CaB_2C_2: Reinvestigation of a Semiconducting Boride Carbide with a Layered Structure and an Interesting Boron/Carbon Ordering Scheme[†]

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Calcium diboride dicarbide, CaB_2C_2, was synthesized as a crystalline powder and investigated by electron energy loss spectroscopy, X-ray powder diffractometry, conductivity measurements, and LMTO band structure calculations. A new structure model was derived, and the crystal structure was refined by Rietveld methods in the tetragonal space group $I4/mcm$ (No. 140, $a = 537.33(1)$ pm and $c = 741.55(2)$ pm, $Z = 4$). The boron and carbon atoms are well ordered within layers consisting of four- and eight-membered rings. A convincing coloring scheme is proven by the detection of a superstructure reflection. An earlier assignment of the compound into the LaB_2C_2 structure family (space group $P\bar{4}2c$ or $P4_2/mmc$, respectively) has been shown to be incorrect. LMTO band structure calculations suggest semiconducting behavior for CaB_2C_2, which has been confirmed by conductivity measurements.

Introduction

In 1986, Burdett, Canadell, and Hughbanks[1] reported on the correlation of symmetry and electronic stability of the coloring of an extended network. They chose CaB_2C_2 as an example of a compound with a crystal structure consisting of layers that contain boron and carbon atoms following a certain ordering scheme and metal atoms between these 48^2 nets. Two possibilities of B/C ordering within the layers were discussed (Figure 1). The authors concluded, that a certain (Figure 1a) arrangement of the boron and carbon atoms excluding homoatomic interactions within the layer should be more stable than the one (Figure 1b) which has been found for the MB_2C_2 structure family (M = Y,[2,3] La,[4] Pr, Gd, Er, Yb, Dy, Ho, Nd, Eu, Ca[5]). Performing “extended Hückel” band structure calculations, they predicted a difference in the electrical properties for compounds crystallizing according to one or the other possible B/C ordering model: semiconducting behavior was assumed for CaB_2C_2 with the electronically stabilized atomic arrangement (Figure 1a).

The synthesis of CaB_2C_2 was published by Bréant et al. in 1978.[5] The crystalline powder was described being isotypic with other diboride dicarbides and crystallizing with the LaB_2C_2 crystal structure (Figure 1b). No further experimental investigation of CaB_2C_2 concerning its composition and its actual crystal structure, its structure refinement, or its electrical behavior has been reported since then.

The contradictory situation concerning the B/C coloring scheme in LaB_2C_2 structures was discussed again by Bauer, Halet, and Saillard,[6] who quoted unpublished experimental work of Pöttgen,[3] dealing with the Y compound and apparently confirming the LaB_2C_2 structure model. This work should help to further elucidate the question of the correct LaB_2C_2 structure type when completed. Recently, an ordering scheme according to Figure 1a was published for the Ce compound.[7]

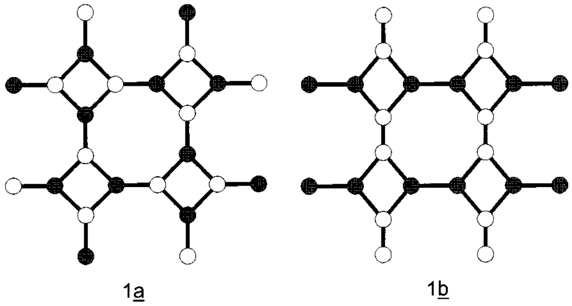

Figure 1. B/C ordering scheme within a layer: (a) arrangement favored according to theoretical considerations;[1] (b) arrangement found for LaB_2C_2[4] (B, gray; C, white).

