Structural Phase Transitions in CaC_2

Michael Knapp[b, c] **and Uwe Ruschewitz***[a]

Abstract: Pure CaC_2, free of CaO impurities, was obtained by the reaction of elemental calcium with graphite at 1070 K. By means of laboratory X-ray and synchrotron powder diffraction experiments, the phase diagram was investigated in the temperature range from 10 K to 823 K; this confirmed the literature data that reported the partial coexistence of up to four modifications. Aside from a cubic high-temperature modification CaC_2 IV ($Fm\bar{3}m$, $Z=4$) and the well-known tetragonal modification CaC_2 I ($I4/mmm$, $Z=2$), a low-temperature modification CaC_2 II ($C2/c$, $Z=4$) that crystallizes in the ThC_2 structure type and a metastable modification CaC_2 III ($C2/m$, $Z=4$) that crystallizes in a new structure type were found. It was shown that phase transition temperatures as well as the relative amounts of the various CaC_2 modifications depend upon the size of the crystallites, the thermal treatment, and the purity of the sample, as a comparison with technical CaC_2 confirmed.

Keywords: calcium · carbides · phase transitions · solid-state structures · synchrotron powder diffraction

Introduction

CaC_2 was prepared for the first time in 1890 by the reaction of calcium oxide or carbonate with carbon and magnesium.[1] A few years later, it was shown that CaC_2 can also be synthesized in an electrical arc by reacting calcium oxide or carbonate with sugar coal.[2] In the first structural investigation a body centered tetragonal unit cell was found,[3] and it then followed that calcium carbide crystallizes in a distorted rock-salt structure with C_2 dumbbells aligned along the tetragonal c axis. This was confirmed later on by neutron powder and X-ray single-crystal diffraction experiments.[4, 5] Franck and co-workers[6, 7] and, in more detail, Bredig[8] investigated the phase diagram of CaC_2. Aside from the tetragonal room-temperature modification named CaC_2 I, they found a cubic high-temperature modification CaC_2 IV, a low-temperature modification CaC_2 II, and a fourth modification CaC_2 III, which was assumed to be metastable. CaC_2 IV can be described as a rock-salt structure with Ca^{2+} in the Na^+ positions and the centers of gravity of the disordered C_2 dumbbells in the Cl^- positions.[9, 10] The crystal structures of CaC_2 II and III were investigated by means of single-crystal X-ray diffraction.[10, 11] On the assumption that CaC_2 II and CaC_2 III were changed by mistake in these publications, the low-temperature modification II was refined in the space group $B2_1/c$ ($Z=8$) and the metastable modification III in the space group $C\bar{1}$ ($Z=8$). But careful examination of these results[12] shows that CaC_2 II can be described in the space group $C2/c$ and is isotypic to the room-temperature modification of ThC_2.[13] This was also assumed in a recent publication[5] based on the indexing of a X-ray powder pattern and is further confirmed by the low-temperature modifications of SrC_2[14] and BaC_2,[15] which also crystallize in the ThC_2 structure type. A close inspection of the refinement results on metastable CaC_2 III suggests that a twinned crystal was investigated, as several unusual reflection extinctions can be found in the published F_o/F_c list.[10] This is further confirmed by the fact that a powder pattern calculated from the resulting crystal structure is not in agreement with the original data.[7] Therefore the crystal structure of metastable CaC_2 III is still unknown.

As several publications have shown that the existence of the different modifications of CaC_2 is highly dependent upon impurities like oxygen, nitrogen, or sulfur,[16] a new synthesis was developed which allows the preparation of polycrystalline CaC_2 almost free of any impurities. Extensive structural investigations on these powders using temperature-dependent laboratory X-ray and synchrotron diffraction methods allowed the determination of the crystal structure of metastable CaC_2 III as well as a description of the stability ranges of the

---

[a] Prof. Dr. U. Ruschewitz
Institut für Anorganische Chemie
Universität zu Köln, Greinstrasse 6
50939 Köln (Germany)
Fax: (+49) 221-470-5083
E-mail: uwe.ruschewitz@uni-koeln.de

[b] Dipl.-Phys. M. Knapp
Technische Universität Darmstadt
Institut für Materialwissenschaft
Petersenstrasse 23, 64287 Darmstadt (Germany)

[c] Dipl.-Phys. M. Knapp
c/o HASYLAB at DESY, Notkestrasse 85
22603 Hamburg (Germany)

0947-6539/01/0704-0874 \$ 17.50+.50/0

different modifications, which were compared with technical CaC_2. The results of these investigations will be given in the following section.

Results and Discussion

Crystalline powders of CaC_2 almost free of any impurities were obtained by the reaction of elemental calcium with graphite. The resulting samples are gray to almost white; the color depends upon the reaction conditions. X-ray powder investigations (Huber G 645) on these samples at 295 K revealed that CaC_2 exists in at least three modifications at ambient conditions. Most of the remaining reflections, which could not be assigned to the well-known modification I (*I*4/*mmm*, $Z = 2$, $a = 388.6$ pm, $c = 640.1$ pm), were indexed in a monoclinic *C*-centered cell ($a = 664.4$ pm, $b = 419.9$ pm, $c = 733.1$ pm, $\beta = 107.3°$). In agreement with our results on SrC_2[14] and BaC_2,[15] it was assumed that this unit cell represents the low-temperature modification II of CaC_2, which crystallizes in the ThC_2 structure type.[13] This was confirmed by a Rietveld refinement. A powder pattern calculated from these structural results reproduced nicely the pattern given in the literature.[6] But there were still some reflections, which could not be assigned to CaC_2 I and II or any possible impurity phase. To get more information about this unknown phase, high-resolution powder diffraction measurements using synchrotron radiation were taken at beamline B2 (Hasylab, Hamburg/Germany). A comparison of the laboratory and synchrotron X-ray data is shown in Figure 1. These sections of the resulting powder patterns show nicely the better resolution and reflection/background ratio of the synchrotron data. From these data, a monoclinic *C*-centered unit cell was found for the remaining reflections ($a = 722.9$ pm, $b = 385.2$ pm, $c = 737.6$ pm, $\beta = 107.3°$). The volume was in agreement with four formula units CaC_2 per unit cell, and the extinction conditions made the space groups *C*2/*m*, *C*2, and *Cm* possible. Le Bail extraction[17] in the space group *C*2/*m* using the respective routines in the GSAS program package[18] and subsequent direct methods using Sirpow 92[19] led to the solution of the crystal structure. In contrast to the crystal structure, which was obtained by Vannerberg,[10] a powder pattern calculated on the basis of these structural results reproduces the data given in the literature.[7] In Table 1, the results of the Rietveld refinement on CaC_2 at ambient temperature are summarized, and some interesting interatomic distances are given in Table 2.[20]

