Superconductivity in the superhard boride WB_{4.2}

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Abstract
We show that the superhard boride WB_{4.2} is a superconductor with a \(T_c\) of 2.05(5) K. Temperature-dependent magnetic susceptibility, electrical resistivity, and specific heat measurements were used to characterize the superconducting transition. The Sommerfeld constant \(\gamma\) for WB_{4.2} is 2.07(3) mJ mol\(^{-1}\) K\(^{-2}\) and the \(\Delta C/\gamma T_c\) = 1.56, which is somewhat higher than what is expected for weakly coupled Bardeen–Cooper–Schrieffer type superconductors. The \(H_{c2}\) versus \(T\) plot is linear over a wide temperature range but does show signs of flattening by the lowest temperatures studied and therefore the zero temperature upper critical field (\(\mu_0H_{c2}(0)\)) for WB_{4.2} lies somewhere between the linear extrapolation of \(\mu_0H_{c2}(T)\) to 0 K and expectations based on the Werthamer–Helfand–Hohenberg model.

Keywords: superconductivity, superhard, tungsten deficient, boride

Introduction
High superconducting transition temperatures may be anticipated for borides due to boron’s light mass and strong B–B covalent bonding, which yields high vibrational frequencies. Superconductivity has been discovered in metal diborides like MgB\(_2\) (\(T_c = 39\) K [11]), (Mo\(_{68}\)Zr\(_{22}\)B\(_{38}\)) (\(T_c = 8.2\) K [2]), NbB\(_2\) (\(T_c = 52\) K [3]) and various other ternary borides [4–7]. Often the superconducting early transition metal ‘diborides’ are deficient in metal content, such as is seen in Nb_{0.70}B\(_2\), which is deficient in Nb [8–10]. The metal deficiencies can sometimes be described by the general formula \(T_{1-x}B_{2+3x}\) where every time a transition metal (\(T\)) is removed, 3 B atoms are added to the structure. Moreover, in these metal borides, boron atoms are likely to bond strongly with each other and form various molecule-like boron clusters, such as in the honeycomb lattice sheets of boron in MgB\(_2\).

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The strong B–B covalent bonding is not only attractive in superconducting materials but also in superhard materials, which have been extensively studied, especially for their practical use as cutting tools, abrasives, or wear-resistant coatings in various industrial applications [11–19]. Diamond and a variety of light-element compounds, although superhard materials, have practical and synthetic limitations for some applications [20–23] motivating the search for other types of superhard materials [24] like metal borides, which are an important class of superhard materials that can be easily applied as cutting tools, abrasives, or wear-resistant coatings in various industrial applications [11–19].
has been of particular interest because most other transition metals besides tungsten cannot tolerate higher boron contents and therefore exist as diborides [31, 32]. Most studies since the discovery of WB$_4.2$ [33] have found the crystal structure to have hexagonal symmetry, but there are a range of reported formulas such as WB$_4$ [32], WB$_{4.92}$ [34], W$_{1.3}$B$_3$ [35], or WB$_{4.2}$ [36]. The lattermost case is most consistent with our work.

Here we report the crystal structure and basic superconducting properties of the superhard boride WB$_{4.2}$. Our single crystal x-ray diffraction characterization shows, in agreement with earlier work, that WB$_{4.2}$ crystallizes in the space group $P6_3/mmc$ (No. 194) and has a crystal structure that is derived from the simple diborides but with a systematic W-deficiency-B$_3$ substitution—each missing W atom in the 2b position is replaced by three B atoms in the 6h position. Different experiments show sharp and reproducible superconducting transitions at about 2 K for WB$_{4.2}$. Temperature-dependent magnetic susceptibility, electrical resistivity and specific heat measurements were used to characterize the superconductor. WB$_{4.2}$ is a Bardeen–Cooper–Schrieffer (BCS)-type superconductor with an upper critical magnetic field, $H_{c2}(0)$, that is between that predicted by the standard WHH equation and the result of using a linear extrapolation of $H_{c2}(T)$ to zero temperature.

