Conventional superconductivity properties of the ternary boron-nitride Nb$_2$BN

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Abstract
The superconducting bulk properties of ternary Nb$_2$BN are confirmed and described by means of magnetization, electronic transport and specific heat measurements. BCS conventional superconductivity is found with $T_c = 4.4$ K. Critical fields of $H_{c1}(0) = 93$ Oe and $H_{c2}(0) = 2082$ Oe are extrapolated by magnetic and resistivity measurements. The specific heat data reveal $\gamma = 6.3 \text{ mJ mol}^{-1} \text{ K}^{-2}$ and $\beta = 0.293 \text{ mJ mol}^{-1} \text{ K}^{-4}$, in good agreement with the BCS theory.

Keywords: superconductivity, BCS superconductivity, boron nitrides, BCS theory, conventional superconductors

(Some figures may appear in colour only in the online journal)

1. Introduction

Among the known ternary carbides, Mo$_2$BC deserves attention due its superconducting behaviour with a $T_c$ ranging from 5 to 7.5 K [1, 2]. Mo$_2$BC has an orthorhombic symmetry [3] (no. 63, space group cmcm) with $a = 3.086$, $b = 17.35$ and $c = 3.047$ Å. Figure 1 illustrates this structure, where distorted Mo$_6$ octahedron layers are separated from each other by zig-zag B chains which pass through the trigonal prisms of Mo atoms [4]. Carbon atoms are located at the centres of the Mo octahedrons [5, 6]. Several efforts [6–9] have been made to enhance the superconducting properties of this compound by inducing chemical pressure with transition elements such as M = Zr, Rh, Nb, Hf, Ta and W at the Mo sites. While the $T_c$ of Mo$_{2-x}$M$_x$BC decreased with increase of $x$ for all the alloys, only the Rh-containing alloy [9] showed an increase up to $T_c = 9$ K.

After the discovery of Mo$_2$BC, a boron-nitride with nominal Nb$_2$BN composition was synthesized for the first time [10] as a thermodynamically stable compound at 1200 °C. In this compound the Nb atoms are arranged in similar distorted octahedra and are separated by zig-zag B chains as in Mo$_2$BC and the N atoms occupy the same positions as the C atoms. The lattice parameters of Nb$_2$BN are quite similar to those of Mo$_2$BC, being $a = 3.17$, $b = 17.85$ and $c = 3.11$ Å. Superconductivity with critical temperature close to 2.2 K was reported in the Nb$_2$BN$_x$ ($x$ undetermined) compound. However, other properties such as specific heat or resistivity were not investigated by the authors in order
to confirm bulk superconductivity. In this context our results show unambiguously bulk superconductivity at 4.4 K in single phase polycrystalline samples of Nb$_2$BN.

2. Experimental details

Polycrystalline Nb$_2$BN samples were synthesized by the conventional powder solid state reaction method. High purity 300 mesh Nb (99.99) and hexagonal BN (99.999) were used. To ensure good quality of the primary reaction the BN was degassed at 1000 °C in vacuum for 24 h before its usage. Stoichiometric amounts (Nb 2:1 BN) of the reagents were weighed, mixed on an agatar mortar and pressed (4 tons) into pellets of cylindrical shape. The compressed mixture was sealed in quartz tubes under 1 bar argon atmosphere and heated at 1200 °C. After each seven days of annealing the samples were quenched, ground, pressed and encapsulated again to be treated at 1200 °C. A complete reaction was obtained only after 28 days of annealing.

X-ray diffraction patterns were collected with a PANalytical Empyrean x-ray diffractometer using CuK$_\alpha$ radiation. Rietveld refinements [11] were calculated using the Fullprof suite considering an error of $\chi^2 \leq 2$ as the minimum standard. Magnetic, electric and thermal initial characterizations were made using a Quantum Design PPMS Evercool II. Magnetization ($M$) measurements were obtained using a commercial VSM magnetometer (Quantum Design) in a DC external field of 50 Oe in zero-field-cooling (ZFC) and field-cooling (FC) conditions, in a temperature range ($T$) from 2 to 20 K. Magnetization ($M$) versus applied field ($H$) data were acquired at constant temperatures between 2 and 5 K. Electrical resistivity measurements were performed between 1.8 and 300 K using the conventional four-point method. Thin Cu wires were welded to a regular shaped sample and served as the voltage and current leads, using a high purity Ag epoxy. Applied magnetic fields were also used to estimate the upper critical field. The superconducting critical temperature ($T_c$) was defined as the transition midpoint. Heat capacity measurements were made using the relaxation method on a piece cut from the sample on a calorimetric probe coupled to the PPMS system in a temperature range from 2 to 10 K.

