Boron–Carbon Order in CeB_2C_2**

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Infinite, planar, π-conjugated systems are of interest for their electronic properties and intercalation chemistry. Graphite and BN both contain hexagonal networks of fused aromatic 6π-electron rings, with alternating B and N atoms in the latter case.[1] However, the isoelectronic BC^- sheets found in CaB_2C_2 and LnB_2C_2 (Ln = lanthanide, Y) were found to contain 4.8^2 nets of fused 4π and 8π rings stacked directly above one another with the cations between the eight-membered rings of successive layers.[2–5] This structure has a basic tetragonal cell with $a \approx 3.8$ and $c \approx 4$ Å (the interplanar spacing). The only nonisostructural analogue is ScB_2C_2, which contains a planar arrangement of five- and seven-membered rings.[6]

Two important structural features of the LnB_2C_2-type structures were uncertain. The first is whether the B and C atoms are a) paired or b) alternate within the eight-membered rings (Figure 1). The latter arrangement has an enlarged

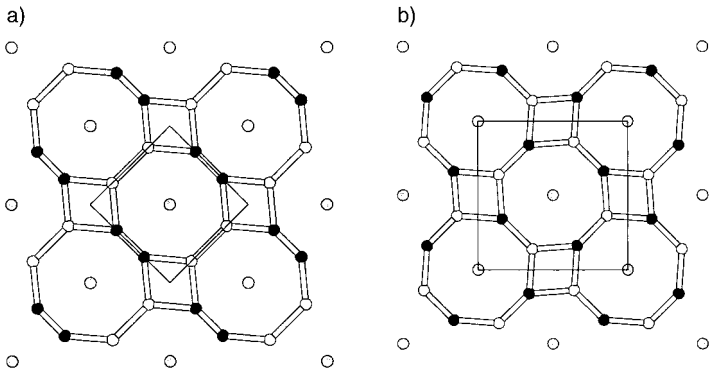

Figure 1. Alternative models for the BC^- planes in CeB_2C_2 with the unit cells (Ce: grey, B: white, C: black). Type (a) contains bonded B–B and C–C pairs, whereas only B–C bonds are present in type (b).

tetragonal cell with $a' \approx \sqrt{2}a$. The second uncertainty is whether the B/C atoms in successive layers are stacked directly or alternate in the z direction, which doubles the c-axis periodicity. Published single-crystal X-ray diffraction studies on YB_2C_2,[3] CaB_2C_2,[4] and LaB_2C_2[5] reported that the layers are of type (a) and alternate in the z direction to give an $a \times a \times 2c$ tetragonal cell. However, calculations of the BC^- layer band structure by Burdett et al.[7] using extended Hückel theory indicate that arrangement (b) should be more stable as it produces a large band gap of approximately 2.8 eV. The authors of this paper concluded that "a careful reexamination of the LnB_2C_2 structures is warranted".

As part of a study of the low-temperature electronic and magnetic properties of the LnB_2C_2 compounds, we performed a definitive structure determination on CeB_2C_2 using powder neutron diffraction. This is preferable even to single-crystal X-ray methods, as the X-ray diffraction is dominated by the heavy Ce atom and gives almost no contrast between B and C. The isotopes of natural boron, which consists of 20% ^{10}B and 80% ^{11}B, scatter neutrons quite differently. ^{10}B is strongly neutron absorbing and has a small coherent scattering length of $b \approx 0.4$ fm, whereas ^{11}B is nonabsorbing and has a scattering length (6.66 fm) almost equal to that of carbon (6.65 fm). We therefore carried out neutron diffraction experiments on two samples of polycrystalline CeB_2C_2. One contained natural boron ($b = 5.40$ fm) and provided good contrast between B and C at the expense of strong sample absorption, while the second sample was prepared with 99.1% ^{11}B to give good counting statistics although no B/C contrast is present. The sample preparation, diffraction experiments, and details of the refinement are described in the Experimental Section.