We now describe the synthesis, characterization, crystal structure, and electronic situation of CaB_2C_2, which is the only known ternary boron/carbon compound of an alkaline earth metal besides MgB_2C_2,[8] whose crystal structure exhibits graphite-like B/C nets of the 6^3 type, and BeB_2C_2,[9] which will be discussed later.[10]

Experimental Section

Synthesis. The samples were synthesized from the elements according to the desired stoichiometry Ca:B:C = 1:2:2 (Ca, distilled; B, Chempur, 99.99%; C, Aldrich, 99.95%). The starting mixtures were prepared in an argon glovebox, pressed into pellets, and placed in preboronated tantalum tubes which were arc-welded under helium. After 48 h at 1050 °C, reddish-brown powders of CaB_2C_2 were obtained which proved to be air-sensitive and had to be handled under argon

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[†] Dedicated to Professor Dr. Dr. h.c. mult. Rudolf Hoppe on the occasion of his 77th birthday.

(1) Burdett, J. K.; Canadell, E.; Hughbanks, T. *J. Am. Chem. Soc.* **1986**, *108*, 3971−3976.
(2) Bauer, J.; Nowotny, H. *Monatsh. Chem.* **1971**, *102*, 1129−1145.
(3) Pöttgen, R. Unpublished results.
(4) Bauer, J.; Bars, O. *Acta Crystallogr.* **1980**, *B36*, 1540−1544.
(5) Bréant, T.; Pensec, D.; Bauer, J.; Debuigne, J. *C. R. Acad. Sci. Paris* **1978**, *287*, 261−264.
(6) Bauer, J.; Halet, J.-F.; Saillard, J.-Y. *Coord. Chem. Rev.* **1998**, *178−180*, 723−753.
(7) Onimaru, T.; Onodera, H.; Ohoyama, K.; Yamauchi, H.; Ohashi, M.; Yamaguchi, Y. *J. Phys. Chem. Solids* **1999**, *60*, 1435−1438.
(8) Wörle, M.; Nesper, R. *J. Alloys Compd.* **1994**, *216*, 75−83.
(9) Markovskii, L. Ya.; Vekshina, N. V.; Kondrashev, Yu. D.; Shoganova, I. M. *J. Appl. Chem.* **1966**, *39*, 10−16.
(10) Schmitt, K. Ph.D. Thesis in preparation, Universität Giessen.

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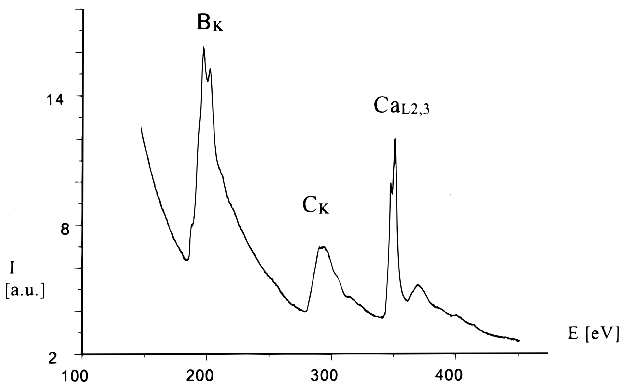

Figure 2. Electron energy loss spectrum showing the $Ca_{L2,3}$, B_K, and C_K edges.

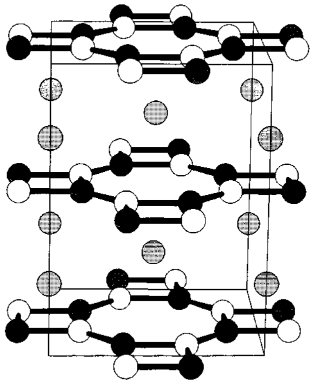

Figure 3. Section of the structure of CaB_2C_2 (Ca, light gray; B, dark gray; C, white; view along [100]).

atmosphere. Their powder diagrams, which were obtained on a Huber Guinier diffractometer G645 using 0.3 mm glass capillaries, allowed a preliminary identification.