Abstract in German: *Durch Umsetzung von elementarem Calcium mit Graphit bei 1070 K konnte reines CaC_2 frei von CaO-Verunreinigungen erhalten werden. Mit Hilfe von Röntgen- und Synchrotronpulverbeugungsuntersuchungen wurde das Phasendiagramm im Temperaturbereich zwischen 10 K und 823 K untersucht, wobei Literaturangaben bestätigt werden konnten, die von der teilweisen Koexistenz von bis zu vier Modifikationen ausgegangen waren. Neben einer kubischen Hochtemperaturmodifikation CaC_2 IV ($Fm\bar{3}m$, $Z = 4$) und der wohlbekannten tetragonalen Modifikation CaC_2 I (I4/mmm, $Z = 2$) wurden eine Tieftemperaturmodifikation CaC_2 II (C2/c, $Z = 4$), die im ThC_2-Strukturtyp kristallisiert, sowie eine metastabile Modifikation CaC_2 III (C2/m, $Z = 4$) gefunden, die in einem neuen Strukturtyp kristallisiert. Es konnte gezeigt werden, daß die Phasenumwandlungstemperaturen als auch die relativen Anteile der verschiedenen Modifikationen von der Kristallitgröße, der thermischen Vorbehandlung als auch der Reinheit der Proben abhängen, wie durch einen Vergleich mit technischem CaC_2 belegt werden konnte.*

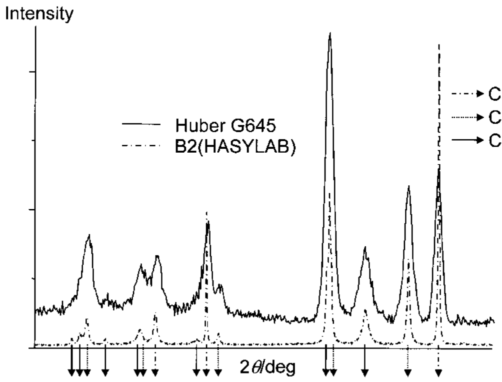

Figure 1. Comparison of sections of powder patterns of CaC_2 taken with laboratory X-ray (Huber G645) and synchrotron radiation (B2, Hasylab) at ambient temperature. The reflections of the modifications CaC_2 I, II, and III are assigned. The range of each powder pattern was chosen so that, despite the different wavelengths of the experiments, the corresponding reflections could be compared (B2: $18.5° < 2\theta < 25.5°$; Huber G645: $24.36° < 2\theta < 33.68°$).

The crystal structures of the four modifications of CaC_2 can be described as a more or less distorted cubic close packing of Ca atoms with the C_2 dumbbells in the octahedral holes. In the cubic high-temperature modification IV ($Fm\bar{3}m$, $a = 589.11(6)$ pm at 803 K, $Z = 4$), these dumbbells are disordered. From powder diffraction data, it is not straightforward to distinguish between a static orientational and a dynamic rotational disorder. But as the halfwidths of the reflections of modification IV are slightly larger than the reflections of modifications I and III just below the transition temperature (see Figure 9), a static disorder can be assumed. In Figure 2, this static disorder of the C_2 dumbbells is depicted, but it has to be mentioned that this is a preliminary picture and more experiments, for example ^{13}C-MAS NMR investigations, are necessary to shed light upon the nature of the disorder of the C_2 dumbbells in the high-temperature modifications IV of CaC_2, SrC_2, and BaC_2.

In the well-known room-temperature modification CaC_2 I, the C_2 dumbbells are aligned along the [001] axis which leads to a distortion of the cubic unit cell to a tetragonal unit cell. The atomic arrangement is shown in Figure 3. For a better comparison, the pseudocubic unit cells are shown in Figures 3, 5, and 6 with a Ca_6 octahedron emphasized. The directions of the axes of the correct unit cells are given at the bottom of each figure. In two theoretical investigations it was found that this ordering of the C_2 dumbbells leads to the most stable structures,[21, 22] but it must be stated that tilting of the dumbbells to a small extent, especially towards a face of the octahedron, produces only slightly less stable structures.[21] The low-temperature modification CaC_2 II crystallizes in the

Table 1. Results and details of X-ray powder investigations on CaC_2 at 295 K [synchrotron radiation, $\lambda = 117.38$ pm, powder diffractometer at beamline B2, Hasylab, Hamburg (Germany)].

