

Synthesis and Crystal Structure of SrC₂

V. Vohn,* M. Knapp,† and U. Ruschewitz*,¹

*Institut für Anorganische Chemie der RWTH Aachen, Professor-Pirlet-Straße 1, D-52056 Aachen, Germany; and †Hasylab at DESY, Notkestraße 85, D-22603 Hamburg, Germany

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Polycrystalline SrC₂ of high purity was prepared by the reaction of elemental strontium with graphite at temperatures of about 970 K. The known tetragonal room-temperature modification (*I4/mmm*, *Z* = 2) was confirmed by synchrotron powder investigations, which revealed a strong anisotropic peak broadening. Temperature-dependent X-ray powder investigations resulted in a first-order phase transition to a cubic high-temperature modification (*Fm $\bar{3}m$* , *Z* = 4) at about 700 K. Below room temperature a monoclinic modification (*C2/c*, *Z* = 4), which is isotypic to the crystal structure of ThC₂ at room temperature, was found. © 2000 Academic Press

Key Words: carbides; phase transition; Rietveld; strontium; synchrotron.

INTRODUCTION

SrC₂ was synthesized for the first time by Moissan at the end of the 1800s (1–3). He reacted Sr(OH)₂ or SrCO₃ with sugar coal in an electrical arc furnace. The first crystallographic investigations using a polycrystalline sample were reported by von Stackelberg (4, 5). He showed that at room temperature SrC₂ as well as CaC₂ and BaC₂ crystallizes in crystal structures that can be described as tetragonally distorted rocksalt variants. The C₂²⁻ dumbbells are aligned along the tetragonal *c* axis in these structures, which were named AC₂ I (*A* = Ca, Sr, Ba). A few years later temperature-dependent X-ray investigations on CaC₂, SrC₂, and BaC₂ were performed (6–8) which revealed a cubic high-temperature modification IV with disordered C₂²⁻ dumbbells for these carbides. Furthermore low-temperature modifications CaC₂ II and SrC₂ II as well as a metastable CaC₂ III were found but their crystal structures remained unknown. Just recently we showed that such a low-temperature modification II also exists for BaC₂ (9). Its crystal structure could be solved and refined from neutron diffraction data on a polycrystalline sample showing that the low-temperature modification of BaC₂ is isotypic with the room-temperature modification of ThC₂ (10).

¹To whom correspondence should be addressed. Fax: (+49) 241-8888288. E-mail: Uwe.Ruschewitz@ac.rwth-aachen.de.

In the following a new synthesis of SrC₂ will be presented which leads to polycrystalline samples of high purity. These samples were used for structural investigations at high and low temperatures. Furthermore an unexpected peak broadening of some reflections of the room-temperature modification was investigated by high-resolution synchrotron experiments.

EXPERIMENTAL

1. Synthesis

Polycrystalline samples of SrC₂ were prepared by the reaction of elemental strontium (ABCR, 99.95%) with graphite (Fluka, 99.9%) in a graphite cylinder which could be 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 under high vacuum for about 24 h. In a typical experiment, 300 mg of Sr (3.42 mmol) and 76.5 mg of annealed graphite (6.37 mmol) were mixed in a glove box and pressed to pellets of \varnothing 10 mm. The pellets were transferred into the graphite cylinder, which was closed with the lid. Under argon atmosphere the cylinder was placed in a horizontal tube furnace. The reaction temperature of 970 K was held for about 15 h in a weak argon stream. The products were allowed to cool in the argon atmosphere and were transferred to a glove box, where all further handling was carried out. The resulting powder was slightly gray to almost white, depending upon the reaction conditions. No impurities could be found by X-ray powder diffraction.

2. Structural Investigations

X-ray powder investigations between 295 and 833 K were carried out with a Huber G644 Guinier diffractometer (CuK α ₁ radiation, Ge monochromator, scintillation counter). The heating equipment provided by Huber consists of a corundum bow with a thermocouple surrounded by a cylinder of X-ray transparent capton foil. After careful grinding the sample was sealed in a capillary (\varnothing 0.3 mm, LINDEMANN glass) under purified argon gas. Powder

patterns were taken at room temperature ($24^\circ \leq 2\theta \leq 56^\circ$) and at 773 K ($24^\circ \leq 2\theta \leq 68^\circ$). Furthermore, the sample was heated from room temperature to 833 K and vice versa in steps of 30 and 20 K, respectively ($23^\circ \leq 2\theta \leq 32^\circ$).

