The Crystal Structure of Calcium Carbide III

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The crystal structure of CaC_2 III has been determined from three-dimensional X-ray data. The structure is built up of calcium and carbide ions arranged in a more complicated way than in the ordinary tetragonal calcium carbide structure.

The crystal structure of tetragonal face-centered calcium carbide, CaC_2 I, was determined by von Stackelberg[1]. The cell dimensions were found to be $a = 5.48$ and $c = 6.37$ Å. There are 4 formula units in the cell. The carbide (C_2^{2-}) ions have their length axis in the z-axis direction, see Fig. 2c. The distances between the carbon atoms in a carbide ion were found by v. Stackelberg to be 1.4 Å. However, in a recent investigation made by neutron diffraction, Atoji and Medrud[2] found the much more probable distance of 1.20 Å. This is in accordance with distances found in organic acetylidic compounds[3]. Earlier Dehlinger and Glockner[4] had described a cubic calcium-carbide structure. Their investigation was criticised by Herman[5] and v. Stackelberg[1]. This structure has nothing to do with the cubic face-centered high temperature modification found by Bredig[6]. The axes in the crystal structure of the latter compound were determined to be 5.92 Å. The structure is only stable above $450° \pm 20°$. On cooling according to Frank, Bredig and co-workers[7-9] and to Bredig[6], this structure may yield two modifications with low symmetry, CaC_2 II and CaC_2 III, which are both metastable in the temperature interval $0°-450°C$. They are transformed into CaC_2 I by grinding. Below 0°C, CaC_2 II is said to be the stable modification. When the carbide is contaminated by sulphur, the modifications CaC_2 II and CaC_2 III are not formed when CaC_2 IV is cooled below 450°; instead CaC_2 I is obtained. When cyanamide and sulphur are present, CaC_2 II is formed. This structure is said to be able to incorporate about 5 mole % cyanamide ions at 450°C. When only cyanamide is present, CaC_2 III is formed. However, Bredig has earlier claimed that CaC_2 II and not CaC_2 III is formed in the presence of cyanamide[6]. While the actual investigation was still in progress, a similar view was presented by Bochert and Röder[10]. They found that CaC_2 IV was stable above 435°C. This phase was transformed into CaC_2 III when no impurities were present, into CaC_2 II when cyanamide and sulphur were present, and into CaC_2 I when sulphur

was the only contamination. They also found that III is transformed into I above 30°C under high pressure. Below 30°C, II is formed.

Later Nast and Pfab reported [11],[12] a fifth modification of CaC_2, the X-ray pattern of which was very similar to that of Cu_2C_2. This work has been seriously criticised by Bredig [13],[14], on good grounds according to this author's opinion.

According to Bochert and Röder [10] both CaC_2 II and CaC_2 III have tetragonal symmetry. CaC_2 II: $a = 23.40$ Å, $c = 22.31$ Å, and CaC_2 III: $a = 23.40$ Å, $c = 22.87$ Å.

PREPARATION OF THE COMPOUND

4 g calcium metal, granular, was mixed with 2 g graphite. The mixture was heated in an induction furnace of Philips' construction. A graphite crucible was used. The induction coil and the crucible were inserted in a glass flask (Fig. 1). The air was removed from the flask with the aid of a stream of argon gas. When the air had been carefully removed, the current was turned on and the temperature was gradually raised to about 1 800°C. This temperature was not enough to melt the carbide formed. The crystals obtained were rather small and had grown together in great aggregates. They were unsuitable for X-ray work. After many unsuccessful attempts it became clear that the temperature must be increased to the melting point in order to get better single crystals. In these experiments the radiation losses set the upper temperature limit. The radiation losses were considerably decreased by putting on a layer of zirconium oxide powder outside the induction coil. In this way the temperature was raised to above 2 200°, which was enough to melt the carbide. After a few attempts rather good crystals were obtained, suitable for single crystal work. The compound obtained consists of small transparent light-brown to colourless crystals. In addition there were black coloured grains, probably consisting of graphite.
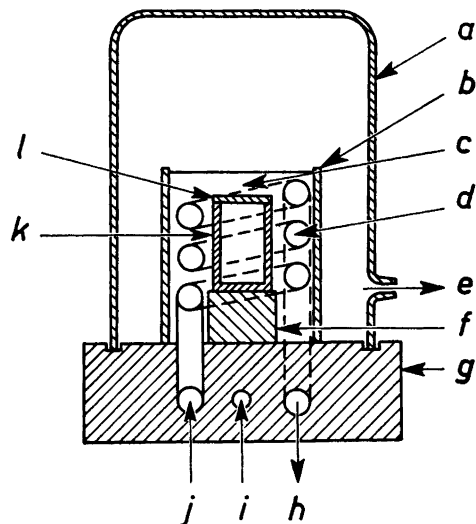
Fig. 1. Section through the induction furnace. Between the cover of zirconium oxide and the heating coil zirconium oxide powder is packed. a) Glass flask, b) cover of zirconium-oxide, c) zirconium oxide powder, d) heating coil, e) outlet for argon, f) cylinder of boron nitride, g) soap stone, h) water outlet, i) inlet for argon, j) water inlet, k) grafite crucible, l) cover of boron nitride.

