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Possible Superhardness of CrB_4

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Ⓢ *Supporting Information*

ABSTRACT: Chromium tetraboride [orthorhombic, space group *Pnnm* (No. 58), $a = 474.65(9)$ pm, $b = 548.0(1)$ pm, $c = 286.81(5)$ pm, and R value (all data) = 0.041], formerly described in space group *Immm*, was found not to be superhard, despite several theory-based prognoses. CrB_4 shows an almost temperature-independent paramagnetism, consistent with low-spin Cr^I in a metallic compound. Conductivity measurements confirm the metallic character.

Chromium boride coatings were reported to have excellent adhesive wear resistance because of their high hardness.[1] As described earlier,[2] chromium tetraboride (CrB_4) remained a sleeping beauty from 1968[3,4] until recently, when several groups recognized it as being interesting in terms of structure and properties. Although the title compound had raised the interest of theoreticians as an analogue to the hypothetical tetragonal carbon net[5] and as a potentially superhard material,[6] its experimental investigation was hampered by the inaccessibility of monophasic samples of CrB_4 until we obtained single crystals.[2] Recently, Niu et al. obtained crystalline, multiphase powder samples and used transmission electron microscopy to show that CrB_4 actually crystallizes in the orthorhombic space group *Pnnm*,[7] a space group closely related to the space group *Immm*, which was formerly used to describe the orthorhombic structure of CrB_4 (Figure 1). Niu et al. explained why the differentiation between the two space groups cannot be proven based on X-ray diffraction data, and they predicted the title compound's superhardness,[7] as does a very recent article by Gou et al.[8]

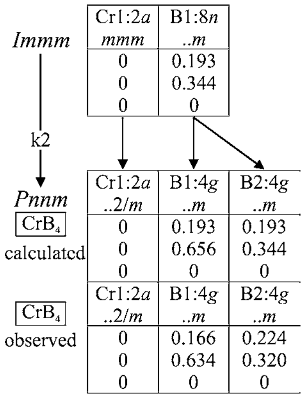

Figure 1. Group−subgroup relationship[12,13] between the two structural descriptions of CrB_4.

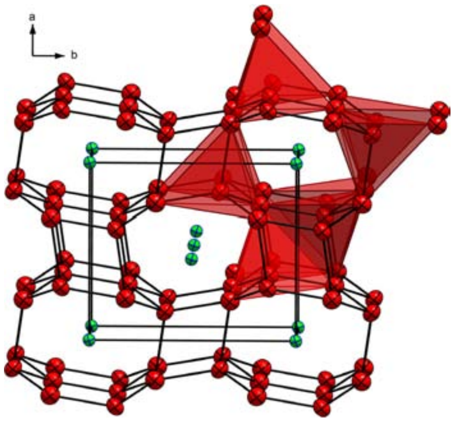

Figure 2. Crystal structure of CrB_4, showing boron atoms as red connected spheres and chromium atoms as green spheres (anisotropic ellipsoids of the displacement parameters are drawn at the 99% probability level).

We repeated the single-crystal structure refinement based on the orthorhombic space group suggested by Niu et al.,[7] and we were able to confirm its correctness. The intensities of superstructure reflections are almost 20 times weaker than the averaged intensity of all reflections. The relevant structural data were derived (Figure 2 and Tables 1 and 2). As stated before, the structure of CrB_4 is highly unusual because it does not consist of electron-deficient polyhedra with the multicenter bonding that is typical for boron-rich compounds with three-dimensional boron-atom frameworks.[9−11] The structure proposed earlier[2−4] is essentially correct, but the corner- and edge-sharing BB_4 tetrahedra that constitute the boron-atom framework are slightly more distorted than was previously believed. It should be noted that the *Immm* and *Pnnm* descriptions of CrB_4 do not correspond to two different phases.

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Table 1. Details on the Data Collection and Structure Refinement of CrB_4. Numbers in Bold from Density Functional Theory Calculations are from Density Functional Calculations

structural formula	CrB_4
cryst syst, space group	orthorhombic, *Pnnm* (No. 58)
lattice parameters *a*, *b*, *c*/pm	474.65(9), 548.0(1), 286.81(5)
	472.6, 547.4, 285.0
formula units	2
cell volume/10^{-6} pm^3	74.61(2)
calcd density/g cm^{-3}	4.240
temperature/K	293(2)
radiation, wavelength/pm	Mo Kα, 71.073
θ range/deg	5.7−34.4
no. unique reflns/param	187/18
μ/mm^{-1}, abs corr	6.987, numerical[a]
cryst shape, size/mm^3, color	needle, 0.30 × 0.18 × 0.10, metallic
R1 (unique reflns)	0.0411
wR2 (unique reflns)	0.0484
GOF (unique reflns)	0.955
electron density min/max	−0.651/0.698

[a] *X-AREA*, *X-RED*, and *X-SHAPE*; Stoe & Cie: Darmstadt, Germany, 2009.

Table 2. Positional and Displacement Parameters of CrB_4 (U_{ij} Values in pm^2)[a]

atom	Wyckoff site	*x*/*a*, *y*/*b*, *z*/*c*	U_{11}, U_{22}, U_{33}, U_{23}, U_{13}, U_{12}, U_{eq}
Cr	2a	0, 0, 0	18(3), 11(3), 11(3), −2(4), 0, 0, 13(2)
B1	4g	0.1661(8), 0.6344(7), 0	53(14),63(16), 20(15), 17(13), 0, 0, 45(8)
		0.1643, 0.6333, 0	
B2	4g	0.2240(8), 0.3204(7), 0	50(14), 51(14), 75(17), −18(13), 0, 0, 58(8)
		0.2236, 0.3209, 0	

[a] Figures in brackets are standard deviations that refer to the last digit. Numbers in bold are from density functional theory calculations.