Analysis. The absence of an excess of Ca was proven by suspending a sample in liquid ammonia, which did not turn blue. To determine the accurate composition, we performed an electron energy loss spectroscopy (EELS) experiment (Gatan PEELS666 spectrometer). Thin specimens were placed on a lacey carbon coated copper TEM grid and set in a transmission electron microscope operated at 300 kV (Philips CM30). The $Ca_{L2,3}$, B_K, and C_K edges were registered within one range and their quantitative analysis was performed with the EL/P3.0 program (Gatan). Magnetic measurements on a Faraday balance indicate the presence of a small amount of ferromagnetic impurities within the otherwise diamagnetic sample. This can be explained by the contact between the starting material calcium and the iron-containing distillation vessel.

Structure Determination and Refinement. High-resolution X-ray powder diffraction experiments were done on a Huber Guinier powder diffractometer G644 using an airtight flat plate sample holder in transmission collection mode (quartz monochromator, range 6−100° 2θ, step width 0.016°, data collection time 60 s/step, 5×10^{-5} mbar). Structure refinements were done using the program GSAS.[11] The background was corrected using a 12 parameter cosinus Fourier series. The profile function used is a modified pseudo-Voigt function with four parameters refined. The cutoff for peaks is 0.1% of the peak maximum. To save parameters, the boron and carbon atoms were refined with a common thermal displacement parameter. In addition, the zero point and a scale factor were refined.

Conductivity Measurements. For conventional four-probe conductivity measurements a powder pellet was prepared and investigated between 58 and 298 K.

Band Structure Calculations. Self-consistent LMTO band structure calculations were performed using the program Tight-Binding LMTO Vers. 4.7.[12] Here, the density functional theory is used with the local density approximation in form of the linear muffin-tin orbital method in the atomic spheres approximation.[13−15] For reciprocal space integrations the tetrahedron method was used with 349 irreducible *k* points within the Brillouin zone.[16]

Results and Discussion

To establish the stoichiometrical composition of the investigated substance, EEL spectra were recorded for several particles. An example is shown in Figure 2, exhibiting the $Ca_{L2,3}$, B_K, and C_K edges. Within the experimental error the quantification of the recorded edge intensities confirms the desired composition of Ca:B:C = 1:2:2 (C/B ratio is 0.93 ± 0.15, Ca/B ratio is 0.48 ± 0.07).

Our crystal structure work was started by calculating theoretical powder patterns for various known structure models. So far, at least three structure models have been proposed for members of the LaB_2C_2 structure family: The first is based on a small unit cell with dimensions of approximately $380 \times 380 \times 360$ pm ($Z = 1$, possible space group $P422$).[17] Second, it has been suggested that the unit cell must be enlarged by multiplying the lattice constants *a* and *b* by the factor $\sqrt{2}$ ($Z = 2$, $540 \times 540 \times 360$ pm, possible space group $P4/mbm$).[18] This setting allows a carbon/boron ordering scheme according to the theoretical predictions of Burdett et al.[1] For the Ca compound, the arrangement should manifest itself by semiconducting behavior. Bauer and Bars[4] described the refinement of the second structure model being unstable for a LaB_2C_2 single-crystal data set. These authors chose a third possibility and refined LaB_2C_2 in $P\bar{4}2c$ using an unit cell doubled along *c* ($Z = 2$, $382.18(6) \times 382.18(6) \times 792.4(1)$ pm). Here, the B/C layers are turned around 90° along *c* with respect to each other. The B/C ordering within the layers corresponds to the scheme which should be energetically less stable due to homoatomic B−B and C−C interactions. This structural arrangement is characterized by a band overlap at the Fermi level.[1] Except for the scandium compound,[19] Bauer and Bars[4] claimed the third structure model to be valid for all other known diboride dicarbides including the calcium compound.[5] The space group later was corrected by Parthé et al. from $P\bar{4}2c$ into $P4_2/mmc$.[20] Reflections, which would indicate the correctness of one of the proposed superstructures, have never been measured.