Table 1. Chemical composition and density of CaC₂ III.

Sample	% Ca	% C_2^{2-}	density
I	60.8	36.8	2.16
II	61.2	36.9	2.15
Calculated	62.5	37.4	2.17

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 a sample. The calcium content was determined volumetrically by titration of the precipitated oxalate with permanganate. The specific gravity was determined by a method given by Schrewelius [15].

THE DETERMINATION OF THE CRYSTAL STRUCTURE

The structural investigation was based on single crystal methods. The single crystals were rotated about the c-axes and Weissenberg photographs were taken for all zones detectable with $CuK\alpha$ radiation. The reflexion intensities were estimated by visual comparison with known scales and corrected by Lorentz and polarization factors. The crystals were mounted inside capillary tubes in order to prevent atmospheric attack.

The unit cell was proved to be monoclinic with

$$a = 8.36 \pm 0.02 \text{ Å}$$
$$b = 4.20 \pm 0.01 \text{ Å}$$
$$c = 11.25 \pm 0.03 \text{ Å}$$
$$\beta = 96.3° \pm 0.5$$

The space group is No 14 $B2_1/c$. A primitive cell could of course have been chosen by taking [101] and [$\bar{1}$01] as principal axes, but as this structure contains a cubic super-structure with $a = 5.9$ Å, the actual choice is easier to visualize. The single crystals, obtained from the melt at about 2 000°C, do not consist of CaC₂ III but of CaC₂ IV. These crystals are then transformed into CaC₂ III. It is obvious since the single crystals are not destroyed, that the crystal structure of CaC₂ IV and CaC₂ III must be very similar.

As the measured density is 2.15, there are eight formula units in the elementary cell.

The unit cell dimensions are not in accordance with those found by Bochert and Röder [10]. It is very probable that these authors have not used a perfect single crystal but a twin.

The calcium atom parameters were calculated from Patterson syntheses. The 2-dimensional synthesis gave too bad resolution to be used, so it was necessary to calculate a complete 3-dimensional synthesis. From the known calcium parameters the sign of every reflexion could be calculated. The positions of the atoms could now be calculated from a 3-dimensional Fourier synthesis.

In order to get better parameters for the carbon positions, a 3-dimensional difference synthesis was also performed.