3. Results and discussion

Figure 2 shows the diffraction pattern of a typical Nb$_2$BN sample after 28 days of heat treatment. All reflections can be indexed with the orthorhombic Mo$_2$BC structure with space group $cmcm$ and without any trace of secondary phases within the limits of this technique. Rietveld refinements led to the following occupancies: Nb-1 atoms occupy the 4c (0, 0.721, 0.25), Nb-2 atoms occupy the 4c (0, 0.3139, 0), N atoms occupy the 4c (0, 0.192, 0) and B atoms the 4c (0, 0.4731, 0.25) positions. These results are in good agreement with those reported earlier [10]. The Nb-1 bonding distances are slightly different (2.22 and 3.01 Å) from the original Mo-1 bonding distances (2.11 and 3.086 Å) in Mo$_2$BC.

The temperature dependence of the magnetization in zero-field-cooled (ZFC) and field-cooled (FC) conditions was measured using an applied magnetic field of 50 Oe and is presented in figure 3. In both ZFC and FC a clear superconducting transition can be seen around 4.4 K. The superconducting volume fraction (~60%) can be estimated within the Meissner state through the dependence of $M$ versus $H$, since the value of the superconducting state susceptibility (perfect diamagnetism) is $-1/4\pi$, according to the CGS system. Note that even without considering the demagnetization size susceptibility factor, this result suggests bulk superconductivity. On the FC curve, the flux expulsion of about 7% indicates a strong flux pinning, as expected. The inset of figure 3 displays the isothermal $M$ versus $H$ at $T = 2$ K which shows a type II superconductivity behaviour.

The typical temperature dependence of the resistivity of Nb$_2$BN is shown in figure 4. A sharp resistivity transition
Figure 4. Electrical resistivity ($\rho$) versus temperature of Nb$_2$BN from 2 to 300 K displaying the characteristic superconducting transition at 4.4 K. The inset shows the evolution of $T_c$ with different applied fields.

Figure 5. The temperature dependence of $H_{c2}$ and $H_{c1}$ of Nb$_2$BN. Experimental points taken from $M$ versus $H$ and $R$ versus $T$ are marked as dots. The red line represents the GL fit for $H_{c1}(T)$ and the black line corresponds to the WHH fit for $H_{c2}(T)$.

close to 4.4 K (at $\rho = 0$, $\Delta T_c \sim 0.1$ K) is clearly observed at zero applied magnetic field which indicates the high quality of the obtained samples. These results are consistent with those obtained in magnetization measurements. The inset in figure 4 shows the resistivity dependence on the applied magnetic field.

An estimate of the upper critical field at 0 K ($\mu_0 H_{c2}(0)$) can be made through the Werthamer, Helfand and Hohenberg (WHH) theory [12] represented by equation (1). According this theory $\mu_0 H_{c2}(0)$ can be estimated inside the limit of a short electronic mean-free path (dirty limit) and is given by

$$\mu_0 H_{c2}(0) = -0.693 T_c (dH_{c2}/dT)_{T=T_c}. \quad (1)$$

The temperature dependence of $\mu_0 H_{c2}(T)$ is shown in figure 5 where the black line represents the conventional fitting of $\mu_0 H_{c2}(0)$ obtained using equation (1). The critical field $H_{c2}(0)$ is estimated to be $\sim 2082$ Oe, a value that suggests a type II superconductivity. Another estimate of $H_{c2}(0)$ was obtained by using the data of magnetization versus applied field at different temperatures as shown in figure 6. The criterion followed consisted of taking the corresponding field of $H_{c2}(T) = 0$ for the given temperature, plotting and fitting the values with equation (1) to obtain $H_{c2}(0)$. The result is completely consistent with the resistivity method.

The lower critical field ($H_{c1}(0)$) was extrapolated from the applied magnetic field dependence of the magnetization at several temperatures shown in figure 6(a), using the Ginzburg–Landau equation [13] $H_{c1}(T) = H_{c1}(0)(1 - (T/T_c)^2)$, which gives $H_{c1}(0) \sim 93$ Oe. The values of $H_{c1}$ were determined by examining the divergence from linearity of the slope of the magnetization curve (figure 6b), using the criterion $\Delta M = 10^{-3}$ emu for the difference between the Meissner line and the magnetization signal. The calculated values of $H_{c1}(0)$ and $H_{c2}(0)$ allow us to estimate the coherence length and penetration depth using the Ginzburg–Landau (GL) formulæ [13],

$$\mu_0 H_{c1}(0) = \frac{\phi_0}{2\pi \lambda_0^2}, \quad (2)$$

$$\mu_0 H_{c2}(0) = \frac{\phi_0}{2\pi \xi_0^2}, \quad (3)$$

Figure 6. Magnetization versus applied field taken at constant temperatures from 2 to 4 K. The dashed line illustrates the criterion used to determine the difference between $M$ and the linear behaviour below $H_{c1}$. The lower critical field ($H_{c2}(0)$) is estimated to be $\sim 2082$ Oe, a value that suggests a type II superconductivity. Another estimate of $H_{c2}(0)$ was obtained by using the data of magnetization versus applied field at different temperatures as shown in figure 6. The criterion followed consisted of taking the corresponding field of $H_{c2}(T) = 0$ for the given temperature, plotting and fitting the values with equation (1) to obtain $H_{c2}(0)$. The result is completely consistent with the resistivity method. The lower critical field ($H_{c1}(0)$) was extrapolated from the applied magnetic field dependence of the magnetization at several temperatures shown in figure 6(a), using the Ginzburg–Landau equation [13] $H_{c1}(T) = H_{c1}(0)(1 - (T/T_c)^2)$, which gives $H_{c1}(0) \sim 93$ Oe. The values of $H_{c1}$ were determined by examining the divergence from linearity of the slope of the magnetization curve (figure 6b), using the criterion $\Delta M = 10^{-3}$ emu for the difference between the Meissner line and the magnetization signal. The calculated values of $H_{c1}(0)$ and $H_{c2}(0)$ allow us to estimate the coherence length and penetration depth using the Ginzburg–Landau (GL) formulæ [13],