For CaB_2C_2, we were not able to confirm any of these structural models by refining our X-ray powder data. Rietveld refinements of the different atomic arrangements proved to be unstable. We therefore developed a new structure model shown in Figure 3.[21] It contains both features of Burdett's[1] suggestions (B/C ordering) and the "Bauer model"[4] (arrangement of the layers in respect to each other). Hereby, homoatomic interactions are minimized in all three dimensions and the structure should be electrostatically favored compared with the earlier models.

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(11) Larson, A. C.; Von Dreele, R. B. Program GSAS, Los Alamos, NM, 1985.

(12) Andersen, O. K. Program Tight-Binding LMTO Vers. *4.7*, Stuttgart, Germany, 1994 (updated 1998).

(13) Andersen, O. K. *Phys. Rev. B* **1975**, *12*, 3060−3083.

(14) Andersen, O. K.; Jepsen, O. *Phys. Rev. Lett.* **1984**, *53*, 2571−2574.

(15) Jepsen, O.; Andersen, O. K. *Z. Phys. B* **1995**, *97*, 35−47.

(16) Jepsen, O.; Andersen, O. K. *Solid State Commun.* **1971**, *9*, 1763−1767.

(17) Smith, P. K.; Gilles, P. W. *J. Inorg. Nucl. Chem.* **1967**, *29*, 375−382.

(18) Smith, P. K. Ph.D. Thesis, University of Kansas, 1964; quoted according to ref 4.

(19) Smith, G. S.; Johnson, Q.; Nordine, P. C. *Acta Crystallogr.* **1965**, *19*, 668−673.

(20) Cenzual, K.; Gelato, L. M.; Penzo, M.; Parthé, E. *Acta Crystallogr.* **1991**, *B47*, 433−439.

(21) Hundt, R. Program KPLOT, Bonn, Germany, 1979.

Table 1. Crystal Data and Structure Refinement Parameters

empirical formula	CaB_2C_2
fw	85.72
temp (K)	296.2(5)
radiation	Cu Kα_1
wavelength (Å)	1.54056
cryst system	tetragonal
space group (no.)	*I*4/*mcm* (140)
unit cell dimens (pm)	$a = 537.33(1)$ $b = 537.33(1)$ $c = 741.55(2)$
V (Å^3)	214.103(1)
Z	4
μ (cm^{-1})	24.78
density/calcd (g/cm^3)	2.66
used 2θ range (deg)	20−100
no. obsd reflns	39
no. refined (struct determining) params	7
R_{wp}^{a}	0.093
R_p^{a}	0.073
D_{dw}^{a}	1.74
χ^2 ^{a}	1.3

[a] $R_p = \Sigma|I_o - I_c|/\Sigma I_o$, $R_{wp} = \sqrt{(M/\Sigma(wI_o^2)}$, $\chi^2 = M/(N_{obs} - N_{var})$, $D_{dw} = \Sigma(\Delta_i/\sigma_i - \Delta_{i-1}/\sigma_{i-1})^2/\Sigma(\Delta_i/\sigma_i)^2$ (I_o,I_c = intensity observed/calculated, M = minimization function, w = weight factor, N_{obs}, N_{var} = number of observations/parameters, $\Delta = I_o - I_c$).

Table 2. Positional and Thermal Displacement Parameters (10^4 pm^2) for CaB_2C_2

	x/a	*y/b*	*z/c*	$U_{eqv/iso}$^{a}
Ca	0	0	0.25	0.009
C	0.345(3)	0.845(3)	0	0.005(2)
B	0.141(3)	0.641(3)	0	0.005(2)

[a] U_{Eqv} for Ca $^1/_3$ of the diagonalized matrix; $U_{11} = 0.003(1)$, $U_{33} = 0.021(2)$.