Table 2. Observed and calculated structure factors for CaC$_2$ III

$h\ k\ l$	F_{obs}	F_{calc}	$h\ k\ l$	F_{obs}	F_{calc}
4 0 0	19.0	− 16.2	$\bar{9}$ 2 1	8.4	− 7.9
8 0 0	6.7	+ 7.4	2 2 2	9.0	− 4.6
2 0 2	9.5	+ 7.3	$\bar{2}$ 2 2	7.3	+ 5.5
$\bar{2}$ 0 2	6.6	− 10.3	6 2 2	8.4	+ 4.8
6 0 2	8.1	− 8.3	$\bar{6}$ 2 2	5.2	− 6.1
$\bar{6}$ 0 2	7.8	+ 11.4	1 2 3	8.5	+ 8.0
$\overline{10}$ 0 2	8.2	− 10.4	$\bar{3}$ 2 3	4.3	+ 4.7
4 0 4	15.0	+ 15.7	5 2 3	10.2	− 9.9
$\bar{4}$ 0 4	10.9	+ 10.2	$\bar{7}$ 2 3	2.6	− 4.6
$\bar{8}$ 0 4	4.4	− 5.2	0 2 4	4.3	+ 8.5
2 0 6	8.4	− 7.3	4 2 4	9.4	− 7.7
$\bar{2}$ 0 6	8.2	+ 11.6	8 2 4	5.6	+ 5.1
6 0 6	8.3	+ 5.6	$\bar{8}$ 2 4	4.3	− 3.3
$\bar{6}$ 0 6	7.8	− 12.2	$\bar{1}$ 2 5	15.0	+ 12.4
			3 2 5	8.8	+ 8.7
2 1 0	17.9	− 19.8	$\bar{5}$ 2 5	10.0	− 10.0
6 1 0	10.4	+ 9.3	7 2 5	5.7	− 4.3
10 1 0	6.8	− 4.5	$\bar{9}$ 2 5	—	—
1 1 1	5.3	+ 7.0	2 2 6	4.9	+ 4.5
$\bar{3}$ 1 1	8.1	− 8.7	$\bar{2}$ 2 6	5.6	− 6.1
5 1 1	2.1	− 2.8	6 2 6	4.3	− 3.6
$\bar{7}$ 1 1	5.1	+ 6.0	$\bar{6}$ 2 6	4.5	+ 6.4
9 1 1	2.2	+ 2.1			
0 1 2	7.0	+ 7.4	2 3 0	1.1	+ 1.5
4 1 2	12.8	− 6.8	6 3 0	1.8	− 1.5
$\bar{4}$ 1 2	8.0	+ 9.5	1 3 1	8.6	− 9.9
8 1 2	8.2	+ 7.8	$\bar{3}$ 3 1	11.8	+ 12.8
$\bar{8}$ 1 2	7.7	− 9.8	5 3 1	6.8	+ 5.7
1 1 3	2.7	− 3.6	$\bar{7}$ 3 1	13.4	− 11.0
3 1 3	6.3	+ 6.0	0 3 2	4.7	− 2.1
$\bar{5}$ 1 3	1.2	+ 2.5	4 3 2	4.5	+ 1.9
7 1 3	5.8	− 5.8	$\bar{4}$ 3 2	2.8	− 1.7
$\bar{9}$ 1 3	1.3	− 3.0	$\bar{1}$ 3 3	7.2	+ 6.9
2 1 4	14.7	+ 15.9	3 3 3	9.8	− 10.1
$\bar{2}$ 1 4	9.8	+ 12.6	$\bar{5}$ 3 3	5.2	− 5.2
6 1 4	10.8	− 10.8	7 3 3	10.6	+ 10.7
$\bar{6}$ 1 4	5.6	− 6.3	2 3 4	1.7	− 1.4
10 1 4	—	—	$\bar{2}$ 3 5	3.5	− 1.6
1 1 5	6.2	− 7.3	6 3 4	1.6	+ 1.2
$\bar{3}$ 1 5	6.8	+ 7.3	$\bar{6}$ 3 4	2.9	+ 1.6
5 1 5	3.6	+ 3.7	1 3 5	11.3	+ 11.8
$\bar{7}$ 1 5	3.6	− 4.6	$\bar{3}$ 3 5	12.9	− 12.5
0 1 6	8.1	− 8.5	5 3 5	9.0	− 7.2
4 1 6	7.6	+ 5.4	$\bar{7}$ 3 5	8.5	+ 8.6
$\bar{4}$ 1 6	7.1	− 10.6	0 3 6	—	+ 1.8
8 1 6	5.4	− 5.1	4 3 6	2.0	− 1.7
$\bar{8}$ 1 6	6.8	+ 9.6			
			0 4 0	3.2	− 4.7
0 2 0	7.8	− 10.6	4 4 0	1.6	+ 3.5
4 2 0	9.4	+ 7.5	$\bar{1}$ 4 1	11.7	+ 9.8
8 2 0	6.1	− 4.3	3 4 1	7.1	+ 6.7
$\bar{1}$ 2 1	11.4	− 12.3	$\bar{5}$ 4 1	12.5	− 10.3
3 2 1	7.9	− 6.7	7 4 1	2.2	− 4.4
$\bar{5}$ 2 1	12.4	+ 11.6	2 4 2	1.6	− 0.4
7 2 1	5.2	+ 3.9	6 4 2	2.4	+ 1.4

