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Beryllium Boride Carbide

The η^6,η^1-Coordination of Beryllium Atoms in the Graphite Analogue BeB_2C_2**

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Dedicated to Dr. Joseph Bauer on the occasion of his 65th birthday

The coordination of beryllium ions in homoleptic beryllocene, $[Be(C_5H_5)_2]$, has for decades been the subject of debate and theoretical as well as experimental investigations. It was not until quite recently that Schurko and co-workers[1] were able to show beyond doubt that Be is present in $[Be(C_5H_5)_2]$ in the η^5,η^1-coordination mode, which is consistent with the octet rule for Be. We have now found an analogous disposition for Be in a solid-state compound, namely BeB_2C_2, in which six-membered rings of boron/carbon (B/C) layers coordinate to beryllium atoms in a η^6,η^1 fashion.

BeB_2C_2 is the first boride carbide with slipped 6^3 B/C layers as in graphite. Initially, we were unable to determine its structure with diffraction methods; we thus solved the structure by means of electron energy loss spectroscopy (EELS)—whereby a combination of theoretical and experimental methods was indispensable for the analysis of the energy loss near-edge structure (ELNES)—and further refinement was achieved by X-ray powder diffractometry.

This beryllium diboride dicarbide is one of two compounds that were described in the Be–B–C system about forty years ago.[2] But although this substance was accessible as a single crystal (and its diffraction diagram was indexed in the Laue class 6/*mmm*, $a = 1082$ pm, $c = 618$ pm), its structure had not been resolved before now. Indications from EELS[3] that BeB_2C_2 is isostructural to LiBC could not be confirmed from X-ray powder diffractometry. LiBC and MgB_2C_2 crystallize in layer structures in which the boron and carbon atoms form covalent, two-dimensional, planar (in analogy to the hexagonal boron nitride) or slightly corrugated networks of condensed six-membered rings.[4,5] Similar structures are interesting in the context of the discussion of high-temperature superconductors,[6] since they are topologically closely related to MgB_2.[7]

We were recently able to show that it is possible to distinguish between several possible structural models for MB_2C_2 compounds (M = Ca, La) by comparing the experimental fine-edge structures of the B_K ionization edges with those obtained by DFT calculations.[8] This result was later confirmed by independent DFT calculations.[9] The fine-edge structure of the B_K edge in borides and boride carbides is highly variable with respect to weak structural and electronic influences.[10]

The work described herein derives an otherwise inaccessible, coherent structural model for BeB_2C_2 by calculating the energy loss near-edge structures (obtained with the WIEN2k software)[11] for a number of atomic distributions. The structure was then refined on the basis of X-ray powder diffractograms and confirmed by theoretical quantum calculations.

We were able to obtain BeB_2C_2 in the form of a crystalline powder at a temperature of 1950 °C. With EELS, the Be/B/C ratios were established to be 1:2:2. The diffractograms, which were obtained by high-resolution Guinier diffractometry and $Cu_{K\alpha 1}$ irradiation (flat specimen, transmission) as well as on the synchrotron (Hasylab, DESY, $\lambda = 113.96101$ pm, Ge(111) double monochromator, Ge(111) analyzer, capillaries, Debye–Scherrer geometry), did not permit us to find a solution for the structure.[12] Although it was possible to index the diffractograms for the first time in an orthorhombic crystal system similarly to those of magnesium diboride dicarbide (space group no. 64, *Cmce*, $a = 1083.7$, $b = 939.6$, $c = 613.6$ pm; compare MgB_2C_2: $a = 1092.2$, $b = 946.1$, $c = 745.9$ pm), the distortions of the network obtained by Rietveld refinement of the analogous structural model did not make sense, and the difference Fourier maps for the structure model without cations showed no atomic positions for the beryllium atoms.

The measured B_K ionization edges of the compounds LiBC, MgB_2C_2, and BeB_2C_2 are very similar to one another (Figure 1). If one calculates the B_K fine-edge structures of LiBC and MgB_2C_2 on the basis of structures described in the literature and then compares these with the experimental ELNES, the agreement is very convincing (Figure 2a,b). On the other hand, the structural models of LiBC and MgB_2C_2 do not allow a correct simulation of the experimental B_K ELNES of BeB_2C_2 (Figure 2c). As soon as the B/C layers are slipped with respect to each other, however, to make a B/C arrangement analogous to that of graphite, the agreement becomes striking between the ELNES calculated on the basis of this structural model and the experimental one. This is true for the B_K as well as for the C_K ionization edges (Figure 3a,b). One

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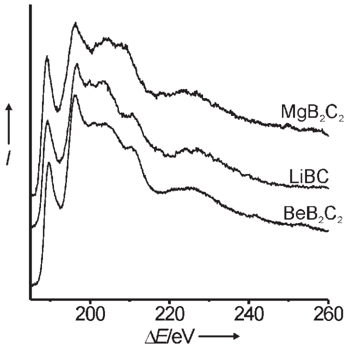

Figure 1. B_K ionization edges for BeB_2C_2 (bottom), LiBC (middle), and MgB_2C_2 (top).