Boron−boron distances were refined to values between 174.3(6) and 186.8(6) pm, and chromium−chromium distances amount to 286.81(5) pm. The small shift of the boron atoms that occurs when the lower symmetric space group is chosen does not influence the conclusions drawn earlier from theoretical calculations. Density functional theory calculations using the techniques described earlier[2] confirm that the compound is a metal. The computed cell parameters and atomic positions closely match those determined experimentally. The Bader charge is consistent with a formal oxidation state of I, which is also suggested by the nature of the density of states.

Because the chromium atoms are coordinated with two sets of boatlike six-rings of boron atoms similar to the metal-atom coordination in RuB_2 and OsB_2,[14] it seemed reasonable to expect high hardness and ultra-incompressibility for CrB_4, as was described for OsB_2.[15] Therefore, the Vickers hardness (H_V) of the CrB_4 crystals was measured using a LECO M-400 G2 microhardness tester (Figure 3). At least seven indentations were made at loads of 0.1 kg (0.98 N) and 0.2 kg (1.96 N) with a 15 s loading time. Only two indentations were made at 0.5 kg (4.9 N) load because of the limited sample surface. The obtained H_V values of 26.1 (±1.0), 24.8 (±0.4), and 23.3 (±0.7) GPa at 0.1, 0.2, and 0.5 kg, respectively, indicate high hardness but not superhardness of CrB_4.

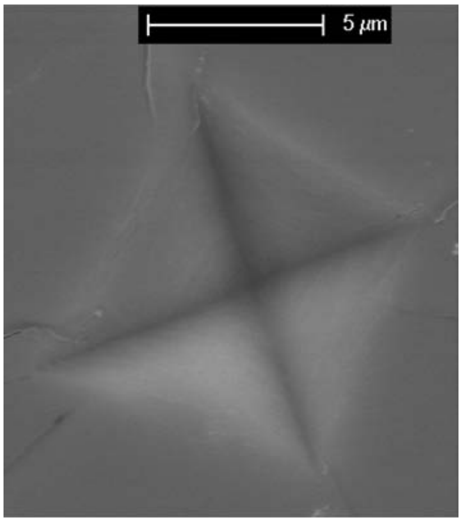

Figure 3. Scanning electron microscopy image of a typical Vickers indentation produced on a CrB_4 crystal by a 0.2 kg load.

Such values are slightly higher than those typical for chromium borides with other compositions (for example, values given in ref 16) but below the theoretically estimated values of 43−48 GPa.[6,7] This could reflect the general difficulty of estimating hardness from first-principles calculations. The measurements of H_V presented are orientation-averaged values of an agglomerate of single crystals. It is possible that other tests, e.g., nanoindentation, might result in higher values. The high values of elastic moduli predicted for CrB_4 are pending experimental verification.

CrB_4 shows an almost temperature-independent paramagnetism (4.56 mg sample of several single crystals; field of 50 Oe; Figure 4), consistent with the chromium oxidation state being close to low-spin d^5 in a metallic system. Small amounts of impurities are visible at low temperatures.

The electrical properties of CrB_4 were investigated on needle-shaped single crystals and on a compressed bulk powder

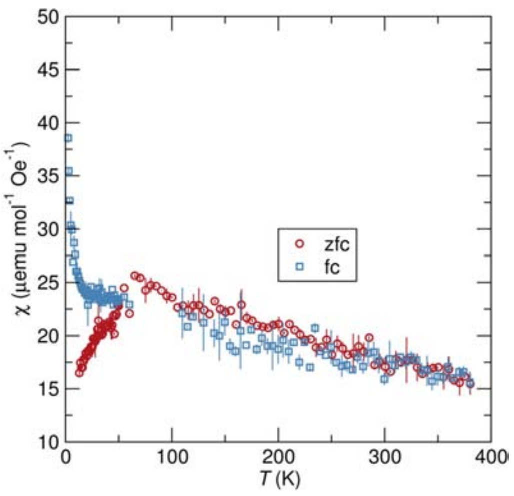

Figure 4. Magnetic measurement of CrB_4 displaying almost temperature-independent paramagnetism. The divergence in the zero-field-cooled and field-cooled traces at low temperatures is due to adventitious magnetic impurities.

by the four-probe method. CrB_4 turned out to be a conductor with metallic characteristics. In all measurements (see the Supporting Information), an increase of the resistivity with increasing temperature was observed. This is valid for a single crystal in the needle direction but also for the compressed powder. Here, texture effects bring the needle-shaped crystals into a preferred orientation parallel to the compressed disk, the direction in which the conductivity was determined. We conclude that the conduction characteristics are also metallic perpendicular to the needle axes. The specific conductivity is estimated to 5.2×10^{-6} Ω m, which is comparable to the conductivity of graphite.

In conclusion, CrB_4 is a hard, paramagnetic, and metallic conducting material with a very interesting boron-atom framework. These properties were measured for the first time. The structure of manganese tetraboride (MnB_4) is reported to show a structure very similar to that of CrB_4 and has also been described to be hard, rigid, and strong as well as difficult to synthesize. We will publish our findings on this compound soon.[17]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Conductivity measurements. Further details of the crystal structure investigation(s) may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany [fax (+49)7247-808-666; e-mail crysdata(at)fiz-karlsruhe.de, and url http://www.fiz-karlsruhe.de/request_for_deposited_data.html] upon quoting the CSD number 425106. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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