The powder neutron diffraction patterns of the two CeB_2C_2 samples show superstructure peaks (indicated by arrows in Figure 2a) that are all indexed on a tetragonal $\sqrt{2}a \times \sqrt{2}a \times c$ unit cell. No doubling of the c axis was observed. The

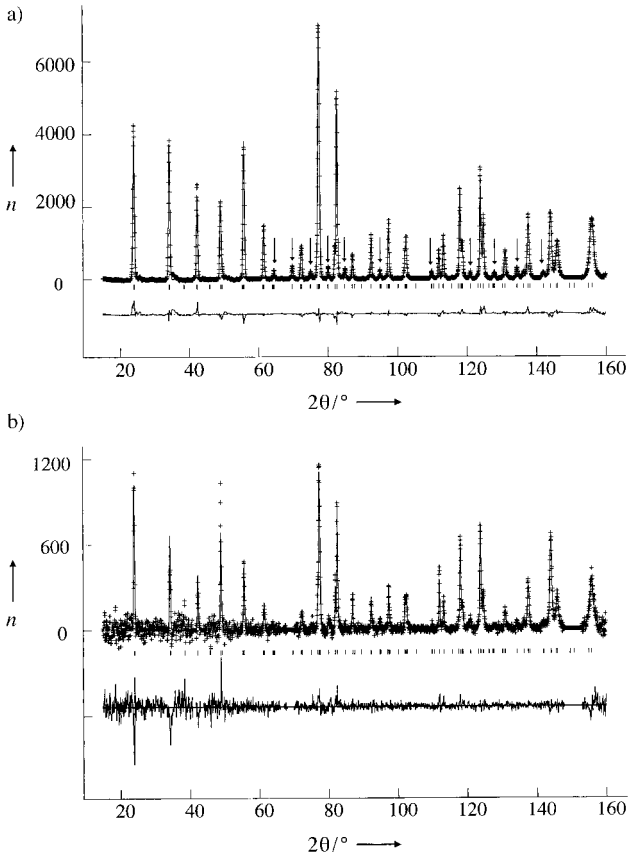

Figure 2. Observed, calculated, and difference neutron diffraction profiles for CeB_2C_2 samples containing 99% enriched ^{11}B (a) and natural boron (b). The backgrounds of approximately 240 counts in (a) and approximately 400 counts in (b) have been subtracted from the plots for ease of comparison. Peaks indicating the enlarged cell (Figure 1b) are indicated by arrows on profile (a).

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arrangement in Figure 1b is confirmed by the Rietveld fits to the two profiles; no significant scrambling of the B/C atoms was found when their site occupancies were refined. The refined coordinates and derived distances and angles are given in Table 1. Figure 1b shows the [001] projection of the

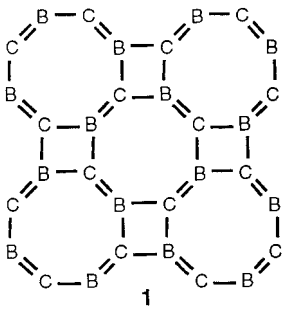
Table 1. Atomic parameters and bond lengths [Å] and angles [°] with multiplicities for the ^{11}B-enriched CeB_2C_2 sample at 15 K.

Atom	Site	x	y	z	U_{iso} [Å^2]
Ce	2(a)	0	0	0	0.0003(2)
B	4(h)	0.36107(9)	0.13894	0.5	0.0027(2)
C	4(h)	0.16060(8)	0.33940	0.5	0.0030(2)
Ce–B	×8	2.8402(2)	C-B-C	×2	130.86(2)
Ce–C	×8	2.7952(2)	C-B-C	×1	98.28(4)
B–C	×2	1.6220(6)	B-C-B	×2	139.14(2)
B–C	×1	1.5312(9)	B-C-B	×1	81.72(4)

The cell is tetragonal, space group $P4/mbm$, with $a = 5.39803(3)$ and $c = 3.84641(3)$ Å.

CeB_2C_2 structure. The information contained in both profiles contributed to the model. The superstructure intensities in the ^{11}B pattern reflect the difference between the pseudosymmetry-related light-atom coordinates (i.e., B:x and C:y) and enables their values to be determined precisely, while the contrast in the natural B pattern assigns the sites to B and C.

This neutron diffraction study demonstrates that the four- and eight-membered rings in the CeB_2C_2 structure consist of alternating B and C atoms, as predicted by Burdett et al.[7] Two types of B–C bonds are present: long bonds (1.62 Å) common to the four-and eight-membered rings, and short bonds (1.53 Å) unique to the eight-membered rings. The difference between these distances shows that the π bonding



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within the layers is predominantly as described by the idealized arrangement of single and double bonds in **1**. The layers essentially consist of fused cyclobutane- and cyclooctatetraene-like rings in which the bond angles are significantly distorted from the ideal values of 90 and 135°. As a result, the Ce atoms located above the centers of the eight-membered rings have slightly shorter contacts to C (2.80 Å) than to B (2.84 Å) in keeping with the greater electronegativity of carbon. These distances are comparable to the mean Ce–C distance of 2.74 Å in the $[Ce(C_8H_8)]^-$ anion.[8] The Ce atoms are packed in an almost perfect simple cubic array; the Ce–Ce distances of 3.82 Å in the *ab* plane and 3.85 Å parallel to *c* are longer than those of 3.64 Å in cubic close-packed Ce metal but still enable metallic Ce–Ce bonding to occur (see below).

