Redlich, Gable, Dunlop & Millar, 1950) with the object of securing basic data required for various applications. In the early stages of this work an investigation of the structure of these complexes was therefore undertaken to determine the molecular configuration and its relation to the stability of the complexes. A brief resumé of these results has already appeared (Smith, 1950). Since the completion of most of this work several additional papers (Zimmerschied, Dinerstein, Weitkamp & Marschner, 1949*a*, *b*, 1950; Schlenk, 1949) on these complexes, including a brief account of the structure determination by C. Hermann (Schlenk, 1949), have appeared. Although the preliminary results of Hermann are in general agreement with those reported in this investigation there are differences in several of the bond distances and parameters. The more detailed structure investigation leads to some additional conclusions, including an explanation of the stability of the complex somewhat different from that presented by Schlenk (1949).

Preliminary crystallographic data

Preliminary X-ray examination of a number of urea complexes of n-hydrocarbons of various chain length C_8–C_{50} by the powder method indicated that they all had a similar structure which was different from that of urea. Similar powder patterns were also obtained with urea complexes of various straight-chain alcohols, acids, esters, etc. The n-hexadecane ($C_{16}H_{34}$)–urea complex was selected for detailed structure investigation because of the relative stability of this complex and the availability of reasonably pure n-hexadecane. Single-crystal work was also carried out with the 1,10-dibromodecane–urea complex.

Long needle-like crystals of the hexadecane–urea complex, hexagonal in cross section, form when n-hexadecane is added to a solution of urea in water, methyl or isopropyl alcohol, etc. The single crystals used for the X-ray work were all grown slowly from

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