

## The Crystal Structure of Calcium Carbide II and IV

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The crystal structure of  $\text{CaC}_2$  II has been determined from two dimensional X-ray data. The structure is built up of calcium and carbide ions arranged in a similar but more complicated way than in  $\text{CaC}_2$  I and  $\text{CaC}_2$  III. The structure of  $\text{CaC}_2$  IV could only be determined from X-ray powder diffraction data. The structure is cubic and disordered.

A review of the literature on the structure of calcium carbide has recently been published in this journal<sup>1</sup>. There seem to exist four modifications, of which  $\text{CaC}_2$  I<sup>2</sup> and  $\text{CaC}_2$  III<sup>1</sup> have previously been investigated and described.  $\text{CaC}_2$  IV<sup>3</sup> is a high temperature modification while  $\text{CaC}_2$  II is a low temperature modification stable only in presence of cyanamide ions ( $\text{CN}_2^{2-}$ )<sup>3</sup>.

### CALCIUM CARBIDE II

*Preparation of the compound.* 4 g calcium carbide, 2 g calcium cyanamide and 0.4 g graphite was heated in an induction furnace<sup>1</sup>.

A graphite crucible was used. The air was removed from the crucible with the aid of a stream of argon gas. The temperature never exceeded 1700°C. If the temperature was raised to above 2000°C, all nitrogen disappeared and on cooling  $\text{CaC}_2$  III was formed.

The compound consisted of small semi-transparent light brown crystals. They were generally not suited for X-ray work but after many fruitless attempts some useful crystals were found.

*Analysis.* The carbide content was determined by measuring the amount of gas liberated when a certain amount of water saturated with acetylene gas was added to the sample. Calcium was determined as oxalate. The nitrogen content could be determined by the ordinary Kjeldahl method. The specific gravity was determined by a method described by Schrevelius<sup>4</sup>.

### The determination of the crystal structure

The structural investigation was based on single crystal methods. The single crystals were mounted inside capillary tubes and rotated about three axes approximately perpendicular to each other. The patterns were generally not of high quality, and twin effects were very common. The reflexion intensities

Table 1. Analysis of CaC<sub>2</sub>(tric.)

Sample	% Ca <sup>2+</sup>	% C <sub>2</sub> <sup>2-</sup>	% CN <sub>2</sub> <sup>2-</sup>	Density
a	60.6	36.4	0.6	2.2
b	60.0	35.6	0.6	2.1
CaC <sub>2</sub> (tric.) calculated	62.5	37.4	—	2.17

were estimated by visual comparison with known scales and corrected by Lorenz and polarization factors.

The unit cell was found to be triclinic with

$$\begin{array}{ll}
 a = 8.42 \pm 0.02 \text{ \AA} & \alpha = 93.^\circ 4 \pm 0.5 \\
 b = 11.84 \pm 0.03 \text{ \AA} & \beta = 92.^\circ 5 \pm 0.5 \\
 c = 3.94 \pm 0.01 \text{ \AA} & \gamma = 89.^\circ 9 \pm 0.5
 \end{array}$$

The space group was chosen to be base centered  $C\bar{1}$ , in order to show the resemblance to the cubic superstructure with  $a = 5.9 \text{ \AA}$ . There are eight formula units in the elementary cell. The calculated density is  $2.17 \text{ g/cm}^3$ , to be compared with  $2.17 \text{ g/cm}^3$  for CaC<sub>2</sub> III<sup>1</sup> and  $2.23 \text{ g/cm}^3$  for CaC<sub>2</sub> I<sup>2</sup>. Approximate calcium atom parameters were calculated from Patterson syntheses. With the aid of these parameters the sign of all the reflexions could be calculated and all the atomic parameters could be calculated from electron density maps. The proposed structure model was then refined with the aid of successive difference syntheses.

The parameter values found were the following:

	<i>x</i>	<i>y</i>	<i>z</i>
4 Ca	0.375	0.141	0.717
4 Ca	0.875	0.109	0.783
4 C	0.066	0.124	0.317
4 C	0.187	0.126	0.192
4 C	0.660	0.090	0.192
4 C	0.590	0.160	0.317

A comparison between observed and calculated structure factors can be found in Table 2. The *R* factor was found to be 0.18.