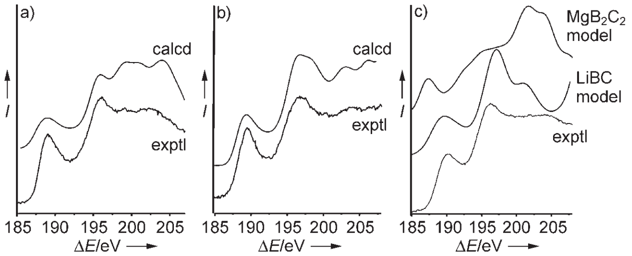

Figure 2. Experimental (bottom) and calculated (top) B_K ELNES for LiBC (a), MgB_2C_2 (b), and BeB_2C_2 (c), calculated using known structure models.

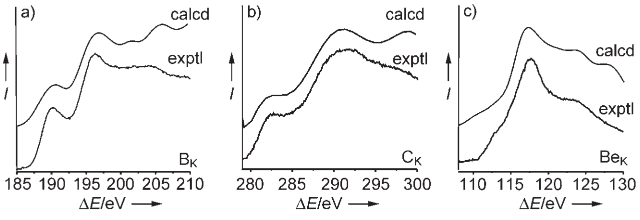

Figure 3. Experimental (bottom) and calculated (top) B_K (a), C_K (b), and Be_K (c) ELNES for BeB_2C_2.

carbon atom of the first layer has to be located above or below the center of a six-membered ring of the second layer, leading to a structure with the space group *Pmmn* ($a = 613.425(5)$ pm, $b = 542.20(3)$ pm, $c = 469.28(3)$ pm), with B and C on one fourfold and two twofold positions each. This structural model is amenable to refinement by the Rietveld method on the basis of synchrotron data (GSAS software[12b]), and the analysis of the difference Fourier maps shows electron density on a *4f* site which corresponds to the position of the beryllium atoms. The complete structure model allows a calculation even of the Be_K ionization edge, which matches the experimental edge quite well (Figure 3c). All positional coordinates and common displacement parameters for each of the elements can be freely refined and lead to a good adjustment of the experimental diffraction data (Figure 4).[13] The B/C layers are planar, as shown in Figure 5. The B–C distances are between 154.4(3) and 159.4(3) pm and can thus be compared to B–C distances in other compounds with B/C layers, for example, CaB_2C_2.[14] The Be ions are η^6-coordinated on one side by three B and three C atoms of one layer, and bound to only one C atom on the other side with a Be–C distance of 181.1(1) pm (Figure 5), which is significantly shorter than the three other Be–C distances (196.3(2)–197.5(2) pm) and the three Be–B distances (201.8(2)–206.8(2) pm). This η^1-coordination mode may be described as a σ Be–C bond, similarly to that described for $[Be(\eta^1\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)]$.[15]

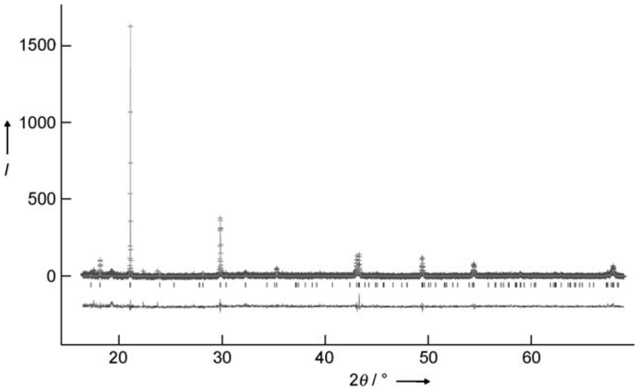

Figure 4. Observed (+) and calculated (solid line) powder pattern for BeB_2C_2 with the difference curve (bottom). The vertical dashes indicate the positions of the reflections. I = intensity.

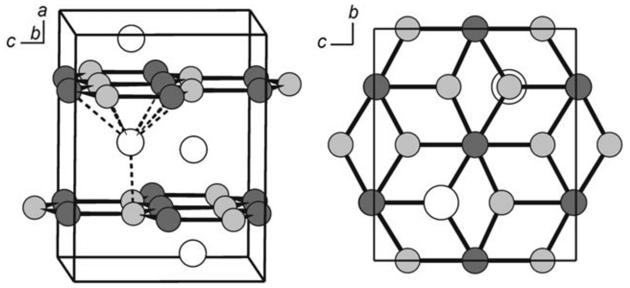

Figure 5. Projection of the unit cell along the crystallographic *b* axis (left) and along the crystallographic *a* axis (right). Be white, B dark gray, C light gray.