**Experimental**

The starting materials for the synthesis of polycrystalline WB$_{4.2}$ were boron (99.5%, chunk, Johnson Matthey Catalog Co.) and tungsten powder (>99.9%, Alfa). The tungsten powder was pressed into a pellet and arc-melted to have a metal chunk for the subsequent melting. The W and B chunks were weighed out in a 1:10 ratio and arc-melted three times in a Zr-gettered Ar atmosphere of ~600 mbar. The arc-melted buttons were flipped between each melting to ensure homogeneous samples. The resulting sample buttons had <1% mass loss and are stable in air over time. High quality samples of WB$_{4.2}$ are only obtained when a significant excess of B is employed, as has been previously reported [36]. The purity of all samples was checked at room temperature using a Bruker D8 Advance Eco Cu $K\alpha$ radiation ($\lambda = 1.5406$ Å) x-ray diffractometer equipped with a LynxEye-XE detector. Single crystals from arc-melted samples were mounted on the tips of Kapton loops and room-temperature intensity data were collected using a Bruker Apex II x-ray diffractometer with Mo $K\alpha_1$ radiation ($\lambda = 0.71073$ Å). All data were collected with 0.5° scans in $\omega$ over a full sphere of reciprocal space with 10 s per frame of exposure time. Data acquisition was carried out using the SMART software. The program VESTA was used to create all crystal structure images [37]. The SAIMT program was used to both extract and correct intensities for polarization and Lorentz effects. XPREP, which is based on face-indexed absorption, was used for numerical absorption corrections [38]. The unit cell was tested for twinning. The crystal structure was then solved using direct methods with the SHELXTL package and the refinement was carried out by full-matrix least squares on $F^2$ [39]. A Rietveld refinement of the room temperature powder x-ray diffraction (pXRD) data was performed using the FullProf Suite program with Thompson–Cox–Hastings pseudo-Voigt peak shapes and the lattice parameters from the single crystal refinement as a starting point.

A superconducting quantum interference device with a $^3$He attachment was used to measure the zero-field cooled (ZFC) temperature-dependent volume magnetic susceptibility from 0.5 to 2.2 K with $H = 20$ Oe as the applied magnetic field. The field-dependent magnetization was measured at 1.4, 1.0, and 0.5 K from 0 to 35 Oe. A physical property measurement system equipped with a resistivity option and $^3$He attachment was used to measure the temperature-dependent electrical resistivity from 300 to 0.5 K under zero applied magnetic field using a standard four probe method. The low

![Figure 1. Rietveld refinement of room temperature powder x-ray diffraction data for WB$_{4.2}$. The red circles are the observed data, the black line is the calculated fit, the dark green vertical bars are the expected Bragg reflections for WB$_{4.2}$, and the light green vertical bars are the expected Bragg reflections for SiO$_2$ (from the mortar and pestle). The asterisk indicates a small amount of boron impurity. Rietveld agreement factors: $\chi^2 = 3.28$; $wR_p = 14.0%$; $R_p = 14.4%$; $R(F^2) = 6.08%$.](image)

| Table 1. Single crystal crystallographic data for WB$_{4.2(1)}$ at 293 (2) K. |
|-----------------|----------------|
| Formula         | WB$_{4.2(1)}$  |
| F.W. (g mol$^{-1}$) | 229.33        |
| Space group     | $P6_3/mmc$ (No.194) |
| $a$ (Å)         | 5.191(6)      |
| $c$ (Å)         | 6.345(8)      |
| $V$ (Å$^3$)     | 148.0(4)      |
| Absorption correction | Numerical |
| Extinction coefficient | 0.014(2) |
| No. reflections; $R_{int}$ | 874; 0.0833 |
| No. independent reflections | 151 |
| No. parameters  | 15            |
| $R_1; wR_2$ ($I > 2\sigma(I)$) | 0.0327; 0.0573 |
| $R_1; wR_2$ (all $I$) | 0.0556; 0.0606 |
| Goodness of fit | 1.130         |
| Diffraction peak and hole (e$^{-}$ Å$^{-3}$) | 2.640; -3.284 |
temperature resistivity was measured under applied magnetic fields ranging from 0 to 600 mT in the temperature region from 0.5 to 2.2 K. The specific heat was measured on a small polished sample of polycrystalline WB4.2 using Apiezon N grease from 3.6 to 0.5 K under zero applied magnetic field.