*Discussion.* The distance between the two carbon atoms in a carbide group was found to be  $1.14 \text{ \AA}$  and  $1.13 \text{ \AA}$ , to be compared with  $1.20$  in CaC<sub>2</sub> I. The difference is not significant. The calcium ions are surrounded by six carbide ions and are in contact with seven carbon atoms. The distances between the calcium ions and carbon atoms are 2.46, 2.55, 2.57, 2.80, 2.82, 2.82 and  $2.90 \text{ \AA}$ . The arrangement can be seen in Fig. 1 and will be discussed below.

Table 2. Observed and calculated structure factors for  $\text{CaC}_2(\text{tric.})$ .

$h$	$k$	$l$	$F_{\text{obs}}$	$F_{\text{calc}}$	$h$	$k$	$l$	$F_{\text{obs}}$	$F_{\text{calc}}$
2	0	0	—	0	0	2	0	—	0
4	0	0	24	-30	0	4	0	41	-41
6	0	0	—	0	0	6	0	—	0
8	0	0	12	+13	0	8	0	15	+18
1	1	0	—	0	0	10	0	—	0
3	1	0	—	0	0	12	0	7	-6
5	1	0	—	0	0	2	1	19	+18
1	1	0	—	+4	0	4	1	—	0
3	1	0	—	0	0	6	1	14	-17
5	1	0	—	0	0	8	1	—	0
0	2	0	—	0	0	10	1	14	+12
2	2	0	14	+16	0	12	1	—	0
4	2	0	—	0	0	14	1	8	-6
2	2	0	14	-19	0	2	1	17	-13
4	2	0	—	0	0	4	1	—	0
6	2	0	16	+23	0	6	1	6	+8
1	3	0	8	+9	0	8	1	—	0
3	3	0	—	0	0	0	2	30	-31
5	3	0	12	-12	0	0	2	—	0
1	3	0	—	0	0	2	2	—	0
3	3	0	—	-6	0	4	2	30	+26
5	3	0	—	0	0	6	2	—	0
0	4	0	43	-41	0	8	2	24	-17
2	4	0	—	0	0	10	2	—	0
4	4	0	15	+26	0	12	2	16	+10
6	4	0	—	0	0	2	2	—	0
2	4	0	—	0	0	4	2	22	+24
4	4	0	25	+21	0	6	2	—	0
6	4	0	—	0	0	8	2	9	-11
1	5	0	—	0	0	10	2	—	0
3	5	0	12	+9	0	2	3	15	-17
5	5	0	—	0	0	4	3	—	0
1	5	0	17	-17	0	6	3	17	+20
3	5	0	—	0	0	8	3	—	0
0	6	0	—	0	0	10	3	11	-16
2	6	0	14	-12	0	2	3	13	+9
4	6	0	—	0	0	4	3	—	0
2	6	0	17	+16	0	6	3	—	-1
4	6	0	—	0	0	0	4	11	+12
6	6	0	18	-20	0	2	4	—	0
1	7	0	11	-12	0	2	4	—	0
3	7	0	—	0	2	0	0	—	0
5	7	0	16	-17	4	0	0	31	-30
1	7	0	—	0	6	0	0	—	0
3	7	0	—	+9	8	0	0	13	+13
5	7	0	—	0	2	0	1	39	-45
0	8	0	19	+18	4	0	1	—	0
2	8	0	—	0	6	0	1	20	+21
4	8	0	15	-16	8	0	1	—	0
2	8	0	—	0	2	0	1	28	-45
4	8	0	—	0	4	0	1	—	0
1	9	0	—	0	6	0	1	19	+19
3	9	0	16	-15	8	0	1	—	0
1	9	0	17	+22	0	0	2	34	-31
3	9	0	—	0	0	0	2	—	0

Table 2. Continued.

<i>h</i>	<i>k</i>	<i>l</i>	$F_{\text{obs}}$	$F_{\text{calc}}$	<i>h</i>	<i>k</i>	<i>l</i>	$F_{\text{obs}}$	$F_{\text{calc}}$
2	0	2	—	0	4	0	2	—	0
4	0	2	28	+ 27	6	0	3	22	- 19
6	0	2	—	0	$\bar{2}$	0	3	15	+ 23
8	0	2	16	- 12	4	0	3	—	0
$\bar{2}$	0	2	—	0	0	0	4	17	+ 12
$\bar{4}$	0	2	18	+ 27	2	0	4	—	0
$\bar{6}$	0	2	—	—	4	0	4	21	- 17
2	0	3	23	+ 23	$\bar{2}$	0	4	—	—