Data range	$18.5^\circ \leq 2\theta \leq 61^\circ$, 10624 data points			
wR_P, R_P, no. of refined parameters	0.1590, 0.1264, 41			
CaC_2 I	tetragonal, *I*4/*mmm* (no. 139), $Z = 2$			
lattice constants [pm]	$a = 388.582(4)$, $c = 640.05(1)$			
ρ_{calcd} [g cm^{-3}]	2.2026(1)			
R_F, no. of refined reflections	0.0883, 17			
	x	*y*	*z*	U_{iso}/pm^2
Ca on 2(a)	0	0	0	341(6)[a]
C on 4(e)	0	0	0.3987(6)	70(10)[b]
CaC_2 II	monoclinic, *C*2/*c* (no. 15), $Z = 4$			
lattice constants [pm, °]	$a = 664.35(2)$, $b = 419.94(1)$, $c = 733.07(2)$, $\beta = 107.257(1)$			
ρ_{calcd} [g cm^{-3}]	2.1798(2)			
R_F, no. of refined reflections	0.1126, 69			
	x	*y*	*z*	U_{iso}/pm^2
Ca on 4(e)	0	0.1852(6)	1/4	341(6)[a]
C on 8(f)	0.284(1)	0.145(1)	0.0581(8)	70(10)[b]
CaC_2 III	monoclinic, *C*2/*m* (no. 12), $Z = 4$			
lattice constants [pm, °]	$a = 722.86(3)$, $b = 385.24(1)$, $c = 737.64(3)$, $\beta = 107.338(3)$			
ρ_{calcd} [g cm^{-3}]	2.1712(3)			
R_F, no. of refined reflections	0.1490, 82			
	x	*y*	*z*	U_{iso}/pm^2
Ca on 4(i)	0.2086(6)	0	0.2486(9)	341(6)[a]
C1 on 4(i)	0.439(2)	0	0.065(3)	70(10)[b]
C2 on 4(i)	0.925(2)	0	0.447(2)	70(10)[b]

[a] Constrained. [b] Constrained.

ThC_2 structure type[13] with C_2 dumbbells that also point towards a corner of the Ca_6 octahedron with a small tilt angle of 12.8°. The definition of the tilt angle α is given in Figure 4. In contrast to theoretical predictions, this tilting leads to an arrangement, in which the C_2 units point towards an edge of the Ca_6 octahedron, but the tilt angle is very small and the octahedron itself very strongly distorted. The main difference between CaC_2 I and CaC_2 II is the fact that the C_2 dumbbells in modification I are aligned along one direction, whereas in modification II they lie in a plane perpendicular to one axis. This arrangement is very similar to the one found for MgC_2.[12, 23] Both structural arrangements are compared in Figure 5. In CaC_2 I, each Ca atom is surrounded by four C_2 dumbbells in a *side-on* and two C_2 dumbbells in an *end-on* coordination that leads to a coordination number 2+8 (Table 2). In CaC_2 II, again each Ca atom is surrounded by four *side-on* and two *end-on* coordinated C_2 dumbbells, but the distortion of the structure leads to a coordination that is better described as a 4+4+2 coordination (Table 2). In MgC_2, each Mg atom is also coordinated by two C_2 dumbbells in an *end-on* and by four dumbbells in a *side-on* fashion, but the coordination number is better described as 2+4+4. Therefore, in this simple picture, CaC_2 II lies in-between CaC_2 I and MgC_2, which seems to point to the fact that mainly the size of the cations influences the stability of the different structures.

Table 2. Selected interatomic distances [pm] in the modifications I, II, and III of CaC_2 at different temperatures [synchrotron powder diffraction data, powder diffractometer at beamline B2, Hasylab, Hamburg (Germany)].

			83 K	295 K	640 K
CaC_2 I	Ca–C	2 *x*, *end-on*	260.5(6)	255.2(4)	261.2(5)
		8 *x*, *side-on*	279.8(1)	282.3(1)	283.7(1)
	C–C		119(1)	129.7(8)	116(1)
CaC_2 II	Ca–C	2 *x*, *end-on*	258.1(5)	256.3(5)	
		2 *x*, *side-on*	265.3(7)	267.3(7)	
		2 *x*, *side-on*	281.5(5)	283.8(5)	
		2 *x*, *side-on*	281.6(5)	282.6(5)	
		2 *x*, *side-on*	308.0(7)	309.7(7)	
	C–C		118.7(9)	122(1)	
CaC_2 III	Ca–C1	*end-on*	268(2)	244(2)	264(3)
		2 *x*, *side-on*	274(1)	295(2)	288(2)
		2 *x*, *side-on*	292(1)	279(1)	278(2)
	Ca–C2	2 *x*, *end-on*	268(1)	263.3(9)	268(1)
		side-on	242(2)	285(2)	281(3)
		side-on	290(2)	270(2)	280(3)
	C1–C1		127(4)	148(4)	106(7)
	C2–C2		118(3)	113(2)	107(4)

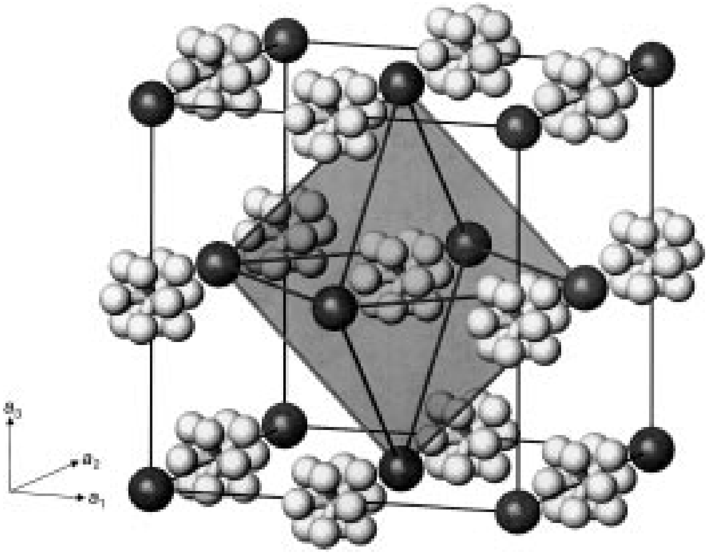

Figure 2. Crystal structure of the cubic high-temperature modification CaC_2 IV (dark circles: calcium; light circles: carbon). The unit cell and one Ca_6 octahedron are outlined. The disorder of the C_2 dumbbells is depicted as a static disorder on several carbon positions (see text).