**Results and discussion**

The crystal structure of WB4.2 was analyzed using single crystal x-ray diffraction, which showed that the superconductor crystallizes in the space group $P6_3/mmc$ (No. 194) with lattice parameters $a = 5.191(6)$ Å and $c = 6.345(8)$ Å, consistent with what has been previously reported [36]. Figure 1 shows a Rietveld refinement of the room temperature pXRD data for WB4.2 using the lattice parameters and the space group from the single crystal refinement as a starting point. It should be noted that there is some SiO2 in the pXRD pattern (indicated by the light green vertical bars in figure 1) that originates from parts of the agate mortar and pestle that intrude during grinding due to the superhardness of WB4.2. The lattice parameters and the W occupancy from both refinements are in good agreement with one another so only the single crystal refinement will be discussed here. The results from the single crystal refinement are shown in table 1 and the atomic coordinates from the same refinement are given in table 2 for WB4.2. The W2 atom position was freely refined, resulting in an occupancy of 0.665, and, consistent with the previous report, three B atoms were found in a triangular arrangement in place of the missing W2 atoms [36]. Figure 2 shows a comparison of the crystal structure of WB4.2 (right) and MgB2 (left). The boron atoms in MgB2 form a honeycomb network, similar to graphite, with the magnesium atoms between the upper and lower six-membered rings that form the hexagonal honeycomb layers. WB4.2 has a similar boron honeycomb with some of the holes between layers fully occupied by only W atoms while other holes can be occupied either by W2 or a B3 triangle. Although the occupancy of 0.665 for the W2 position is within error of a value of 2/3, which has the potential to result in a long range ordered structure, no evidence for W2 ordering is observed, consistent with previous reports [30]. The structure can be considered as either a highly defective or highly non-stoichiometric version of WB2. There is also no crystallographic evidence for a wide range in stoichiometry for this compound [36].

The temperature-dependent volume magnetic susceptibility ($\chi_V$) was measured to characterize the superconducting critical temperature of WB4.2. The ZFC $\chi_V$ versus $T$ (figure 3) shows the first clear deviation from the normal state susceptibility at approximately 2.0 K. The volume magnetization ($M_V$) was measured at 1.4, 1.0, and 0.5 K from 0 to 35 Oe as shown in the inset of figure 3. At low magnetic fields ($H < 15$ Oe) the $M_V$ data collected at 0.5 K was fitted with the linear formula $M(H) = -bH$, where $b$ is the slope of the fitted line. Assuming that the initial linear response to an applied magnetic field is perfectly diamagnetic ($dM/dH = -1/[4\pi(1 - N)]$), we obtained a demagnetization factor $N = 0.55$. The main panel of figure 3 shows the volume magnetic susceptibility in
the presence of a demagnetization effect ($N = 0.55$) and normalized by $4\pi$. The tiny departure of the strongest diamagnetic signal at the lowest temperatures from $-1$, which corresponds to perfect diamagnetism, is most likely due to mass error from working with such a small sample. A rough estimation of the lower critical field at 0.5 K (not corrected for demagnetization) is $H_{c1}(0.5 \text{ K}) = 10 \text{ Oe}.

The inset of figure 4 shows $C_p/T$ versus $T^2$, where the data were fitted above the critical temperature to the equation,

$$
\frac{C_p}{T} = \gamma + \beta T^2,
$$

where $\gamma T$ is the electronic contribution ($C_{el}$) to the specific heat and $\beta T^3$ is the phonon contribution ($C_{ph}$). The slope of the fitted line, $\beta$, is 0.021(1) mJ mol$^{-1}$ K$^{-4}$ and the Sommerfeld parameter, $\gamma$, is calculated to be 2.07(3) mJ mol$^{-1}$ K$^{-2}$. Using $\beta$, the Debye temperature ($\Theta_D$) is calculated to be 780(10) K using the equation

$$
\Theta_D = \left(\frac{12\pi^4}{5nR}\right)^{\frac{1}{3}},
$$

where $R$ is the ideal gas constant 8.314 J mol$^{-1}$ K$^{-1}$ and $n = 5.2$ for WB$_{4.2}$. The Debye temperature is high, which reflects a high concentration of boron in the material. With $\Theta_D$, $T_c$, and assuming $\mu^* = 0.13$, the inverted McMillan formula [41]

$$
\lambda_{ep} = \frac{1.04 + \mu^* \ln\left(\frac{\Theta_D}{1.45T_c}\right)}{(1 - 0.62\mu^*) \ln\left(\frac{\Theta_D}{1.45T_c}\right) - 1.04},
$$