## CALCIUM CARBIDE IV

*Preparation of the compound.* Three specimens containing  $\text{CaC}_2$  I,  $\text{CaC}_2$  II and  $\text{CaC}_2$  III were prepared as described previously.  $\text{CaC}_2$  I contained 4 % CaS as impurity, while  $\text{CaC}_2$  II contained 1.5 %  $\text{CaCN}_2$ . The compounds were heated to 500°C in a high temperature X-ray diffraction unit. At about 450°C  $\text{CaC}_2$  IV is formed from all the modifications. If the temperature is lowered one of the low temperature modifications is formed again. The process is completely reversible. A sample of  $\text{CaC}_2$  IV prepared from  $\text{CaC}_2$  I always yields  $\text{CaC}_2$  I on cooling and so on.

## The determination of the crystal structure

The structural investigation was based on X-ray powder photographs taken with a modified Philips' Diffractometer. The specimen temperature was

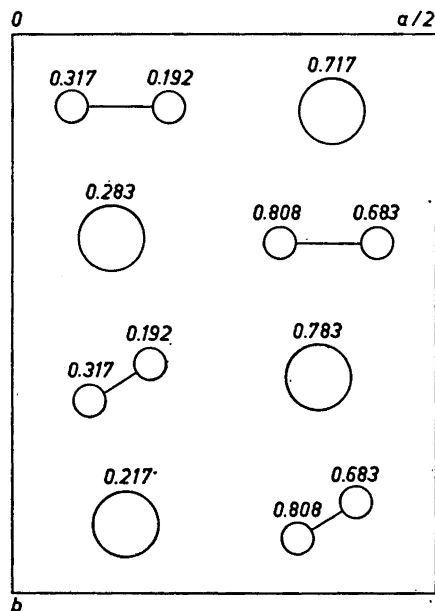
Fig. 1. Projection of the  $\text{CaC}_2(\text{tric.})$  structure on (001).

Table 3. Observed and calculated  $\sin^2\Theta$  values for  $\text{CaC}_2(\text{cub.})$ 

<i>h k l</i>	1		2		3	
	$10^4 \cdot \sin^2\Theta_o$	$10^4 \cdot \sin^2\Theta_c$	$10^4 \cdot \sin^2\Theta_o$	$10^4 \cdot \sin^2\Theta_c$	$10^4 \cdot \sin^2\Theta_o$	$10^4 \cdot \sin^2\Theta_c$
1 1 1	510	513	515	515	513	514
2 0 0	681	684	686	686	683	685
2 2 0	1367	1369	1372	1373	1373	1371
3 1 1	1878	1882	1887	1888	1887	1885
2 2 2			2058	2059		
3 3 1	3257	3251	3259	3260	3259	3257
4 2 0	3422	3422	3430	3432	3422	3427
4 2 2	4100	4106	4116	4118	4100	4112

1.  $\text{CaC}_2(\text{cub.})$  prepared of  $\text{CaC}_2(\text{tric.})$
2.    "               "       "  $\text{CaC}_2(\text{mon.})$
3.    "               "       "  $\text{CaC}_2(\text{tetr.})$

The reflexions 222 and 422 are disturbed by reflexions from calcium oxide.

500°C. Ni-filtered  $\text{CuK}\alpha$  radiation was used and the different peaks were scanned at a speed of  $1/8^\circ$  per minute. The intensities were registered with a Geiger-Müller counter tube. The furnace in which the specimen was placed was very carefully evacuated.

The unit cell was found to be face centered-cubic and the edge length of the elementary cube (Table 3) was

$$a = 5.889 \pm 0.005 \text{ for } \text{CaC}_2 \text{ IV from } \text{CaC}_2 \text{ I}$$

$$a = 5.894 \pm 0.005 \text{ for } \text{CaC}_2 \text{ IV from } \text{CaC}_2 \text{ II and}$$

$$a = 5.886 \pm 0.005 \text{ for } \text{CaC}_2 \text{ IV from } \text{CaC}_2 \text{ III}$$

Table 4. Observed and calculated structure factors for  $\text{CaC}_2(\text{cub.})$ 

<i>h k l</i>	$F_o$	$F_c$			
		1	2	3	4
1 1 1	3.2	4.6	4.6	4.6	4.6
2 0 0	11.4	10.1	10.1	10.1	10.2
2 2 0	8.3	7.9	7.9	7.9	7.8
3 1 1	4.6	5.1	5.1	5.1	5.0
3 3 1	4.7	4.7	4.6	4.7	4.7
4 2 0	5.0	5.0	5.0	5.0	5.1

1. Each carbide ion is assumed to rotate.
2. Each carbide ion is assumed to be parallel to one of the four body diagonals.
3. Each carbide ion is assumed to be parallel to one of the six face diagonals.
4. Each carbide ion is assumed to be parallel to one of the three cubic axes.