Table 2 (continued).

h k l	F_{obs}	F_{calc}		h k l	F_{obs}	F_{calc}
$\bar{6}$ 4 2	2.1	— 2.7		3 4 5	8.9	— 8.2
1 4 3	6.2	— 7.5		$\bar{5}$ 4 5	7.6	+ 9.1
$\bar{3}$ 4 3	6.0	— 5.3				
5 4 3	9.5	+ 9.1		2 5 0	5.6	+ 7.7
0 4 4	3.4	+ 4.0		1 5 1	7.2	+ 5.5
4 4 4	3.0	— 4.1		$\bar{3}$ 5 1	6.6	— 6.3
$\bar{4}$ 4 4	1.9	— 1.9		0 5 2	2.5	— 2.5
6 4 4	—	—		$\bar{1}$ 5 3	4.5	— 4.6
$\bar{1}$ 4 5	7.8	— 10.6		3 5 3	3.7	+ 5.4

The parameters found were the following

	x	y	z
8 Ca	0.375	0.676	0.125
8 C	0.085	0.338	0.155
8 C	0.165	0.163	0.095

A comparison between observed and calculated structure factors can be found in Table 2. The R factor was found to be 0.20.

DISCUSSION

The distance between the carbon atoms was determined to be 1.24 Å, as compared with 1.20 in CaC_2 I. The difference is not significant. The distances (two in each case) between the calcium and carbon atoms are 2.46 Å, 2.69 Å, 2.78 Å, 2.86, Å, 3.72 Å, and 3.28 Å.

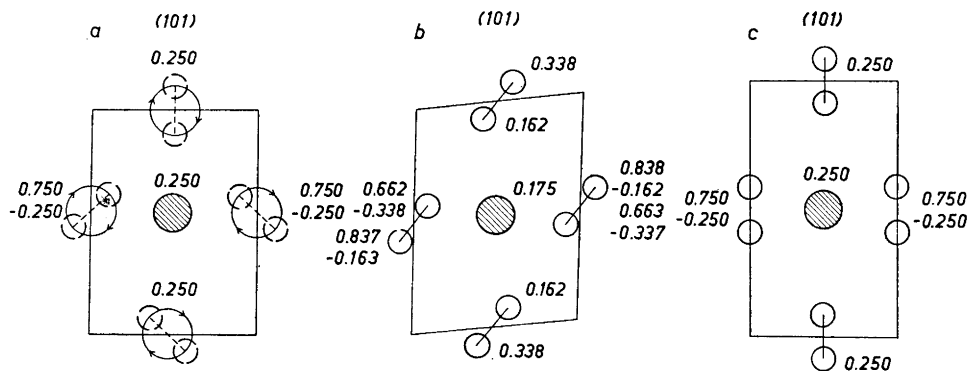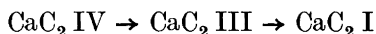A picture of the coordination can be seen in Fig. 2.

Fig. 2. The coordination of carbon atoms (small circles) about the calcium ions (shaded circles) in a) CaC_2 IV, b) CaC_2 III and c) CaC_2 I. In CaC_2 IV, each carbide ion is assumed to rotate freely about its centre main point. The locus of this point is fulldrawn.

The successive transformation

$$CaC_2 \ IV \rightarrow CaC_2 \ III \rightarrow CaC_2 \ I$$

is illustrated in Fig. 2. The similarities between the three structures are very striking.

The observation by Bochert and Röder that CaC_2 III is transformed into CaC_2 I under high pressure is in accordance with the described structure. The calculated density for CaC_2 III is 2.17 g/cm^3, while that of CaC_2 I is 2.23 g/cm^3.

It will be of great interest to study the kind of disorder in CaC_2 IV. Such an investigation will be performed in a short time. The crystal structure of CaC_2 II has also been studied and is now under refinement. It appears to be very similar to that of CaC_2 III. When the two crystal structures mentioned have been determined, a further discussion of the calcium coordination will be performed.

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