can be used to calculate the electron–phonon coupling constant $\lambda_{ep}$ to be 0.43 for WB$_{4.2}$. The Fermi energy $N(E_F)$ is calculated with the formula

$$
N(E_F) = \frac{3\gamma}{\pi^2 k_B^2 (1 + \lambda_{ep})},
$$

to be 0.61 states eV$^{-1}$ per formula unit of WB$_{4.2}$ where $\gamma = 2.07(3)$ mJ mol$^{-1}$ K$^{-2}$, $\lambda_{ep} = 0.43$, and $k_B$ is the Boltzmann constant.

The main panel of figure 4 shows the electronic specific heat divided by temperature ($C_{el}/T$) versus temperature for WB$_{4.2}$ from 0.5 to 3.6 K with zero applied magnetic field showing a large peak in the specific heat. $C_{el}$ was obtained by subtracting the phonon contribution to the specific heat: $C_{el} = C_p - \beta T^3$. The $T_c$ is estimated to be 2.05 K for this data using an equal-area entropy construction (solid black lines), which is close to the critical temperature from the temperature-dependent magnetic susceptibility measurement. Such a large peak in the specific heat due to a significant loss of entropy is an explicit indication that the bulk material is superconducting. The normalized specific heat jump, $\Delta C/\gamma T_c$, is estimated as 1.56 for WB$_{4.2}$, which is near the weak coupling BCS limit of 1.43 [42] and confirms that WB$_{4.2}$ is a bulk superconductor.

Figure 5 shows $C_{el} - \gamma_0 T$ versus $T_c/T$ for WB$_{4.2}$ in the superconducting state under zero applied magnetic field and fitted to the following equation

$$
C_{el} = \gamma_0 T + a^* e^{-\frac{\Delta_0}{T}},
$$

where $\gamma_0 T$ is the electronic contribution to the specific heat originating from impurities in the sample, $\Delta_0$ is the superconducting gap magnitude, and $k_B$ is the Boltzmann constant. The $\Delta_0$ for WB$_{4.2}$ was calculated to be $\Delta_0 = 0.22$ meV and according to BCS theory [42], it is expected to be

$$
2\Delta_0 = 3.5 k_BT_c
$$

for a weak coupling superconductor. The calculated value of the superconducting gap $\Delta_0 = 0.22$ meV (2$\Delta_0 = 0.44$ meV) is less than the weak coupling BCS value of 2$\Delta_0 = 0.62$ meV. The discrepancy may indicate that multiband superconductivity may be present in this material.

Figure 6 shows the temperature-dependent electrical resistivity for WB$_{4.2}$ measured from 300 to 1.7 K. In the normal state, the resistivity changes slightly and the RRR ratio ($\rho_{300}/\rho_{22K}$) is only ~1.3, as is often observed for polycrystalline samples. The inset of figure 6 shows that the resistivity drops to 50% of the normal state value at ~2.1 K (black dotted line) and reaches zero above 2 K. The resistivity transition is sharp and only covers a 0.2 K temperature range. The $T_c$ values from the resistivity, specific heat, and magnetic susceptibility are in agreement.

The inset of figure 7 shows the dependence of the $T_c$ (black line) on the applied magnetic field for WB$_{4.2}$ in the

| Atom | Wyckoff | Occupancy | $x$ | $y$ | $z$ | $U_{eq}$ |
|------|---------|-----------|----|----|----|---------|
| W1   | 2c      | 1         | 2/3| 1/3| 1/4| 0.0029(3)|
| W2   | 2b      | 0.665(8)  | 0  | 0  | 1/4| 0.0038(4)|
| B1   | 12i     | 1         | 0  | 0  | 0  | 0.0005(2)|
| B2   | 6h      | 0.335*    | 0  | 0  | 0  | 0.0008(3)|