The differences are not significant. There must be four formula units in the elementary cell. The relative intensity of a certain reflexion is the same regardless if the sample consists of  $\text{CaC}_2$  I, II, or III. As mentioned the powder pattern is that of a face centered structure. This excludes the possibility that  $\text{CaC}_2$  IV could be isomorphous with pyrite  $\text{FeS}_2$ . The reflexions (210) and (211), which would be fairly strong, are completely absent.

The only possibility is then that the gravity centers of the carbide ions form a face centered structure while the two carbon atoms of each carbide ion must occur in a disordered way around each main point.

This can be the case, if the carbide ions rotate freely. There are, however, other disordered structures which will also give a face centered cubic cell, *e.g.*, if each pair of carbon atoms is oriented parallel to one of the three cubic axes, or if each pair is parallel to one of the four body diagonals, or if each pair is parallel to one of the six face diagonals <sup>7</sup>.

As is clear from Table 4, the calculated structure factors of the four alternatives do not differ appreciably. It must be regarded as impossible to select the correct structure from powder diffraction data only. However, physically there is not a great difference between them. Even if free rotation is not assumed, the disorder at 500°C is certainly dynamic. The only difference would be that the rotation is so strongly hindered that one special orientation is more probable than others.

The calculations are made with the assumption that the distance between the carbon atoms in a carbide group is 1.20 Å.

#### GENERAL DISCUSSION

Since all the known calcium carbide structures have been determined, it is possible to discuss them, especially their conditions of formation, simultaneously.

All the structures are built up of calcium and carbide ions. The structures have similarities with that of rock salt, *i.e.* each calcium ion is surrounded by six carbide ions and each carbide ion by six calcium ions. The coordinating ions form a more or less distorted octahedron.

The tetragonal calcium carbide  $\text{CaC}_2$  I or  $\text{CaC}_2(\text{tetr.})$  is probably the stable room temperature modification <sup>3</sup>, but it is likewise obvious that it is not spontaneously formed without the presence of calcium sulphide <sup>1,3,5</sup>. As the sulphide ion is less space demanding than the carbide ion, it may denote that there are contacts between the carbide ions in the  $\text{CaC}_2(\text{tetr.})$  structure. An incorporation of a small amount of sulphide ions would reduce these contacts and stabilize the structure.  $\text{CaC}_2(\text{tetr.})$  is isostructural with barium peroxide, which structure has been carefully described <sup>8</sup>. In this structure type each cation is surrounded by six anions as mentioned above. The carbide axes are all parallel and also coincident with the fourfold axis, thus the calcium ions are in contact with ten carbon atoms each. If contacts between the anions in this structure are to be avoided, the following relation must hold <sup>9</sup>.

Table 5. The coordination number of the calcium ions and the conditions of formation of the different calcium carbide modifications.

Phase	The coordination number of the calcium ions	Conditions of formation
CaC <sub>2</sub> (cub.)	6	$T > 720^\circ\text{K}$
CaC <sub>2</sub> (mon.)	8	$T < 720^\circ\text{K}$
CaC <sub>2</sub> (tric.)	7	$T < 720^\circ\text{K}$
CaC <sub>2</sub> (tetr.)	10	presence of CaCN <sub>2</sub> $T < 720^\circ\text{K}$ presence of CaS

$$\frac{r_c}{r_a} > 2 \sqrt{\frac{2 + (d/a)^2}{2 + \left(\frac{c}{a} - \frac{2d}{a}\right)^2}} - 1$$

where  $r_c$  = the radius of the cation

$r_a$  = the radius of the anion

$d$  = the distance between the carbon atoms in a carbide group

$a$  = the length of the crystallographic  $a$ -axis

$c$  = the length of the crystallographic  $c$ -axis

In this case  $d$  is 1.20 Å,  $a$  is 3.89 Å, and  $c$  is 6.38 Å. Thus  $r_c/r_a$  must be larger than 0.66 but  $r_c$  is 0.99 Å and  $r_a$  is about 1.55 Å, so  $r_c/r_a$  is only 0.63. Accordingly there are contacts between the carbon atoms in this structure and the role of the sulphide ions can be understood.