Table 3. Selected Bond Lengths (pm) and Angles (deg)

Ca−Ca	370.77(1), 379.95(1)	C−B−C	132(1)
B−C	154.9(8), 159.3(5)	B−C−B	137(1)

Electrostatic interactions are not only reduced within the sheets but also between them. Burdett's principle of alternating the colors is driven even further than it was suggested. The resulting space group is *I*4/*mcm* ($Z = 4$, $a = 537.33(1)$ and $c = 741.55(2)$ pm). With respect to the initial small unit cell the lattice parameters are enlarged by the factor $\sqrt{2}$ for a and b and the factor 2 for c. The Rietveld refinement of this model led to reasonable bond distances and angles (Table 3). Close homoatomic interactions do not occur. The difference between the observed and the calculated diffraction traces is very small (Figure 4). Table 1 contains the crystal data and refinement parameters, and positional and thermal parameters are given in Table 2. The arrangement of alternating boron and carbon atoms along c is a structural feature which is well-known from LiBC[22] and MgB_2C_2.[7]

The LMTO calculation based on our structural data led to a band structure very similar to the one calculated for a B/C sheet by Burdett et al. using the "extended Hückel" method.[1] The total densities of states are shown in Figure 5. The calculated band gap is about 0.8 eV. As expected, the conductivity measurement revealed the presence of a small band gap (0.2 eV) and a temperature dependence of the specific resistivity (Figure 6 shows the range between 256 and 213 K) that is characteristic for semiconductors and that is consistent with the calculations. Hereby, a physical property theoretically predicted for CaB_2C_2 by Burdett et al. has been confirmed experimentally.

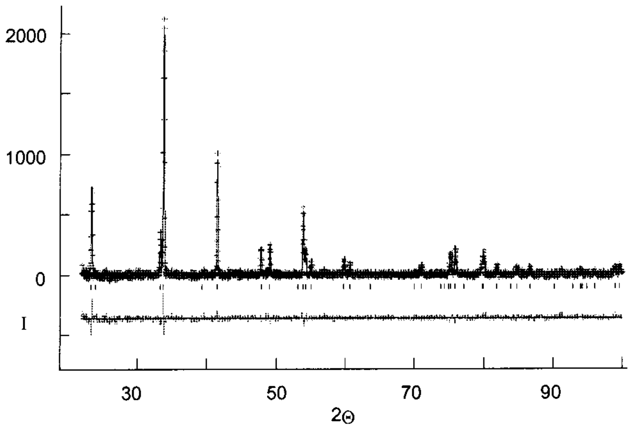

Figure 4. Observed (+) and calculated (solid line) powder diffraction pattern (corrected for the background) with the difference curve (bottom). The vertical dashes indicate the positions of reflections. I = intensity.

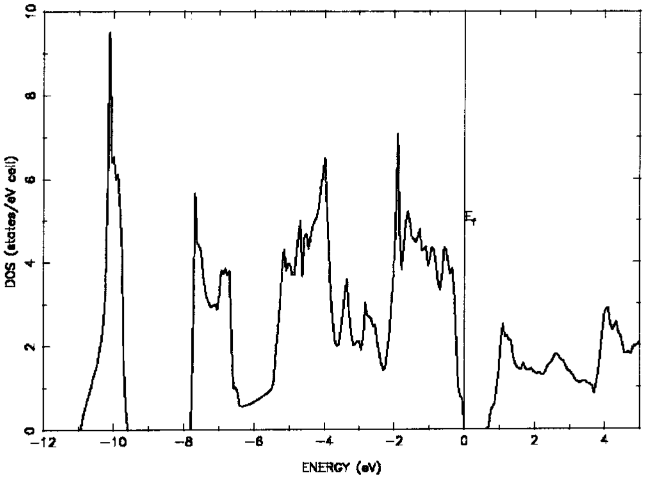

Figure 5. Total densities of states of CaB_2C_2 (energy zero set to the Fermi energy).