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where \( \phi_0 \) is a quantum flux equal to \( 2.068 \times 10^{-15} \) T m\(^{-2} \), which yields \( \xi_0 \approx 425 \) Å and \( \lambda_0 \approx 188 \) nm at 0 K. Using the relation \( \kappa_{GL} = \lambda_0 / \xi_0 \) we obtained the value \( \kappa_{GL} = 4.42 \), which agrees with the previous results indicating a type II superconducting behaviour.

While the magnetization and resistivity suggest bulk superconductivity in Nb\(_2\)BN, an anomaly in the specific heat measurement is necessary for confirmation. Figure 7 displays the specific heat divided by the temperature \( (C_v/T) \) at zero applied magnetic field. A jump in the specific heat is clearly observed at the midpoint of the transition at \( T_c = 4.4 \) K and a small transition length of only \( \Delta T_c \sim 0.3 \) K. The consistency between the magnetization, resistivity, and heat capacity transitions is clear evidence of bulk superconductivity in Nb\(_2\)BN. The normal state specific heat \( (C_v) \) is assumed to have contributions from the standard linear electronic contribution \( (\gamma T) \) term and the cubic phonon \( (\beta T^3) \) term.

In figure 7 the normal state specific heat \( (C_v) \) can be fitted to the expression \( C_v = \gamma T + \beta T^3 \) by a least squares analysis, with resultant values of \( \gamma = 6.3 \) mJ mol\(^{-1} \) K\(^{-2} \) and \( \beta = 0.293 \) mJ mol\(^{-1} \) K\(^{-4} \). The \( \beta \) value corresponds to a Debye temperature of \( \Theta_D \sim 298 \) K. The Sommerfeld coefficient \( \gamma \) suggests a moderated density of states at the Fermi level typical of other transition-metal superconductors.

A subtraction of the phonon contribution from the total specific heat allows analysis of just the electronic contribution \( (C_e) \), displayed here as \( C_e/T \) versus \( T \) in figure 8. The analysis of the specific heat anomaly shows the magnitude of the jump at \( T_c \) to be \( \Delta C_e/T_c \sim 0.88 \), which is significantly smaller than the weak coupling BCS limit of 1.43. However, this apparent inconsistency is related with the superconducting fraction estimated from the magnetization measurement displayed in figure 3. Although the reason for the estimated value from the specific heat measurement diverging from BCS prediction is not obvious, the size of the jump strongly suggests that the superconducting behaviour is in a BCS weak coupling limit.

\[ T_c = \frac{\Theta_D}{1.45} \exp \left\{ \frac{-1.04(1+\lambda)}{\lambda - \mu^* (1+0.62\lambda)} \right\}. \]  

(5)

Indeed, the exponential behaviour of the electronic component in the superconducting state is in good agreement with the BCS theory as shown in the inset of figure 8. The linear behaviour of the logarithmic scale versus \( T_c/T \) is totally consistent with the BCS prediction of a superconducting state below \( T_c \). Comparison with the BCS formula for \( C_v \) below \( T_c \) gives

\[ \frac{C_v}{\gamma T_c} = 8.5e^{\frac{0.62\Delta_0}{k_B T_c}}, \]

(4)

which yields an energy gap \( (\Delta_0) \) of 0.65 meV for \( T \to 0 \) and \( 2\Delta_0/k_B T_c = 3.45 \), which again is a signal of a weak BCS coupling value. Then, all the results from the specific heat suggest that Nb\(_2\)BN is a conventional BCS superconducting material. In all BCS superconductors the Cooper pairing is phonon mediated and the dimensionless electron–phonon constant \( \lambda \) can be determined by the McMillan equation [14]:

4. Conclusions

In this paper the superconducting properties of Nb\(_2\)BN were explored. Conventional bulk superconductivity was found at \( T_c = 4.4 \) K with superconducting critical fields of \( H_{c1}(0) = 93 \) and \( H_{c2}(0) = 2082 \) Oe. The results suggest a conventional type II superconductivity with \( \kappa_{GL} = 4.42 \) and bulk superconductivity was confirmed through specific heat measurements, showing values of \( \gamma = 6.3 \) mJ mol\(^{-1} \) K\(^{-2} \) and \( \beta = 0.293 \) mJ mol\(^{-1} \) K\(^{-4} \) in good agreement with the BCS theory.

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