* The W2 position occupancy is freely refined, but the fractional occupancy of the B2 site is constrained such that the occupancy of B2 = 1 − occupancy of W2, as described in previous studies [36]. The positional parameters of B2 are freely refined.
temperature range from 0.5 to 2.2 K under applied magnetic fields ranging from 0 to 600 mT. The $T_c$ steadily decreases with increasing applied field, as expected, and the last instance where the resistivity drops to below 50% is for $T_c = 0.62$ K with $\mu_0 H = 500$ mT. The thus-determined upper critical fields ($\mu_0 H_{c2}$) plotted as a function of the estimated $T_c$ values were plotted in the main panel of figure 7 and fitted to a line with slope $d\mu_0 H_{c2}/dT = -0.33$ T K$^{-1}$. For many superconductors, the zero temperature upper critical field $\mu_0 H_{c2}(0)$ can be estimated with the Werthamer–Helfand–Hohenberg (WHH) [43] equation given by:

$$\mu_0 H_{c2}(0) = -A T_c \frac{d\mu_0 H_{c2}}{dT} \bigg|_{T=T_c},$$

where $A$ is $-0.693$ for the dirty limit and taking $T_c$ as $\sim 2.05$ K for WB$_{4.2}$. Based on this model, the $\mu_0 H_{c2}(0) = 0.47$ T (indicated by the blue closed circle in figure 7), however the last measured $\mu_0 H_{c2}$ value is $0.50$ T which is already above the WHH-predicted upper critical field of 0.47 T. The nearly linear $H_{c2}(T)$ over a broad temperature range that we observe has been seen previously for Fe based superconductors [44, 45] and also for Nb$_2$Pd$_{0.81}$S$_5$ [46] and claimed to originate from the multiband superconductivity effect. The resulting $\mu_0 H_{c2}(0)$ for WB$_{4.2}$ is therefore most likely somewhere between the linear extrapolation to 0 K (0.71 T) and that predicted by the WHH model (0.47 T). Taking $\mu_0 H_{c2}(0) = 0.71$ T as the upper limit, the approximate coherence length can be calculated by using the Ginzburg–Landau formula $\xi_{GL}(0) = \{\phi_0/[2\pi H_{c2}(0)]\}^{1/2}$, where $\phi_0 = h/2e$ and is found to be $\xi_{GL}(0) = 26$ nm. All physical parameters for WB$_{4.2}$ are gathered in table 3.
We report superconductivity in the superhard material WB₄.2 and confirm that this material crystallizes in the hexagonal space group P6₃/mmc using room-temperature single crystal x-ray diffraction data. This material is non-stoichiometric via W deficiency, where for every missing W atom, three B atoms are inserted into the structural cavity in its place. The superconducting transition occurs at about 2 K and is characterized through temperature-dependent magnetic susceptibility, electrical resistivity, and specific heat measurements. WB₄.2 is shown to be a BCS-type weak coupled superconductor based on the calculated superconducting parameters. The $\mu_0 H_{c2}(0)$ value is between the value predicted using the WHH model and that of a linear extrapolation of $\mu_0 H_{c2}(T)$ to 0 K. This material appears to be an example of a highly non-stoichiometric, metal deficient, early transition metal diboride superconductor.

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Table 3. Normal and superconducting state parameters for WB₄.2.

| Parameter | Unit   | Value  |
|-----------|--------|--------|
| $T_c$     | K      | 2.05(5) |
| $\mu_0 H_{c2}(0)$ | T | 0.71 |
| $\lambda_{sp}$ | — | 0.43 |
| $\Delta_{Gf}(0)$ | nm | 26 |
| $\gamma$ | mJ mol⁻¹ K⁻² | 2.07(3) |
| $\beta$ | mJ mol⁻¹ K⁻⁴ | 0.021(1) |
| $\Theta_D$ | K | 780(10) |
| $\Delta C / T_c$ | — | 1.56 |
| $\Delta \rho$ | meV | 0.22 |
| DOS(E_F) | states eV⁻¹ f.u.⁻¹ | 0.61 |

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Conclusions

The materials synthesis was supported by the Department of Energy, Division of Basic Energy Sciences, Grant DE-FG02-98ER45706, and the property characterization at Princeton was supported by the Gordon and Betty Moore Foundation EPiQS initiative, Grant GBMF-4412. The research at the Gdansk University of Technology was supported by the National Science Centre, Grant UMO—2016/22/M/STS/00435. The work in the Department of Chemistry at LSU was supported by the US Department of Energy under EPSCoR Grant No. DE-SC0012432 with additional support from the Louisiana Board of Regents. The authors declare that they have no competing interests.