X-ray investigations at low temperatures between 295 and 10 K were performed on a Huber G645 Guinier diffractometer ($\text{CuK}\alpha_1$ radiation, Ge monochromator, scintillation counter) with a closed-cycle cryostat. A specially designed flat sample holder (11) was used for the measurements, which was filled in a glove box in an argon atmosphere. Powder patterns were taken at room temperature ($20^\circ \leq 2\theta \leq 100^\circ$) and at 10 K ($10^\circ \leq 2\theta \leq 100^\circ$). Furthermore, the sample was cooled from room temperature to 10 K and vice versa in steps of 10 and 20 K, respectively, taking patterns between $23^\circ \leq 2\theta \leq 32^\circ$.

A high-resolution experiment was performed on the powder diffractometer at beamline B2 ($\lambda = 117.38$ pm, Ge(111) double monochromator, focused beam, NaI detector)

(12) at room temperature (HasyLab, Hamburg/Germany). The sample was measured in a capillary (\varnothing 0.7 mm, LINDEMANN glass), sealed in an argon atmosphere. The pattern was taken between $18.5^\circ \leq 2\theta \leq 58.5^\circ$ in steps of $2\theta = 0.008^\circ$.

All measurements were analyzed by the Rietveld method using the GSAS suite of programs (13).

A Raman spectrum of SrC_2 was recorded on a Dilor XY triple spectrometer (argon laser: $\lambda = 514.5$ nm, $P = 50$ mW). The sample was measured in an NMR capillary (Wilmad "Economy") sealed under argon.

STRUCTURAL INVESTIGATIONS AT ROOM TEMPERATURE

The aim of this contribution was the investigation of the high- and low-temperature modifications of SrC_2 . Therefore, patterns at room temperature were taken only to check