The atomic arrangement of the previously unknown crystal structure of metastable CaC_2 III is depicted in Figure 6. The existence of two crystallographic independent sites for the C_2 dumbbells is the characteristic feature of this crystal structure, which represents to our knowledge a new structure type. Again both dumbbells are tilted compared with the dumbbells in CaC_2 I, but their tilting is different. The $(C1)_2$ dumbbell is pointing towards a corner of the Ca_6 octahedron with a very small tilt angle of only 4.7° from the ideal orientation, and hence this arrangement is comparable to the one found for CaC_2 I. Unlike the $(C1)_2$ dumbbell with an orientation towards a corner of the octahedron, the $(C2)_2$ dumbbell in

0947-6539/01/0704-0876 $ 17.50+.50/0

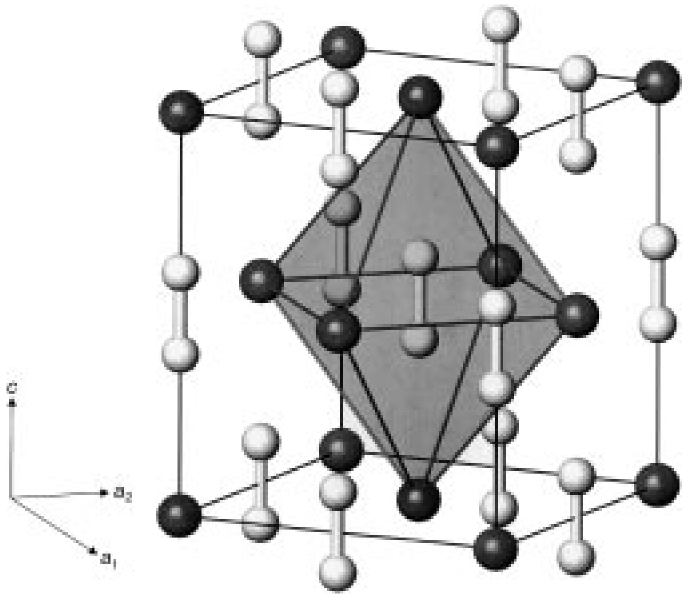

Figure 3. Crystal structure of the tetragonal modification CaC_2 I (dark circles: calcium; light circles: carbon). A pseudocubic unit cell and one Ca_6 octahedron are outlined. The directions of the lattice parameters of the tetragonal unit cell can be seen at the bottom left.

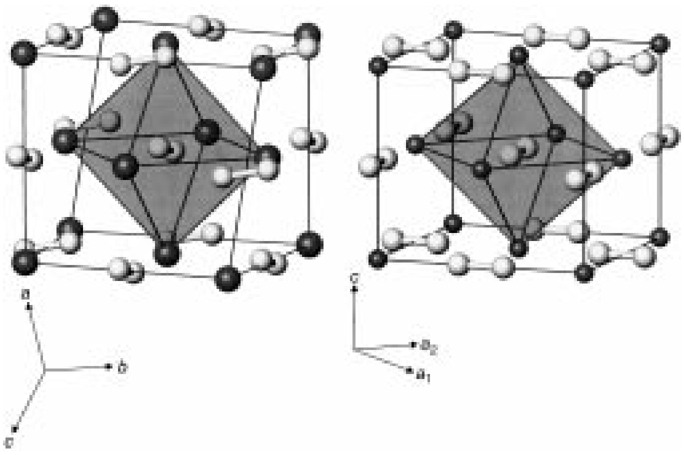

Figure 5. Crystal structures of the low-temperature modification CaC_2 II (on the left; dark circles: calcium; light circles: carbon) and MgC_2 (on the right; dark circles: magnesium; light circles: carbon). Pseudocubic unit cells and one $Ca(Mg)_6$ octahedron are outlined. The directions of the lattice parameters of the monoclinic (CaC_2 II) and the tetragonal (MgC_2) unit cells can be seen at the bottom.

CaC_2 IIIis pointing towards an edge of the Ca_6 octahedron with a tilt angle of 39.9°. According to the theoretical calculations,[21, 22] this arrangement should be unfavorable, which could hence be an explanation for the metastable nature of modification III. But it should be mentioned that the theoretical calculations are based on simplified structures using an undistorted Ca_6 octahedron. However, in the real structures these Ca_6 octahedra as well as the surrounding Ca_8 cubes are strongly distorted, as can be seen in Figures 5 and 6. For CaC_2 III, a new coordination of the Ca atoms is found. Each Ca atom is surrounded by five C1 and four C2 atoms. Three of the C_2 dumbbells are coordinated *side-on* and three *end-on* so that the coordination number 9 results (Table 2). Again this different coordination seems to display the unusual structural properties of metastable CaC_2 III.

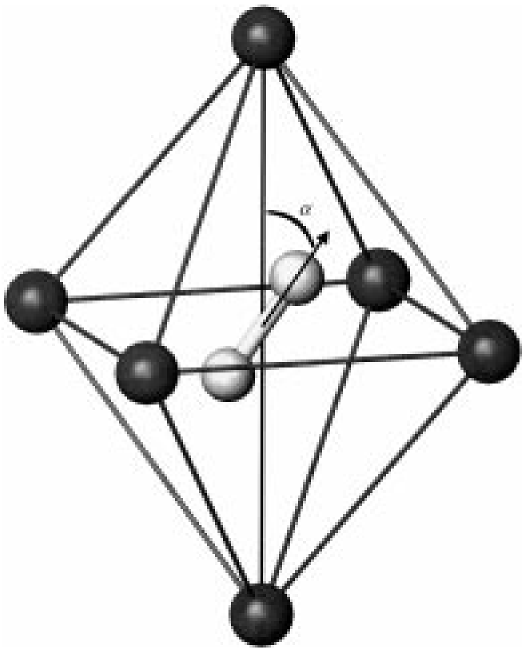

Figure 4. Definition of the tilt angle α.