Comparative DFT calculations[16] for the geometry-optimized structure models in *Pmmn* (this work) and *Cmce* (MgB_2C_2-like) show, as mentioned above, an energy preference for the former (514 meV per formula unit). Indeed, full geometric optimizations of the two arrangements with no symmetry imposed indicate that the structure with initial *Cmce* symmetry strongly distorts towards a more stable arrangement (of $P2_1/c$ symmetry) in which the atomic connectivity of the Be atoms is reduced and comparable to that observed in the structure with *Pmmn* symmetry. Calculations on a structure with initial *Pmmn* symmetry, however, lead to hardly any modification of the geometry. This result shows unambiguously that the η^6,η^1-coordination mode of Be is strongly energetically favored over the η^6,η^6 mode in BeB_2C_2. With a computed band gap of about 1 eV, BeB_2C_2 is expected to be an electrical semiconductor.

The density of states (DOS) of BeB_2C_2 is compared for both space groups, *Pmmn* and *Cmce*, in Figure 6. The stability of the *Pmmn* structure is directly related to the nature and the number of the states at the Fermi level (ε_F). Examination of the projected DOS indicates that the participation of beryllium is weaker around ε_F for the slipped-sandwich η^6,η^1 arrangement than for the symmetrical-sandwich η^6,η^6 arrangement. In other words, just the existence of a band

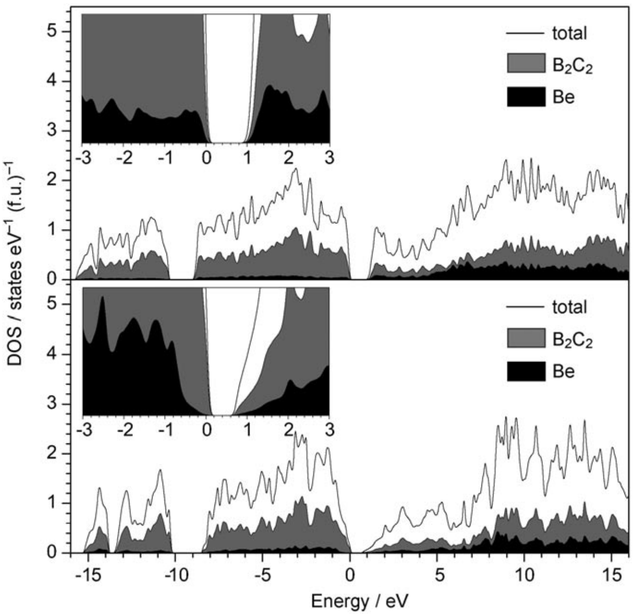

Figure 6. Total and projected densities of states of BeB_2C_2 with *Cmce* (top) and *Pmmn* (bottom) symmetry. The Fermi-level region is enlarged in the inset. f.u. = formula unit.

gap does not explain the higher stability of the *Pmmn* model for BeB_2C_2 with respect to the *Cmce* model. Both structures exhibit a band gap at ε_F, consistent with the "Zintl formula" $[Be^{2+}(B_2C_2)^{2-}]$. The *Pmmn* structure gains additional stability from the η^1 Be–C bonding interactions, which strengthen the covalent character of the compound, and from the lower steric repulsion between the B/C layers, as in beryllocene.[15] Stronger covalent interactions between Be and the B/C layers lead to some destabilization in energy of the Be–B/C antibonding states and some stabilization of the bonding states, thus diminishing the DOS around ε_F.

This is thus the first solution of a crystal structure by the unusual combination of the two methods "theory-supported ELNES" and "high-resolution powder diffractometry". The stability of the crystal structure determined in this way is supported by theoretical calculations. The structural chemistry of BeB_2C_2 is the first of a compound in the Be–B–C system to be determined, which also reveals a fascinating analogy between the molecular and solid-state chemistry of beryllium.

Experimental Section

Caution: Beryllium and beryllium compounds are highly toxic and may act as human carcinogens. Handling of such substances should only be performed in consideration of the required safety precautions.

The samples were synthesized from the elements according to the desired stoichiometry Be/B/C = 1:2:2. The starting mixtures were prepared under argon in a glovebox, pressed into pellets, and heated for 1 h to 1950 °C in an induction furnace (BN crucible inside a graphite crucible).

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