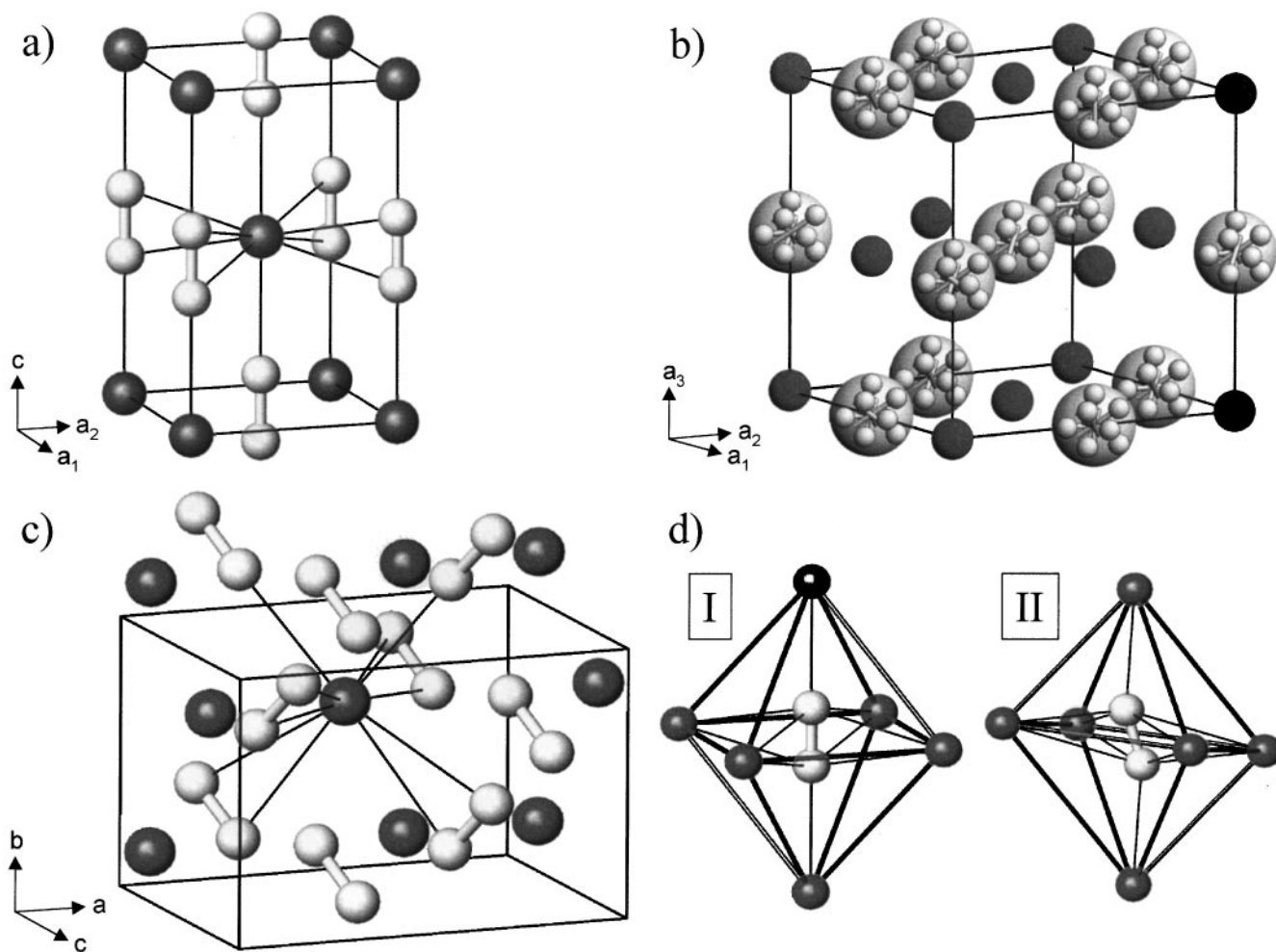


FIG. 1. Crystal structures of the different modifications of SrC_2 (Sr, dark spheres; C, light spheres). The unit cell and the C-C triple bonds are emphasized. (a) SrC_2 I, room-temperature modification ($I4/mmm$, $Z = 2$); the carbon surrounding of one Sr atom is marked. (b) SrC_2 IV, high-temperature modification ($Fm\bar{3}m$, $Z = 4$); the disordering of the C_2^{2-} dumbbells is outlined. (c) SrC_2 II, low-temperature modification ($C2/c$, $Z = 4$); the carbon surrounding of one Sr atom is marked. (d) The octahedral Sr surrounding of the C_2^{2-} dumbbells in the modifications SrC_2 I and II.

the quality of the sample prior to heating or cooling. The known tetragonal modification of SrC₂ at room temperature (*I4/mmm*, $Z = 2$, see Fig. 1a) could be confirmed and no SrO impurities were detected in the diffraction patterns. But one reflection at $2\theta \approx 28.6^\circ$ (CuK α_1 radiation) was found which could not be assigned to the tetragonal modification. Furthermore, the *h0l* and *hkl* reflections of the tetragonal modification were broadened compared to the *00l*, *h00*, and *hk0* reflections. This effect was more pronounced on the Huber G645 with a flat sample than on the Huber G644 with a capillary due to the lower resolution of the latter configuration. As this effect could point to a monoclinic distortion of the tetragonal unit cell with an angle β close to 90° , refinements in the space group *I2/m* were performed. They resulted in a monoclinic angle $\beta = 90.54(1)^\circ$ and an improvement of the residual values by 1–2%. But no splitting of reflections even at high angles was found. Therefore a high-resolution diffraction pattern was taken with synchrotron radiation. Again *h0l* and *hkl* reflections showed a severe broadening, but even with the highest possible resolution and at high angles a splitting of reflections could not be observed. Therefore the model of a monoclinically distorted structure had to be dismissed instead of an anisotropic reflection broadening. A comparable broadening has also been found for some rare earth carbides (14) and in a less pronounced form for CaC₂, BaC₂, and some alkali metal hydrogen acetylides (15). The reason for this reflection broadening is unknown, but it might be due to changes in crystallinity during a phase transition. In Fig. 2 the full widths at half-maximum (fwhm's) of SrC₂ I reflections are shown as a function of the diffraction angle 2θ . It is obvious that *hk0*, *h00*, and *00l* reflections show the expected increase of the half-width with increasing θ , whereas no such almost linear dependence has been found for the broadened reflections *h0l* and *hkl*. From this point it was