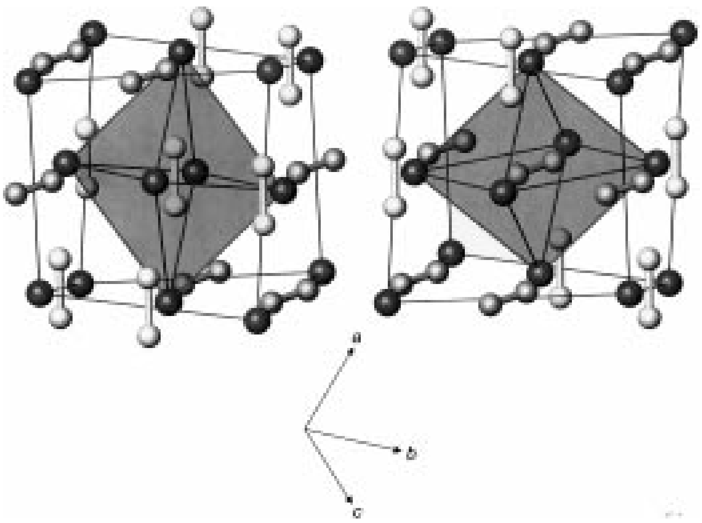

Figure 6. Crystal structure of the metastable modification CaC_2 III (dark circles: calcium; light circles: C1; gray circles: C2). A pseudocubic unit cell and one Ca_6 octahedron around C1 (on the left) and C2 (on the right) are outlined. The directions of the lattice parameters of the monoclinic unit cell can be seen at the bottom.

To obtain more information about the phase diagram of CaC_2, temperature-dependent powder diffraction patterns with laboratory X-ray instruments (Huber G644, G645) were measured between 10 K and 823 K. Furthermore, two high-resolution powder diffraction patterns were recorded at 83 K and 640 K using synchrotron radiation (B2, Hasylab). To get an impression of the quality of the data, the refinement results of the low-temperature investigation are shown in Figure 7.

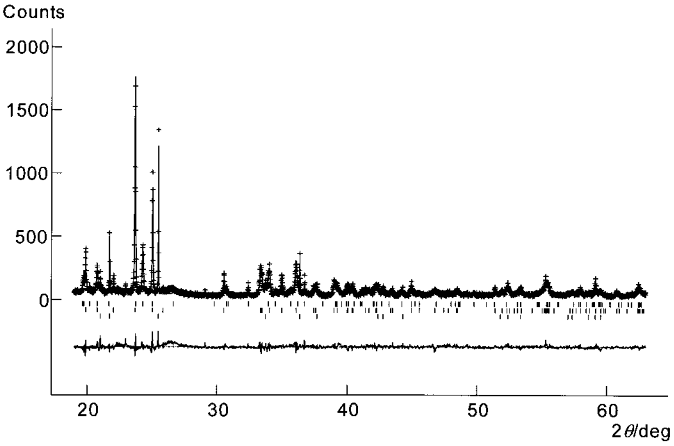

Figure 7. Synchrotron powder diffraction pattern of CaC_2 at 83 K (Hasylab, powder diffractometer at beamline B2). The observed (+) and calculated patterns (solid line) as well as the difference between the two are shown. Vertical bars mark the positions of reflections of CaC_2 III, CaC_2 II, and CaC_2 I (from above).

The experiment with synchrotron radiation at 83 K revealed that CaC_2 I, II, and III also coexist at this temperature, but their relative amounts had changed.[24] The results are given in Table 3. It is evident that CaC_2 I transforms into CaC_2 II with decreasing temperature, whereas the relative amount of CaC_2 III does not change. This is in agreement with the results on SrC_2 and BaC_2, for which a transformation of modification I into II was also found at low temperatures. But a complete transition into modification II was never observed.

Table 3. Composition [wt. %] of pure and technical CaC_2 at different temperatures.

	CaC_2 I	CaC_2 II	CaC_2 III	CaO
pure CaC_2				
83 K	14.8(2)	62.5(2)	22.7(2)	–
295 K	32.2(2)	46.3(2)	21.5(2)	–
640 K	57.3(2)	–	42.7(3)	–
technical CaC_2				
10 K	71.0(3)	20.0(8)	1.7(9)	7.3(5)
295 K	78.0(2)	14.8(7)	1.9(8)	5.3(4)

The refinement of the synchrotron data taken at 640 K[25] showed that modification II had completely transformed into modification I and III so that at this temperature only CaC_2 I and CaC_2 III coexist (Table 3). But it has to be mentioned that the relative amounts as well as the transition temperatures of the different modifications of CaC_2 do not only depend upon the purity of the sample, but also on the size of the crystallites in the powder and the thermal treatment. The size of the crystallites mostly affects the I → II transition, as already mentioned by Bredig[8] and in our work on SrC_2[14] and BaC_2.[15] Therefore all synchrotron measurements were performed on samples from the same preparation.

Most of the resulting C–C bond lengths are in good agreement with the expected value for a C–C triple bond (120 pm)[26] taking the respective standard deviations into account (Table 2). The smaller values that result from the high-temperature data are indicative of an increasing disorder of the C_2 dumbbells around their center of gravity. However, the C–C bond lengths for CaC_2 I (295 K) and CaC_2 III (295 K) are surprising. We think that this is an artifact of the refinement because of strong overlaps of some reflections. Furthermore, an anisotropic reflection broadening was found for CaC_2 I, which was especially marked at ambient temperature. Even when using the appropriate functions in the GSAS program,[18] perfect refinement was not obtained, which could account for the unusual distances. The anisotropic reflection broadening of CaC_2 I is similar to the one found for SrC_2 I; this is even stronger for the latter and has been discussed elsewhere.[14] As the standard deviations for the interatomic distances in CaC_2 III are very high (Table 2), we do not discuss the changes in the Ca–C distances caused by temperature in too much detail, but the data seem to point to an unusual reorientation of the structure upon cooling.