A surprising feature of the CeB_2C_2 structure is that the B/C atoms in successive layers are stacked directly above each other. An alternating arrangement along *c* would be expected from electrostatic principles and is observed in BN.[1] The coordination of the layers to the Ce atoms may favor the direct stacking structure through hybridization of the BC^- π and Ce d electron states.

The large band gap calculated for the observed arrangement (b) of the BC^- layers prevents more than two electrons being donated from each cerium atom to the borocarbide layer. The charge distribution is thus described as $Ce^{3+}B_2C_2^{2-}e^-$ with the surplus electron in the Ce metal d band. This is supported by the high metallic conductivity of CeB_2C_2; the resistivity (measured in the [110] direction on a single crystal by the conventional four-probe dc method) falls from 48 mΩ cm at 300 K to 2 mΩ cm at 4 K. Further evidence for metal–metal interactions comes from our magnetic neutron diffraction studies on other LnB_2C_2 compounds. The Ln = Tb–Tm phases display both commensurate and sinusoidally modulated incommensurate magnetic structures at low temperatures, characteristic of RKKY interactions between localised $4f^n$ configurations mediated by the conduction electrons. Full details of these magnetic structures will be published elsewhere.

Experimental Sction

Polycrystalline samples of CeB_2C_2 were prepared by arc-melting 3-g pellets of the powdered elements (99.9% Ce, submicron 99.999% graphite, <2 μm 96% amorphous boron) on a water-cooled copper hearth in an argon atmosphere. The samples were remelted several times to improve homogeneity. Powder neutron diffraction patterns were collected on instrument D2b at the ILL, Grenoble. The samples were placed in a vanadium can (diameter 10 mm) within a He cryostat. The profile was recorded in the range $2\theta = 0–160°$ with a neutron wavelength of 1.5943 Å. Data were collected from the natural-boron sample at 4 K for 5 h and from the ^{11}B sample at 15 K for 6 h. An absorption correction was applied to the data from the natural-boron sample. Rietveld analysis[9] with the GSAS package[10] enabled both profiles to be fitted simultaneously with a single set of atomic positions. Small regions of the natural-boron profile were excluded due to the presence of an unidentified second phase, and because of scattering from the cryostat, the region between $2\theta = 148$ and 153° was excluded for both samples. The final model gave $R_{wp} = 8.1$, $R_p = 6.5$, $R_{F^2} = 13.7\%$ for the natural-boron sample, $R_{wp} = 7.1\%$, $R_p = 5.3\%$, $R_{F^2} = 6.4\%$ for the ^{11}B sample, and an overall $\chi^2 = 9.6$.

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[1] R. S. Pease, *Acta Crystallogr.* **1952**, *5*, 356.
[2] a) P. K. Smith, P. W. Gilles, *J. Inorg. Nucl. Chem.* **1967**, *29*, 375–382; b) N. A. Fishel, H. A. Eick, *J. Inorg. Nucl. Chem.* **1969**, *31*, 891–893; c) J. Bauer, J. Debuìgne, *C. R. Acad. Sci. Ser. C* **1972**, *274*, 1271–1275; d) E. T. Bezruk, L. Ya. Markovskii, *Zh. Prikl. Khim. Moscow* **1972**, *45*, 3–6; e) P. K. Smith, PhD thesis, University of Kansas (USA), **1964**.
[3] J. Bauer, H. Nowotny, *Monatsh. Chem.* **1971**, *102*, 1129–1145.
[4] T. Bréant, D. Pensec, J. Bauer, J. Debuigne, *C. R. Acad. Sci. Ser. C* **1978**, *287*, 261–264.
[5] J. Bauer, O. Bars, *Acta Crystallogr. Sect. B* **1980**, *36*, 1540–1544.
[6] G. S. Smith, Q. Johnson, P. C. Nordine, *Acta Crystallogr.* **1965**, *19*, 668.
[7] J. K. Burdett, E. Canadell, T. Hughbanks, *J. Am. Chem. Soc.* **1986**, *108*, 3971–3976.
[8] K. O. Hodgson, K. N. Raymond, *Inorg. Chem.* **1972**, *11*, 3030.
[9] H. M. Rietveld, *J. Appl. Crystallogr.* **1969**, *2*, 65–71.
[10] A. C. Larson, R. B. Von Dreele, *Los Alamos Laboratory Rep. No.* La-UR-86-748, **1987**.

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