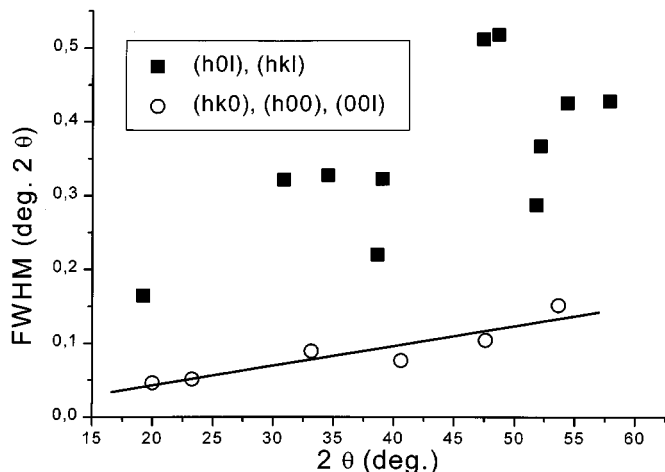


FIG. 2. Full widths at half-maximum (fwhm) of SrC₂ I depending upon the diffraction angle 2θ (Hasyllab, powder diffractometer at beamline B2).

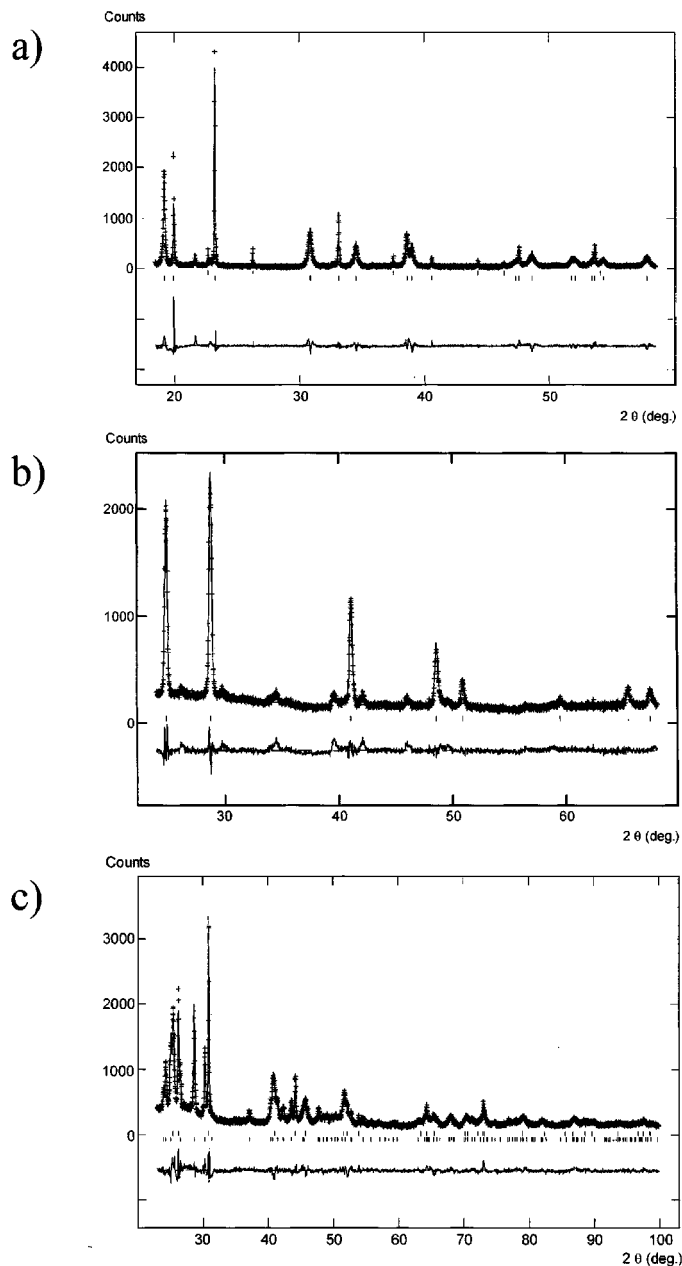


FIG. 3. X-ray diffraction patterns of SrC₂ at different temperatures. The observed (+) and calculated patterns (solid line) as well as the difference between the two are shown. Vertical bars mark the positions of reflections. (a) Pattern at 295 K (Hasyllab, powder diffractometer at beamline B2); the positions of the reflections of SrC₂ I (lower bars) and SrO (upper bars) are marked. (b) Pattern at 773 K (Huber G644); the positions of the reflections of SrC₂ IV are marked by vertical bars (the weak reflections of SrC₂ I have not been included in the refinement). (c) Pattern at 10 K (Huber G645); the positions of the reflections of SrC₂ I (upper bars) and SrC₂ II (lower bars) are marked.

already clear that a Rietveld refinement of the diffraction pattern would be difficult even by applying the anisotropic broadening functions implemented in GSAS (13). The results of the best refinement are shown in Fig. 3a; some

TABLE 1
Details and Results of the X-Ray Powder Investigations on SrC₂ at 295 K (Synchrotron Radiation, $\lambda = 117.38$ pm, Powder Diffractometer at Beamline B2, Hasylab)

Space group	I4/mmm (No. 139), Z = 2				
Lattice constants	$a = 411.43(2)$ pm, $c = 676.60(4)$ pm, $V = 0.11452(1)$ nm ³				
Data range	$18.5^\circ \leq 2\theta \leq 58.5^\circ$, 5001 data points				
Refined parameters	16				
Refined reflections	18				
wR_p , R_p , R_{Bragg}	0.1976, 0.1531, 0.0386				
Atomic Coordinates and Isotropic Thermal Parameters					
	x	y	z	U_{iso} (pm ²)	
Sr	2(a)	0	0	0	265(7)