In triclinic calcium carbide CaC<sub>2</sub> II or CaC<sub>2</sub>(tric.), the six carbide ions surround the calcium ion, forming a distorted octahedron. Each calcium ion is in contact with seven carbon atoms. As mentioned the structure is related to the rock salt structure. Now there are two highly symmetric structures containing spherical cations and dumb-bell anions, which are also strongly related to the rock salt structure, *viz.* the pyrite structure and the low temperature sodium cyanide structure<sup>10</sup>. The former is cubic while the latter has a monoclinic structure, but the axes are directly comparable. In the pyrite structure the dumb-bell axes are parallel with the body diagonals in the cubic elementary cell. In the sodium cyanide structure they are parallel with the longest face diagonal in the monoclinic cell. In the former structure the cations become effectively six-coordinated, while in the latter the cations are eight-coordinated.

In triclinic calcium carbide half of the carbide ions are parallel to two of the body diagonals in the cubic subcell, while the other half are parallel to two of the face diagonals in the cubic subcell. The result is that the calcium ions have seven nearest neighbours. The carbon atoms are coordinated by three or four calcium ions. In the first case the carbon atom is surrounded by a tetrahedron consisting of the three calcium ions and the other carbon atom of the

carbide group. In the latter case an irregular tetrahedron is formed by the four calcium ions only.

The structure is stabilized by the incorporation of cyanamide ions. These ions certainly replace carbide ions situated in "pyrite" positions, for there the corresponding cation-anion distance is very little sensitive to changes in the distance between the coordinating atoms belonging to the same anion.

Monoclinic calcium carbide  $\text{CaC}_2$  III,  $\text{CaC}_2(\text{mon.})$  is formed spontaneously when pure calcium carbide is cooled below  $450^\circ\text{C}$ . It is very doubtful whether it is really metastable at this temperature, but Bredig reports that it is transformed into  $\text{CaC}_2(\text{tetr.})$  by grinding at temperatures between  $200$  and  $350^\circ\text{C}$ <sup>3</sup>.

As usual the calcium and carbide ions are six-coordinated and the structure is thus related to the rock salt structure. A calcium ion is surrounded by eight carbon atoms forming a structure similar to a dodecahedron. Four of the carbon atoms belong to different carbide groups and lie in about the same plane as the calcium ion. Thus they form a nearly regular square. The other four carbon atoms belong to two carbide ions and are also situated approximately in one plane, perpendicular to the one first mentioned. Thus the structure is very similar to that of the low temperature modification of sodium cyanide.

Each carbon atom is surrounded by four calcium ions, forming a very distorted tetrahedron.

The coordination in the cubic calcium carbide  $\text{CaC}_2$  IV or  $\text{CaC}_2(\text{cub.})$  is less well established. The orientation of the carbide ions is disordered, probably by rotation, but it may also be a completely disordered pyrite structure. The great solubility of calcium cyanamide in calcium carbide above  $450^\circ\text{C}$  may then easily be accounted for. In the latter case every calcium ion would be octahedrally surrounded by six carbon atoms. Then the change in the coordination number of the calcium ions is quite in order. At temperatures above  $450^\circ\text{C}$  the coordination number is six, just below  $450^\circ\text{C}$  it is eight and at still lower temperatures it grows to ten. The triclinic calcium carbide which is only stable in presence of cyanamide ions may be regarded as a hybrid of ordered cubic calcium carbide and monoclinic calcium carbide.

The structures of the strontium and barium carbides are less well established, but the different occurring phases have been characterized with the aid of their X-ray powder patterns<sup>3</sup>. The tetragonal and cubic phases are known and, besides, strontium carbide in the presence of cyanamide ions forms a phase, which must be very similar to the triclinic calcium carbide. No phase corresponding to the monoclinic structure seems to exist. This is to be expected. As strontium and barium ions are larger than calcium ions the ten-coordination in the tetragonal phase is energetically more favourable than the eight-coordination in the monoclinic phase (see above).

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