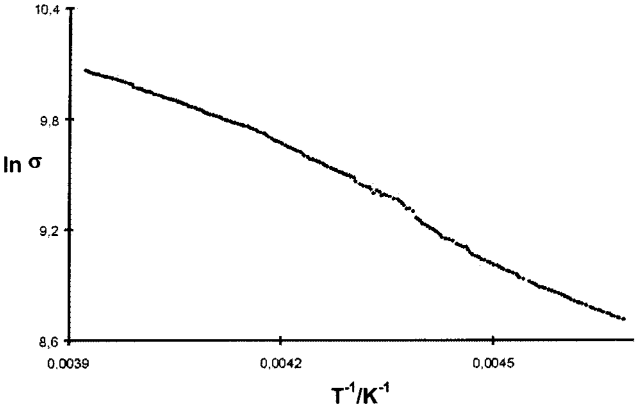

Figure 6. Logarithm of the electrical conductivity of CaB_2C_2 plotted vs reciprocal temperature. σ = specific conductivity, and T = temperature.

Finally, we proved the correctness of our structure model by a long-time data collection for a small range of the powder pattern. By simulating theoretical powder patterns for the four structure models under discussion, we showed that our new atomic arrangement should manifest itself by a very small reflection at about 39° 2θ, which does not appear in one of the traces calculated for former models. This is shown in the upper part of Figure 7. We were able to detect the 211 reflection at

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[22] Wörle, M.; Nesper, R.; Mair, G.; Schwarz, M.; von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1153−1159.

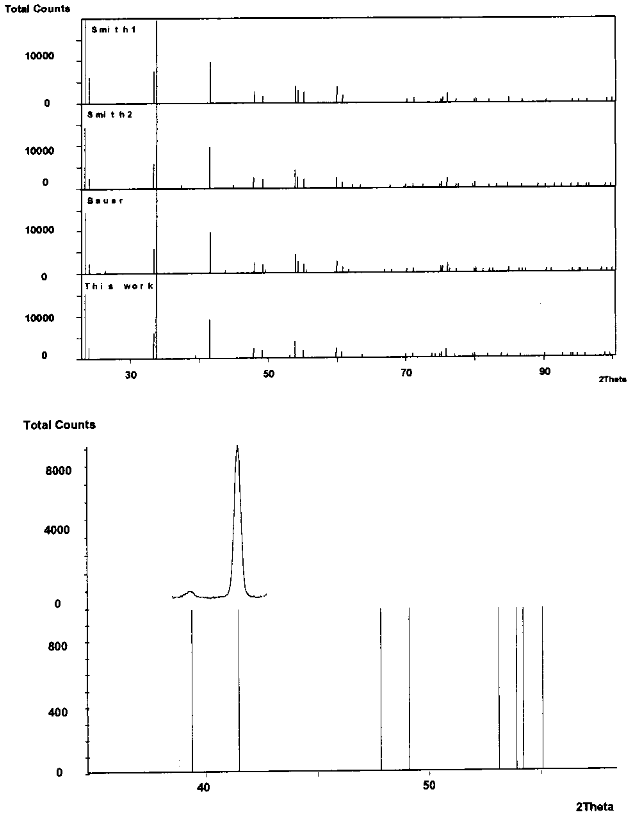

Figure 7. Comparison of the simulated reflection patterns for three structural models for the LaB$_2$C$_2$ structure type and the crystal structure of CaB$_2$C$_2$ (above) and recording of the superstructure reflection (bottom).

39.3° 2θ, which would not occur at this position if one of the former MB$_2$C$_2$ structural models were applicable for CaB$_2$C$_2$ (Figure 7).

The total energy values for the two structure models from the literature that allow B/C ordering[4,18] and our model were obtained from LMTO calculations. A comparison of these values allows one to evaluate the stability of the different atomic arrangements due to their different electronic structures. In fact, the least stable structure model appears to be the model allowing homoatomic interactions, followed by the model with B/C alternation within but not between the sheets (ΔE is about 7 eV). Our structure is slightly more stable than the latter (ΔE is about 1 eV).