C	4(e)	0	0	0.412(1)	360(40)
Selected Interatomic Distances (pm)					
Sr–C	278.5(8)	2 ×, end-on		C–C	120(2)
Sr–C	297.0(2)	8 ×, side-on			

details are summarized in Table 1. From the wR_p and R_p values and the difference curve between the measured and the refined pattern (Fig. 3a) it can be seen that there are some problems in modeling the profile of the pattern, but the structural details are well described as represented by the very good R_{Bragg} factor and the C–C distance of 120(2) pm, which is in very good agreement with the expected value for a C–C triple bond (CaC₂ 119.1 pm (16), acetylene 120.5 pm (17)). It should be noted that the high quality of the synchrotron data (low background, high resolution) made weak reflections of SrO visible which could not be found in the laboratory X-ray patterns. From the Rietveld refinement an SrO content of 3.0(2) wt% was obtained.

STRUCTURAL INVESTIGATIONS AT HIGH TEMPERATURES

A polycrystalline sample of almost white SrC₂ was used to investigate its structural behavior above room temperature. It was known from the literature that SrC₂ transforms into a cubic high-temperature modification (SrC₂ IV) at about 643 K (8). In Fig. 4 the volume and the lattice parameters of SrC₂ are depicted as functions of the temperature. From these measurements a transition temperature of about 700 K was found which is slightly larger than the value given in the literature. It is not clear whether this effect must be attributed to different setups of the measurements or the higher purity of the sample investigated in this contribution. For BaC₂ we have also found a transition temperature which is about 100 K higher than the value given in the literature (9). The $V = f(T)$ diagram in Fig. 4a shows