To follow the influence of the thermal treatment, a sample was heated in a capillary in a Guinier diffractometer (Huber G644) from 323 K to 823 K in steps of 10 K and cooled to 333 K again in steps of 10 K. The volumes of the modifications I, III, and IV as a function of the temperature are given in Figure 8 for the heating cycle (for a better comparison the volume of CaC_2 I was doubled). It can be seen that the volumes increase with increasing temperature, and that at the transition temperature of about 763 K a jump in the curve is observed; this points to a first-order transition for the I → IV and III → IV transitions. These transition temperatures seem to be slightly different, which is not evident from the diffraction experiments, but it is suggested by preliminary DSC (differential scanning calorimetry) measurements and results by Meyer and Glaser.[27] Another interesting feature of Figure 8 is the fact that the volume of CaC_2 III is larger than the volume of CaC_2 I at all temperatures investigated. Thus, CaC_2 I has the highest density; the densities of CaC_2 II and III are almost the same.

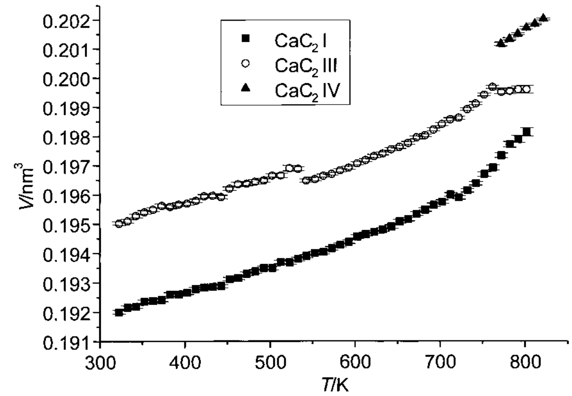

Figure 8. High-temperature phase transition of CaC_2. The temperature dependence of the cell volume of CaC_2 I (volume doubled), CaC_2 III, and CaC_2 IV is shown.

In Figure 9, a contour plot of the diffraction patterns taken between 323 K ($N = 1$), 823 K ($N = 51$), and 333 K ($N = 100$) is shown; the strongest reflections of CaC_2 I, III, and IV are marked. The transitions I → IV and III → IV can be seen

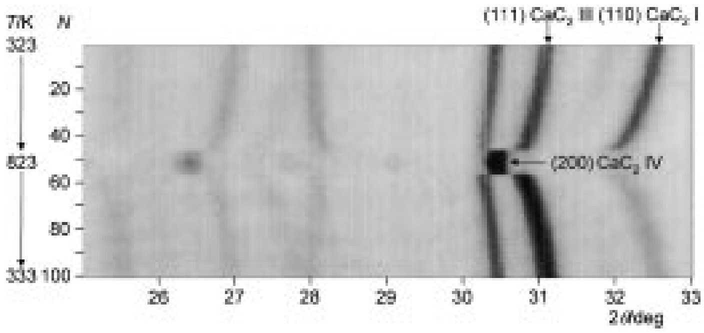

Figure 9. Contour plot of the diffraction patterns (Huber G644) taken upon heating ($N = 1-51 \Rightarrow 323-823$ K) and cooling ($N = 51-100 \Rightarrow 823-333$ K). The strongest reflections of CaC_2 I, III, and IV are marked. The data are not corrected (see Experimental Section).

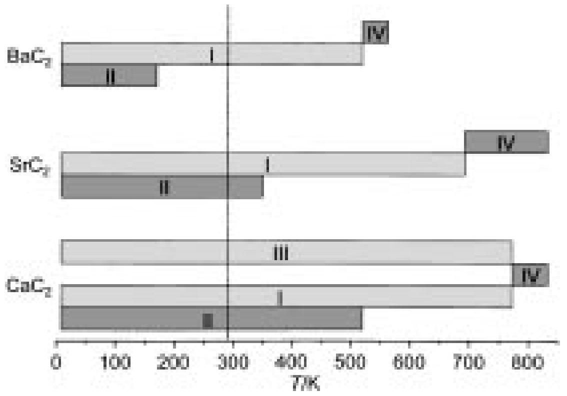

Figure 10. Phase diagrams of CaC_2, SrC_2, and BaC_2.

nicely. Furthermore, it is evident that after cooling the relative amounts of CaC_2 I and CaC_2 III have changed: the strongest reflection of CaC_2 I (110) has decreased in its intensity, whereas the strongest reflection of CaC_2 III (111) has increased in its intensity. This seems to be indicative of Ostwald step rule behavior, and this means that on slow cooling the metastable modification CaC_2 III is obtained first. This effect has been investigated in more detail by Meyer and Glaser, and has resulted in a sample that contained CaC_2 III almost free of any other CaC_2 modifications.[27]

After the crystal structures of all CaC_2 modifications had been solved and their relative amounts in the pure sample determined, it was interesting to compare these results with technical CaC_2. This is shown in Table 3. The relative amounts of the different modifications in pure CaC_2 have already been discussed, but it is intriguing that technical CaC_2 consists, at ambient temperature, mainly of CaC_2 I with minor amounts of CaC_2 II, III, and CaO. This changes only slightly upon cooling and heating. These results were confirmed by Raman spectroscopic investigations at ambient temperature. For technical CaC_2, only one signal for the C–C stretching vibration was found (1860 cm^{-1}), which was therefore assigned to modification I. For the pure sample, a similar value with a medium intensity was found (1858 cm^{-1}) so that the stronger signal at 1869 cm^{-1} had to be assigned to CaC_2 II. No signals were found for modification III as they are either too weak or they overlap with the signals of the other modifications. These assignments are in agreement with the data given in the literature.[5]