The structure of CaB$_2$C$_2$ has been observed to resemble to the structure of CaB$_6$.[23] Topological similarities between crystal structures can be expressed by group−subgroup relations between their space groups. A graphical representation of these relations helps to understand the hierarchical ordering of crystal structures which is a main goal in crystal chemistry. A well-established method to visualize the group−subgroup relations and the necessary information of the respective crystallographic steps (“Bärnighausen family tree”) is shown in Figure 8 for CaB$_6$ → CaB$_2$C$_2$.[24] It demonstrates the close crystallographic relationship between the two structures. First, the cubic symmetry of the hexaboride has to be lowered by removing two of the octahedral corners from opposite sides of the octahedra. This transition is of the lattice-equivalent type (“translationengleich”),[25] index 3 (t3 from $Pm\bar{3}m$ to $P4/mmm$). Second, by introduction of the B/C ordering scheme, a class-equivalent (“klassengleich”) transition of index 2 is made (k2 to $I4/mcm$). In Figure 8, the symmetry changes are shown and the cell transformations and the relevant Wyckhoff positions are listed.

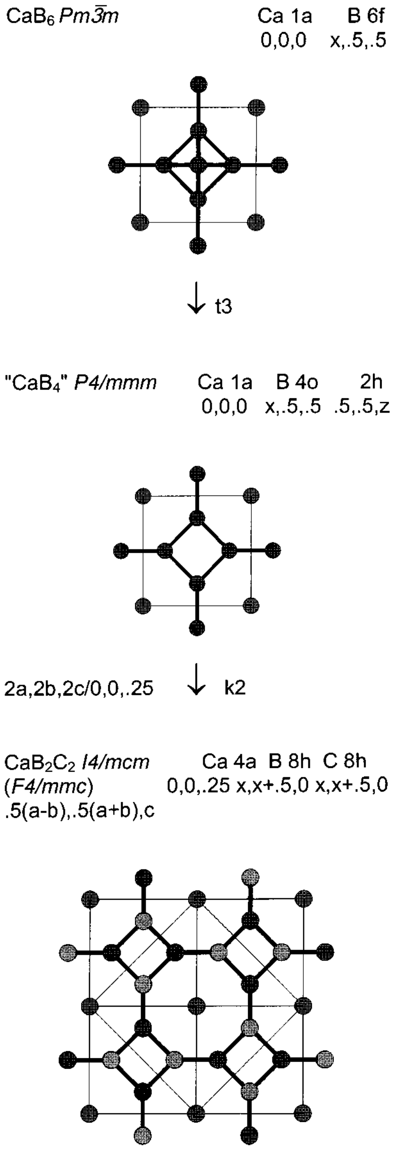

Figure 8. Bärnighausen family tree, demonstrating group−subgroup relations between the CaB$_6$ structure and the CaB$_2$C$_2$ structure.

Conclusion

A new structure model for CaB$_2$C$_2$ has been developed on the basis of a B/C ordering scheme previously suggested by theoretical considerations. The Rietveld refinement of the crystal structure using highly resolved X-ray powder data proved to be stable and led to reasonable atomic distances within the B/C net.

Therefore, we consider our structure determination the most appropriate to define the atomic arrangement in CaB$_2$C$_2$. Band structure calculations on the basis of the new structure data confirm the electronic stability of this model. They indicate semiconducting behavior which is consistent with our measurements. Considering the new experimental evidence on CaB$_2$C$_2$

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(23) von Stackelberg, M.; Neumann, F. *Z. Phys. Chem.* **1932**, *B19*, 314−320.

(24) Bärnighausen, H. *Match, Communications Mathematical Chemistry* **1980**, *9*, 139−175.

(25) *International Tables for Crystallography*; Hahn, T., Ed.; Kluwer: Dordrecht, The Netherlands, 1996; Vol. A.

which we have presented here, a final reinvestigation of the crystal structures of the other members of the MB_2C_2 structure family might be advisable.

Acknowledgment. We thank Prof. Dr. J. Beck for his support, Dipl.-Chem. K. Hofmann for performing the EELS experiment, and Dipl.-Chem. A. Dülmer for his help. This work was supported by the Fonds der Chemischen Industrie and the BMBF under the program “Neue Materialien” and the Deutsche Forschungsgemeinschaft.

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