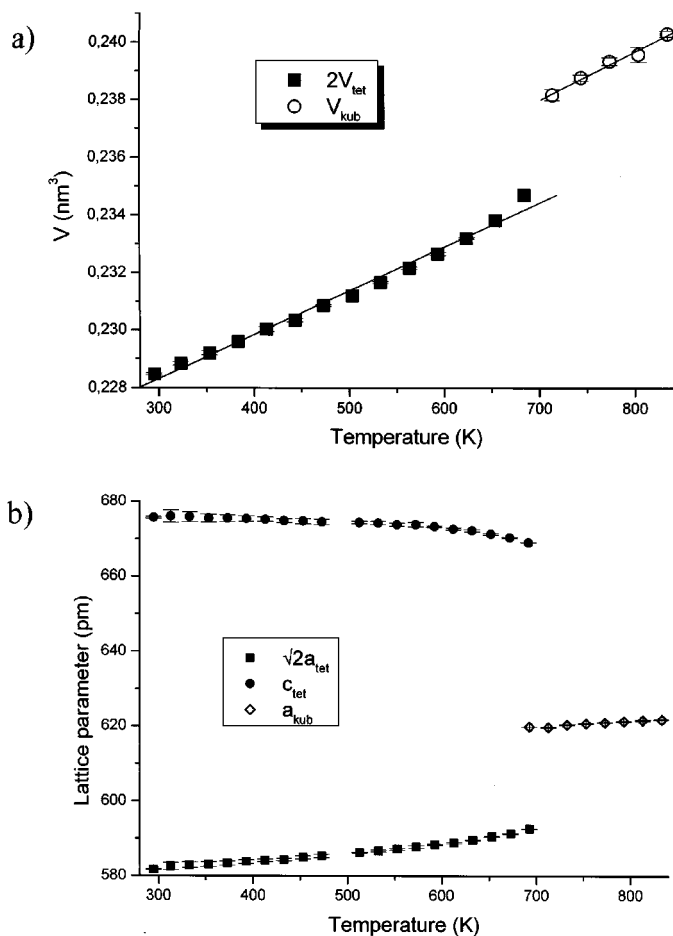


FIG. 4. High-temperature phase transition of SrC₂: (a) the temperature dependence of the cell volume and (b) the lattice parameters is shown.

quite clearly that the phase transition SrC₂ I \rightarrow SrC₂ IV is a first-order transition because of the discontinuity around the transition temperature. This behavior is reversible as a cooling of the sample confirmed (not shown). With respect to the experimental errors no hysteresis could be observed. In Fig. 4b the temperature-dependent behavior of the lattice parameters is plotted: with increasing temperature the a axis increases whereas the c axis decreases. This can be attributed to an increasing vibration of the C₂²⁻ dumbbells toward the (001) plane with increasing temperature. The same effect has been found for BaC₂ (9) and Li₂C₂ (18).

The results of a Rietveld refinement of a X-ray pattern taken at 773 K are summarized in Table 2 and Fig. 3b. The lattice parameter a is in reasonable agreement with the value given in the literature (8). The crystal structure of SrC₂ IV can be described as a rock-salt type structure (Fig. 1b) with Sr²⁺ occupying the Na⁺ positions and disordered C₂²⁻ dumbbells occupying the Cl⁻ positions with their center of gravity. From the diffraction experiments it cannot

TABLE 2
Details and Results of the X-Ray Powder Investigations on SrC₂
at 773 K (Huber G644, CuK α_1 Radiation)

Space group	<i>Fm</i> $\bar{3}$ <i>m</i> (No. 225), <i>Z</i> = 4				
Lattice constants	<i>a</i> = 621.34(6) pm, <i>V</i> = 0.23988(6) nm ³				
Data range	24° ≤ 2θ ≤ 68°, 4401 data points				
Refined parameters	7				
Refined reflections	8				
w <i>R</i> _p , <i>R</i> _p , <i>R</i> _{Bragg}	0.1135, 0.0868, 0.1220				
Atomic Coordinates and Isotropic Thermal Parameters					
	<i>x</i>	<i>y</i>	<i>z</i>	Occ.	<i>U</i> _{iso} (pm ²)
Sr	4(<i>a</i>)	0	0	1	790(20)
C	4(<i>b</i>)	½	½	2 ^{<i>a</i>}	1920(60)

^{*a*}The disordered C₂²⁻ dumbbells were refined by occupying their center of gravity with two carbon atoms. The large *U*_{iso} of the carbon atoms displays the disordering of the C₂²⁻ dumbbells.

be distinguished between a static and a dynamic disordering of the dumbbells.