To summarize the results on CaC_2, the phase diagrams of CaC_2, SrC_2, and BaC_2 are given in the simplified picture of Figure 10. If we keep in mind that the phase transition temperatures depend upon the purity and the crystallite sizes of the sample, the picture given can only be a qualitative one, but it is still very conclusive. For all compounds, a cubic high-temperature modification IV exists, which transforms into a tetragonal modification I. The latter transforms to a monoclinic low-temperature modification II, which is isotypic with ThC_2. But a complete transition was never observed so that I and II coexist. Only for CaC_2 was a fourth modification III found, which is also produced from the cubic high-temperature modification IV and can coexist with I and II in different ratios that depend upon the thermal treatment. This confirms Bredig's assumption that CaC_2 III is metastable.[8] Furthermore it can be seen in Figure 10 that only BaC_2 I is obtained in pure form at ambient temperature.

Experimental Section

CaC_2 of high purity was synthesized by the reaction of elemental calcium (Alfa, 99.99 %) with graphite (Fluka, 99.9 %) in a graphite cylinder, which was closed with a graphite lid. The graphite cylinders were made from electrode graphite (about 99 %). Prior to the reaction, the raw graphite, the cylinder, and the lid were heated to 1070 K in a dynamic vacuum for about 24 hours. In a typical experiment, calcium (0.2318 g, 5.783 mmol) and annealed graphite (0.1384 g, 11.523 mmol) were mixed in a glove box (argon atmosphere) and pressed to pellets of $\phi = 10$ mm. These pellets were transferred into the graphite cylinder, which was closed with the lid. Under an argon atmosphere, the cylinder was heated in a horizontal tube furnace to 1070 K for about sixteen hours. The products were allowed to cool down and transferred to a glove box, in which all further handling was carried out. The resulting powder was gray to almost white; the color depended upon the reaction conditions. No impurities were detected by X-ray powder diffraction. Technical CaC_2 was purchased from Aldrich (pieces, ≈ 8 mm thick, tech.).

Low-temperature X-ray diffraction experiments were carried out on a Huber G645 diffractometer ($Cu_{K\alpha 1}$ radiation, Ge monochromator, scintillation counter, closed-cycle cryostat) in the temperature range 298–10 K in steps of 20 K. A flat sample holder designed for air-sensitive samples was used, which was filled in a glove box. Usually patterns were only taken in a selected 2θ range, but at 298 K and 10 K a complete pattern was recorded ($5^\circ \leq 2\theta \leq 100^\circ$). All data were analyzed with the GSAS software.[18]

For the high-temperature X-ray diffraction experiments, a Huber G644 diffractometer ($Cu_{K\alpha 1}$ radiation, Ge monochromator, Stoe OED detector, Huber furnace) was used. The sample was sealed in a capillary ($\phi = 0.3$ mm) under argon. Patterns were taken between 323 and 823 K in steps of 10 K; both heating and cooling cycles were in the range $22.40^\circ \leq 2\theta \leq 36.78^\circ$ (pure CaC_2) and $20.56^\circ \leq 2\theta \leq 34.94^\circ$ (technical CaC_2). Because of the special camera geometry (Guinier diffractometer with a linear PSD detector), the measured 2θ values had to be corrected with calibrated data. No Rietveld refinement was performed with these corrected data. Instead the 2θ value of each reflection was determined by using a single-peak-fit procedure. The unit cells were refined with the resulting 2θ values. In Figure 9 the noncorrected data are shown.

High-resolution experiments were performed on the powder diffractometer at beamline B2 (Ge(111) double monochromator, focused beam, NaI scintillation counter with analyzer crystal)[28] at Hasylab, Hamburg (Germany). The samples were measured in capillaries ($\phi = 0.7-1.0$ mm) sealed under argon. For the low-temperature measurement, a closed-cycle He cryostat was used. As problems with the cooling system occurred, only a minimum temperature of 83 K was achieved. For the measurement at

640 K a Stoe furnace was used. More details can be found in the refs. [20], [24], and [25]. All data were analyzed with the GSAS software.[18]

The Raman spectra were obtained with a BIO-RAD FT-Raman spectrometer (Nd-YAG laser, $\lambda = 1064$ nm, 50 mW laser power). The samples were sealed in NMR tubes ("Economy", Fa. Wilmad) under argon.

Acknowledgements

We would like to thank Vera Vohn for her help with the synthesis, Dr. Paul Müller for his assistance with the laboratory X-ray experiments, and Dr. Christa Kneip for the Raman spectra. The financial support of the Fonds der Chemischen Industrie and the BMBF is gratefully acknowledged.

---

[1] a) C. Winkler, *Ber. Dtsch. Chem. Ges.* **1890**, *23*, 2642; b) L. Maquenne, *C.R. Acad. Sci.* **1892**, *115*, 558.

[2] a) H. Moissan, *C.R. Acad. Sci.* **1892**, *115*, 1031; b) H. Moissan, *C.R. Acad. Sci.* **1894**, *118*, 684; c) H. Moissan, *Bl. Soc. Chim.* **1894**, *11*, 1002.

[3] a) M. v. Stackelberg, *Naturwissenschaften* **1930**, *18*, 305; b) M. v. Stackelberg, *Z. Phys. Chem. Abt. B* **1930**, *9*, 437.

[4] M. Atoji, R. C. Medrud, *J. Chem. Phys.* **1959**, *31*, 332.

[5] O. Reckeweg, A. Baumann, H. A. Mayer, J. Glaser, H.-J. Meyer, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1686.

[6] H. H. Franck, M. A. Bredig, G. Hoffmann, *Z. Anorg. Allg. Chem.* **1937**, *232*, 61.

