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Crystal Structure Refinement and Bonding Patterns of CrB_4: A Boron-Rich Boride with a Framework of Tetrahedrally Coordinated B Atoms

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S *Supporting Information*

ABSTRACT: Crystals of chromium tetraboride, a recently proposed candidate superhard material, have been grown for the first time to allow for a first structure refinement of the compound [orthorhombic, space group *Immm* (No. 71), $a = 474.82(8)$ pm, $b = 548.56(8)$ pm, and $c = 287.17(4)$ pm, *R* value (all data) = 0.018]. The previously proposed structure model is confirmed, and accurate interatomic distances are presented for the first time. First-principles electronic structure calculations emphasize the unique framework of three-dimensionally linked B atoms that are tetrahedrally coordinated and carry a slightly negative charge. All B−B bonding is of the 2-center 2-electron type. CrB_4 is metallic with a pseudogap at the Fermi level.

Chromium tetraboride, CrB_4, was discovered in 1968, and on the basis of powder data of a mixture of several chromium boride phases, a structure was proposed that consists of three-dimensionally interconnected BB_4 tetrahedra.[1] Not much later, almost the same structure model was suggested for the manganese analogue, MnB_4, based on diffraction data of similar quality.[2] Although the title compound has raised interest of theoreticians as an analogue to the hypothetical tetragonal carbon net[3] (tetragonal diamond) and has been described recently as a potentially superhard material with exceptionally high computed shear moduli,[4] the synthesis of CrB_4 and MnB_4 was never successfully repeated. Samples of sufficient quality for crystallographic examination or property measurement have so far not been obtained. Malychev et al. reported a high-temperature (900 °C) electrochemical synthesis of CrB_4, but no further details of these samples have been made available.[5−8] Some of the phase diagrams of the Cr−B system report a CrB_4 phase to be stable up to 1500 °C.[9,10] The structure of these tetraborides is highly unusual because it does not consist of electron-deficient polyhedra with multicenter bonding that is typical for boron-rich compounds with three-dimensional B atom frameworks.[11−13]

We have grown single crystals of the title compound from the elements chromium (260 mg, Chempur, 99.9%) and boron (216.2 mg, H. C. Starck, 98−99%). A cold-pressed pellet was placed in a silica ampule with 190 mg of iodine as a mineralizer. The ampule was heated to 1027 °C for 14 days and then quenched to room temperature. Single crystals and crystalline powders of CrB_4 proved to be the main product (close to 90% from Rietveld refinement), with about 10% CrB_2 as a second product. Gray-metallic crystals of the title compound (Supporting Information, Figure s1) were mounted on a diffractometer (Fa. Stoe, Darmstadt, IPDS2). The data set was indexed in the orthorhombic crystal system, and the structure determination was performed in space group *Immm*. Results of the structure investigation are given in Tables 1 and 2. The X-ray powder diffractogram displaying results of the two-phase Rietveld refinement is shown in the Supporting Information (Figure s2). The crystal structure is shown in Figure 1. The structure proposed earlier[1] is essentially correct, although interactomic distances are in some error.

The lattice parameters correspond well with those that were recently reported from first-principles calculations,[4] as well as the calculation reported in this work. B−B distances were refined to values between 171.1(8) pm and 184.9(6) pm.

Compared with the distances formerly discussed for CrB_4 (166 and 191 pm),[1,3] those are more realistic values for 2e2c bonds (single) bonds between B atoms. The resulting framework of corner- and edge-connected boron-centered tetrahedra of B atoms is unique in the field of boron-rich materials. As can be seen in Figure 1, the B atom framework consists of boatlike six-rings, corrugated eight-rings, and four-rings that are almost planar. Distorted hexagonal prisms are formed around the Cr atoms. Cr−B distances are 209.9(3) pm (4×) and 221.7(3) pm (8×). As shown in the highlighted part of Figure 1, the coordination of the metal atoms bears similarities to the layered structures of RuB_2 and OsB_2, in which the metal atoms also nestle into boatlike six-rings of B atoms.[14] Such an arrangement has been described as resulting in a particularly strong covalent bonding between metal and B atoms and taken to explain the (anisotropic) ultraincompressibility of OsB_2.[15] In CrB_4, the layers of conjugated six-rings are, of course, also linked in the third direction, thus resulting in a three-dimensional framework that could be described as a tetragonal diamond. The title compound can, therefore, indeed be expected to exhibit a hardness and incompressibility of higher isotropic character than that of osmium and ruthenium diboride.

To better understand the structure and bonding patterns in this important compound, we have carried out first-principles

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Table 1. Details on the Data Collection and Structure Refinement of CrB_4

structural formula	CrB_4
cryst syst, space group	orthorhombic, *Immm* (No. 71)
lattice parameters *a*, *b*, *c*/pm	474.82(8), 548.56(8), 287.17(4)
formula units	2
cell volume/10^{-6} pm^3	74.80(2)
calcd density/g cm^{-3}	4.229
temperature/°C	20(3)
radiation, wavelength/pm	Mo Kα, 710.73
θ range/deg	5.7 − 28.9
no. of unique reflns/param	71/11
μ/mm^{-1}, abs corrn	6.969, refdelf
cryst shape, size/mm^3, color	prism, 0.2 × 0.2 × 0.15, metallic
R (unique reflns)	0.0176
wR2 (unique reflns)	0.0447
GOF (unique reflns)	1.438
electron density min/max	−0.588/+0.365

Table 2. Positional and Displacement Parameters of CrB_4 and U_{iso} Values (pm^2), Defined as One Third of the Track of the Orthogonalized Tensor U_{ij}[a]

atom	Wyckoff site	*x*, *y*, *z*	U_{11}, U_{22}, U_{33}, U_{12}, U_{13}, U_{22}
Cr	2a	0, 0, 0	0.0039(5), 0.0037(6), 0.0045(6), 0, 0, 0
B	8n	0.1933(9), 0.3441(7), 0	0.035(2), 0.029(2), 0.007(2), 0.025(2), 0, 0

[a] Figures in brackets are standard deviations that refer to the last digit.