STRUCTURAL INVESTIGATIONS AT LOW TEMPERATURES

The patterns which were obtained on cooling a polycrystalline sample of SrC₂ below room temperature are shown in Fig. 5. One can see that with decreasing temperature the reflections of a new low-temperature modification (SrC₂ II) increase in intensity. At about 80 K no further increase of

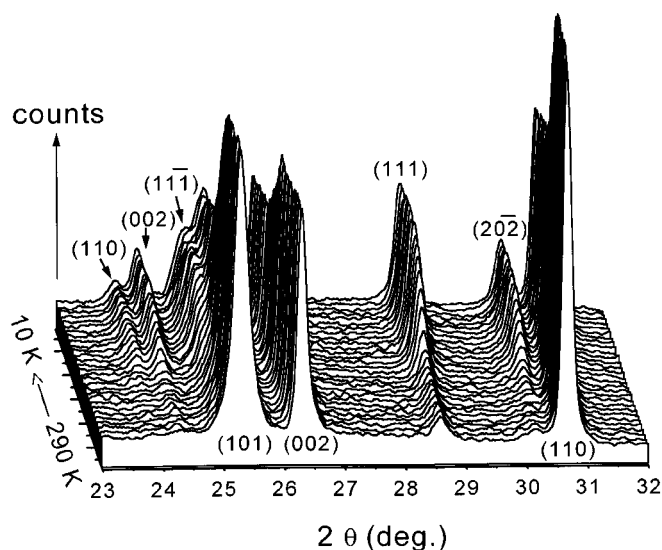


FIG. 5. Low-temperature phase transition of SrC₂: the temperature dependence of the X-ray powder patterns in the range 23° ≤ 2θ ≤ 32° is shown. The indices of SrC₂ I and SrC₂ II are given below and above the patterns, respectively.

these reflections is observed, but the reflections of the room-temperature modification are still visible. Therefore even at very low temperatures both modifications coexist. The ratio of modification II to modification I is about 45:55 based on one formula unit. From Fig. 5 one can deduce that the reflection at 2θ ≈ 28.6° in the room-temperature pattern which could not be assigned to the room-temperature modification SrC₂ I is the strongest reflection of the low-temperature modification SrC₂ II. The low-temperature behavior of SrC₂ is completely reversible, as a measurement heating the sample from 10 K to room temperature confirmed (results are not shown). In the literature a transition temperature of 243 K is given (8), but according to our measurements no sharp transition temperature can be assigned. The same behavior has been found for BaC₂ (9). An interesting fact is the finding that grinding of SrC₂ decreases the transition temperature to about 193 K (8).

A C-centered monoclinic cell was found for the new reflections of the low-temperature modification of SrC₂ using the program DICVOL91 (19). The resulting volume of

TABLE 3
Details and Results of the X-Ray Powder Investigations on SrC₂
at 10 K (Huber G645, CuK α_1 Radiation)

Space group	<i>I4/mmm</i> (No. 139), <i>Z</i> = 2; <i>C2/c</i> (No. 15), <i>Z</i> = 4				
Lattice constants	<i>a</i> = 409.98(3) pm, <i>c</i> = 680.50(7) pm, <i>V</i> = 0.11438(2) nm ³ ; <i>a</i> = 704.55(8) pm, <i>b</i> = 446.81(6) pm, <i>c</i> = 768.36 (9) pm, β = 107.22(1)°, <i>V</i> = 0.23103(5) nm ³				
Data range	23° ≤ 2θ ≤ 100°, 7701 data points				
Refined parameters	23				
Refined reflections	27; 118				
w <i>R</i> _p , <i>R</i> _p , <i>R</i> _{Bragg}	0.0951, 0.0752, 0.0499; 0.0791				
Atomic Coordinates and Isotropic Thermal Parameters					
	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} (pm ²)	
<i>I4/mmm</i>					
Sr	2(<i>a</i>)	0	0	0	215(6) ^{<i>a</i>}
C	4(<i>e</i>)	0	0	0.415(2)	130(40) ^{<i>b</i>}
<i>C2/c</i>					
Sr	4(<i>e</i>)	0	0.1833(7)	¼	215(6) ^{<i>a</i>}
C	8(<i>f</i>)	0.278(3)	0.165(5)	0.061(2)	130(40) ^{<i>b</i>}
Selected Interatomic Distances (pm)					
<i>I4/mmm</i>					
Sr-C	282(1)	2 ×, end-on		C-C	116(2)
Sr-C	295.7(2)	8 ×, side-on			
<i>C2/c</i>					
Sr-C	280(2)	2 ×, end-on		C-C	119(3)
Sr-C	277(2)	2 ×, side-on			
Sr-C	293(3)	2 ×, side-on			
Sr-C	303(2)	2 ×, side-on			
Sr-C	329(2)	2 ×, side-on			