[7] H. H. Franck, M. A. Bredig, K.-H. Kou, *Z. Anorg. Allg. Chem.* **1937**, *232*, 75.

[8] M. A. Bredig, *J. Phys. Chem.* **1942**, *46*, 801.

[9] M. Atoji, *J. Chem. Phys.* **1971**, *54*, 3514.

[10] N.-G. Vannerberg, *Acta Chem. Scand.* **1962**, *16*, 1212.

[11] N.-G. Vannerberg, *Acta Chem. Scand.* **1961**, *15*, 769.

[12] V. Vohn, U. Ruschewitz, *Z. Kristallogr.* **1998**, *Suppl. 15*, 55.

[13] E. B. Hunt, R. E. Rundle, *J. Am. Chem. Soc.* **1951**, *73*, 4777.

[14] V. Vohn, M. Knapp, U. Ruschewitz, *J. Solid State Chem.* **2000**, *151*, 111.

[15] V. Vohn, W. Kockelmann, U. Ruschewitz, *J. Alloys Compds.* **1999**, *284*, 132.

[16] R. Juza, H.-U. Schuster, *Z. Anorg. Allg. Chem.* **1961**, *311*, 62.

[17] A. Le Bail, H. Duroy, J. L. Fourquet, *Mater. Res. Bull.* **1988**, *23*, 447.

[18] A. C. Larson, R. B. v. Dreele, *Los Alamos Nat. Lab. Rep. LA-UR* **1987**, *86*, 748; A. C. Larson, R. B. v. Dreele, *Los Alamos Nat. Lab. Rep. LA-UR PC Version* **1998**.

[19] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* **1994**, *27*, 435.

[20] Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-411 189.

[21] J. F. Long, R. Hoffmann, H.-J. Meyer, *Inorg. Chem.* **1992**, *31*, 1734.

[22] E. Ruiz, P. Alemany, *J. Phys. Chem.* **1995**, *99*, 3114.

[23] P. Karen, A. Kjekshus, Q. Huang, V. L. Karen, *J. Alloys Compd.* **1999**, *282*, 72.

[24] Structural refinement of CaC$_2$ at 83 K: synchrotron radiation, $\lambda = 120.635$ pm, powder diffractometer at beamline B2, Hasylab Hamburg (Germany), $19° \leq 2\theta \leq 63°$, 10 998 data points; CaC$_2$ I: crystal system: tetragonal, space group *I4/mmm* (no. 139), $a = 386.578(8)$ pm, $c = 640.07(2)$ pm, $\rho_{\text{calcd}} = 2.2254(1)$ g cm^{-3}, $Z = 2$, Ca on 2(a), C on 4(e) with $z = 0.407(1)$, 17 reflections, $R_F = 0.0426$; CaC$_2$ II: crystal system: monoclinic, space group *C2/c* (no. 15), $a = 659.95(2)$ pm, $b = 418.99(2)$ pm, $c = 731.09(3)$ pm, $\beta = 107.034(2)°$, $\rho_{\text{calcd}} = 2.2026(4)$ g cm^{-3}, $Z = 4$, Ca on 4(e) with $y = 0.1821(5)$, C on 8(f) with $x = 0.282(1)$, $y = 0.146(1)$, $z = 0.0562(8)$, 69 reflections, $R_F = 0.0580$; CaC$_2$ III: crystal system: monoclinic, space group *C2/m* (no. 12), $a = 720.76(3)$ pm, $b = 382.83(2)$ pm, $c = 736.77(4)$ pm, $\beta = 107.193(3)°$, $\rho_{\text{calcd}} = 2.1921(3)$ g cm^{-3}, $Z = 4$, Ca on 4(i) with $x = 0.1969(7)$, $z = 0.2544(7)$, C1 on 4(i) with $x = 0.421(2)$, $z = 0.021(3)$, C2 on 4(i) with $x = 0.952(3)$, $z = 0.420(2)$, 82 reflections, $R_F = 0.0847$; 44 variables refined, $wR_P = 0.1679$, $R_P = 0.1287$.
Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-411 188.

[25] Structural refinement of CaC$_2$ at 640 K: synchrotron radiation, $\lambda = 114.699$ pm, powder diffractometer at beamline B2, Hasylab Hamburg (Germany), $18° \leq 2\theta \leq 61°$, 10 748 data points; CaC$_2$ I: crystal system: tetragonal, space group *I4/mmm* (no. 139), $a = 392.642(8)$ pm, $c = 638.63(2)$ pm, $\rho_{\text{calcd}} = 2.1620(1)$ g cm^{-3}, $Z = 2$, Ca on 2(a), C on 4(e) with $z = 0.4090(8)$, 18 reflections, $R_F = 0.0822$; CaC$_2$ III: crystal system: monoclinic, space group *C2/m* (no. 12), $a = 725.49(3)$ pm, $b = 390.75(2)$ pm, $c = 738.53(3)$ pm, $\beta = 107.724(2)°$, $\rho_{\text{calcd}} = 2.1349(4)$ g cm^{-3}, $Z = 4$, Ca on 4(i) with $x = 0.2091(7)$, $z = 0.245(1)$, C1 on 4(i) with $x = 0.455(3)$, $z = 0.045(5)$, C2 on 4(i) with $x = 0.934(3)$, $z = 0.443(4)$, 93 reflections, $R_F = 0.2229$, 30 variables refined, $wR_P = 0.1783$, $R_P = 0.1337$.
Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-411 190.

[26] L. Pauling, *The Nature of the Chemical Bond*, 3rd. ed., Cornell University Press, Ithaca, **1960**, p. 230.

[27] H.-J. Meyer, J. Glaser, private communication.

[28] U. Löchner, P. U. Pennartz, G. Miehe, H. Fuess, *Z. Kristallogr.* **1993**, *204*, 1.

Received: July 5, 2000 [F2583]