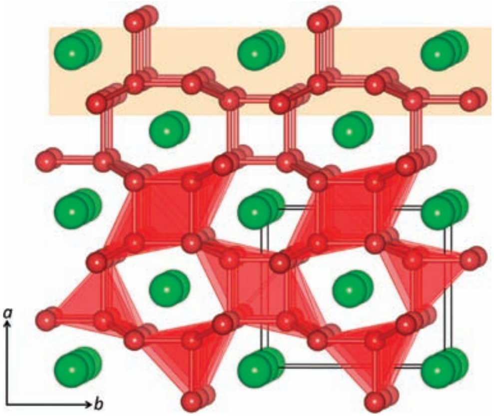

Figure 1. Crystal structure of CrB_4, showing B atoms as red, connected spheres, and Cr atoms as green spheres. A portion of the upper part of the figure is highlighted to accentuate a similarity with the OsB_2 structure.

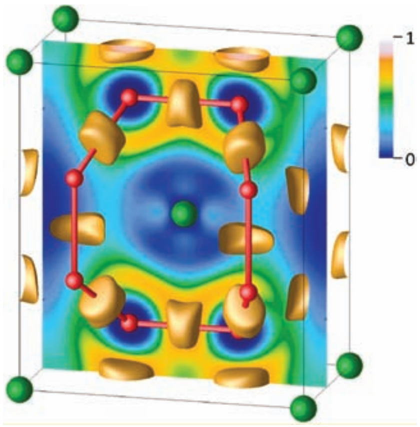

Figure 2. ELF for the valence electrons of CrB_4. Strongly covalent localization between B atoms points to the 2c2e bonding. An isosurface of ELF = 0.75 is displayed within a single unit cell. The ELF plane is projected halfway down the *c* axis of the unit cell and displays a complete absence of localization (covalent bonding) between Cr and B.

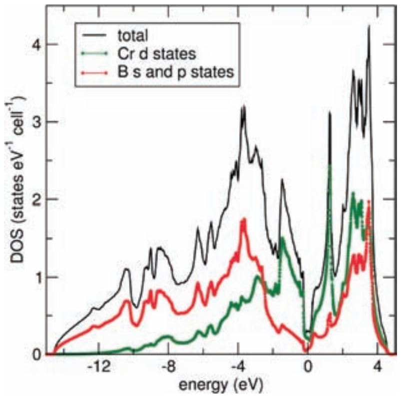

Figure 3. Total and projected DOSs for CrB_4 suggesting metallic behavior and displaying a pseudogap at the Fermi energy.

electronic structure calculations. Geometry optimization was performed using the Vienna ab initio simulation package (VASP)[16] within the generalized gradient approximation of Perdew, Burke, and Ernzerhof.[17] Interaction between the valence and core electrons was described using the projector augmented wave approach,[18,19] and the semicore 3p states of chromium were treated as valence states. The structure was optimized in the crystallographic (rather than primitive) cell using a 10 × 8 × 14 Monkhorst-Pack *k* mesh and a plane-wave energy cutoff of 500 eV. Relaxation was deemed to have converged when forces on all of the atoms were less than 0.01 eV $Å^{-1}$. The geometry-optimized crystal structure in space group *Immm* was as follows: a = 475.0 pm, b = 548.9 pm, and c = 285.3 pm. Cr is on a special position. The position of B optimized to (0.1954, 0.3423, 0). These optimized parameters agree very well with the experimental data reported here (Table 2). Atomic charges determined by the Bader method[20] with the aid of the Bader analysis program[21] suggested a charge close to +0.92 for Cr atoms and −0.23 for B atoms.

Further details of the bonding were obtained by calculating the electron localization function (ELF) within the linear muffin-tin orbital (LMTO) method, as implemented in the Stuttgart TB-LMTO-ASA program.[22] The ELF was employed to understand the localized bonding in the real space of the crystal structure.[23,24] The ELF, which is depicted in Figure 2, supports the picture of localized 2-center 2-electron (2c2e) bonds between the B atoms as opposed to the more delocalized situation that has been observed by experimental electron density analysis for electron-deficient boron clusters.[24−26] The Cr atom does not show a preferred interaction with its neighboring B atoms but might be considered to be octahedrally coordinated by the centers of maximum electron localization with the B atom framework.

LMTO densities of state (DOS) for CrB_4 are displayed in Figure 3 and are in agreement with the results of previous calculations,[4] as well as the VASP calculations performed here. The DOS suggest the presence of a pseudogap at the Fermi level, confirming the stable and metallic character of the compound.

In conclusion, a new synthetic procedure to obtain samples of CrB_4 has been developed. For the first time, it has been possible to obtain excellent structural data based on X-ray single-crystal and powder diffraction data and to refine the crystal structure. Electronic structure calculations confirm the unusual 2c2e tetrahedral network of the potentially superhard material. The availability of single crystals is encouraging from the viewpoint of being able to perform nanoindentation measurements that should help verify the predicted superhard behavior, and these are planned in the near future.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. X-ray crystallographic data in CIF format, photograph of a silica ampule, and a powder pattern. This material is available free of charge via the Internet at http://pubs.acs.org. Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany [fax (+49)7247-808-666; e-mail crysdata(at)fiz-karlsruhe.de; web site http://www.fiz-karlsruhe.de/request_for_deposited_data.html) upon quoting the CSD number 423380.

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