^{*a,b*} Constrained.

the unit cell was almost double the size of the tetragonal unit cell of SrC₂ I, and so four formula units per unit cell were assumed. At this point it was obvious that the low-temperature modification of SrC₂ as well as BaC₂ (8) crystallizes in the monoclinic ThC₂ structure type (10). This assumption was confirmed by the results of a Rietveld refinement; the details are summarized in Table 3 and the quality of the refinement can be seen in Fig. 3c. The resulting structure for SrC₂ II is shown in Fig. 1c. Like in tetragonal SrC₂ I each Sr is surrounded by six C₂²⁻ dumbbells, from which four are coordinated side-on and two end-on, so that a coordination number of 10 results. But a closer look at the Sr–C distances reveals that the 2 + 8 coordination of the room-temperature modification is changed to a 4 + 4 + 2 coordination in the low-temperature form (see Tables 1 and 3). Calculating effective coordination numbers using the ECoN approach (20) leads to 9.86 (295 K, SrC₂ I) and 8.75 (10 K, SrC₂ II).

Considering the standard deviations the C–C distances are in the range expected for a C–C triple bond for both the room-temperature (120(2) pm at 295 K, 116(2) pm at 10 K) and the low-temperature modifications (119(3) pm at 10 K). The Sr surrounding of the C₂²⁻ dumbbells in both modifications is shown in Fig. 1d. In SrC₂ I the dumbbell sits in an elongated octahedron with the dumbbell axis pointing toward the elongated corners of the octahedron. In the low-temperature modification the dumbbell is rotated away from this position by 20.2° toward the plane of the four other Sr atoms. The C atoms now point toward the faces of the octahedron. This is in agreement with theoretical calculations on CaC₂, which gave only slightly less stable configurations for a distortion with the dumbbells pointing toward the faces compared to the undistorted structure (21).

CONCLUSION

We have confirmed that SrC₂ exists in three modifications. At room temperature the well-known tetragonal modification (*I4/mmm*, SrC₂ I) was found, which transforms at about 700 K in a first-order transition to a cubic high-temperature modification with disordered C₂²⁻ dumbbells. The nature of the disordering cannot be elucidated from diffraction experiments. Spectroscopic investigations, especially ¹³C-MAS-NMR measurements, are a useful tool for these phenomena. Some work has already been done in this field (22). At low temperatures a partial transformation of SrC₂ I to a monoclinic low-temperature modification (*C2/c*, SrC₂ II) has been observed. This transformation starts at room temperature and levels out at about 80 K. At this temperature the ratio of both modifications is roughly 1 : 1 based on one formula unit. We did not investigate the influence of the purity and the crystallinity of the sample on both the transition temperature and the ratio of SrC₂ I : SrC₂ II. But our investigations on BaC₂ (9) and older work

on SrC₂ (8) make their influences very likely. The new synthetic route presented allows the preparation of samples of very high purity; the SrO contents is about 3 wt%. Therefore it is not surprising that our transition temperatures differ from the values given in the literature. In all refinements a C–C distance was found that is in agreement with the value expected for a C–C triple bond. This finding is further confirmed by the results of a Raman spectroscopic measurement. The frequency for the C–C stretching vibration was determined to be 1852 cm⁻¹, which is in good agreement with the value given in the literature (23) and expected for a C–C triple bond in an ionic acetylide.

Currently we are investigating the phase transitions of CaC₂ and the crystal structures of its different modifications, which are similar to those found for SrC₂ and BaC₂.

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