Incipient superconductivity in TaB$_2$

D. Kaczmorowski, A. J. Zaleski, O. J. Żogal, and J. Klamut

Institute of Low Temperature and Structure Research, Polish Academy of Sciences,
P.O.Box 1410, 50-950 Wroclaw, Poland

(February 15, 2022)

Magnetic properties of TaB$_2$ were studied by means of DC and AC susceptibility measurements. It has been found that the compound becomes superconducting at $T_c = 9.5$ K. From upper critical field measurements the superconducting parameters have been evaluated, which indicated that TaB$_2$ is a hard type-II superconductor. Possible reasons why superconductivity has not been discovered in previous studies are briefly discussed.

I. INTRODUCTION

The recent discovery of high-$T_c$ superconductivity in MgB$_2$ [1] has raised considerable interest in a search for analogous behavior in similar systems. Although the most natural candidates for such investigations seem to be AlB$_2$-type alkali, alkali earth or group III - element diborides, AB$_2$ (e.g. A = Li, Be, Al), in none of them superconductivity has been found up to now [2] [3] [4]. Moreover, in the solid solutions Mg$_{1-x}$Al$_x$B$_2$ a rapid decrease of superconducting transition temperature is always observed with the increase in the dopant content [2] [4].

Diborides isoostructural to MgB$_2$ form also with transition metals from the IVa, Va and VIa groups of the Periodic Table (T = Ti, Zr, Hf, V, Nb, Ta, Cr, Mo), yet also these compounds have been reported [2] not to show superconductivity down to 0.42 K, with the only exception for NbB$_2$ that becomes superconducting below $T_c = 0.62$ K.

Amidst the TB$_2$ materials, TaB$_2$ seems to be especially interesting due to a unique feature of its (0001) surface being terminated by a graphitic boron layer [5]. The recent electronic structure calculations of the TaB$_2$ (0001) surface have revealed the presence at the Fermi level of a pronounced DOS peak originated predominantly from the B $2p$ orbitals [6]. Due to a strong charge transfer from Ta to B the Ta $5d$ orbitals are lowered in energy and filled with electrons. Interestingly, the resulting band structure is similar to the one derived for MgB$_2$ [7] [8] and favorable of hole superconductivity concept [9]. This striking observation motivated us to re-investigate our TaB$_2$ sample on the context of possible appearance of superconductivity.

II. EXPERIMENTAL

Powder sample of TaB$_2$ was obtained by the borothermic method [10]. The product was checked by chemical analysis, which proved a sample stoichiometry close to the ideal. EDAX studies, performed using a Phillips 515 scanning electron microscope did not reveal any other elements but tantalum. Phase analysis showed a homogeneous material. X-ray diffraction pattern (see Fig. 1) was easily indexed within a hexagonal unit cell with lattice parameters: $a = 308.2$ pm and $c = 324.3$ pm. DC magnetic measurements were carried out using a Quantum Design SQUID magnetometer. The AC susceptibility was measured employing an Oxford Instruments EXA susceptometer. All physical measurements were done on powders freely placed in sample holders.

III. RESULTS

In Fig. 2 is shown the temperature dependence of the magnetization in TaB$_2$ measured in a field of 50 Oe upon cooling the sample in zero (ZFC) and applied (FC) magnetic field. Down to $T_c = 9.5$ K, the specimen investigated shows nearly temperature independent paramagnetism with the magnetic susceptibility of the order of $10^{-5}$ emu/g. However, most strikingly, at the temperature $T_c$ there occurs a clear transition to a diamagnetic state, and the ZFC and FC curves split in a manner characteristic of type-II superconductors, with the weak irreversibility field. Furthermore, the field variation of the magnetization, taken at 1.7 K with increasing and decreasing magnetic field (see Fig. 3), shows highly irreversible properties of the material. The lower critical field estimated from Fig. 3 is about $H_{c1} = 100$ Oe.

The behavior typical of type-II superconductors has been corroborated for TaB$_2$ via the AC magnetic susceptibility measurements ($H = 10$ Oe, $f = 1$ KHz). As seen in Fig. 4, in the normal state the real component of the susceptibility is positive and below about 10 K a sudden drop to negative values occurs. Just below $T_c$ a sharp peak in the imaginary component of the susceptibility is observed, being characteristic of good quality superconducting material.

The onset of superconductivity in the AC susceptibility was used to define the upper critical field $H_{c2}$, and the so-derived temperature dependence of $H_{c2}$ is depicted in Fig. 5. The experimental data can be well described
by the expression: \( H_{c2}(T) = H_{c2}(0)[1-T/T_c]^\beta \), with the least-squares fitting parameters: \( H_{c2}(0) = 23.6 \text{kOe} \) and \( \beta = 2.2 \). It is worthwhile noting that the \( H_{c2}(T) \) variation has a positive curvature, yielding a rather large parameter \( \beta \), which is usually considered as a measure of the material quality. The \( H_{c2}(T) \) dependence derived for TaB\(_2\) differs from that known for conventional low-\(T_c\) superconductors, but rather resembles the behavior typical of rare-earth nickel borocarbides \(^{[3]}\).

\( * \)From the obtained value of \( H_{c2}(0) \) (which is probably the upper estimate of the real value) it is possible to derive the superconducting coherence length \( \xi_0 \) at 13.4 nm. Then, from \( H_{c1} \) and \( \xi_0 \) we estimate the penetration depth \( \lambda_0 = 250 \text{ nm} \) and the Ginzburg-Landau parameter \( \kappa = 18 \). All these superconducting characteristics strongly indicate that TaB\(_2\) may be classified as a hard type-II superconductor.

IV. DISCUSSION

The discovery of superconductivity in TaB\(_2\) below \( T_c = 9.5 \text{ K} \) clearly contradicts previous results obtained for this compound by Leyarovska and Layarovski \(^{[5]}\). It should be emphasized that we have also re-investigated some other transition metal diborides studied by the latter authors (TiB\(_2\), ZrB\(_2\), HfB\(_2\), VB\(_2\), NbB\(_2\)) but only confirmed their conclusions that none of them is superconducting above 1.7 K. Thus, assuming that the previously investigated non-superconducting sample of TaB\(_2\) was of the highest quality, we thoroughly checked our specimen on possible impurities, which might result in spurious superconductivity effect.

As can be inferred from Fig. 1, two very weak impurity lines were indeed observed in the X-ray pattern. Both can be assigned to the equiatomic compound TaB or alternatively, but less likely, to Ta\(_3\)B\(_4\). In order to test a hypothesis that the superconductivity arises due to the presence of small amount of the other tantalum borides, we prepared both these phases and investigated their low-temperature magnetic and electrical properties. Although one of them is diamagnetic, none has proven to be superconducting.

Then, we considered a possibility that the amount of eventual superconducting impurity in our sample is below the detection limit of X-ray diffraction. This latter presumption seems supported by rather weak diamagnetic signal found in the superconducting state. The contamination by non-reacted metallic Ta must be ruled out because the afore-discussed critical temperature and upper critical field are very different than those characterizing pure Ta (\( T_c = 4.4 \text{ K} \) and \( H_{c2} = 0.8 \text{kOe} \)). Although the detailed EDAX measurements of our sample has not revealed the presence of any other elements except Ta, we cannot exclude that it does contain some oxygen or other light elements, which are not seen by EDAX. In such a case the observed superconductivity could be due to very little amount of unknown tantalum oxide or e.g. nitride. Yet, no other Ta-based compounds, reported so far in the literature, fit to the behavior found in the present work. In particular, albeit the superconducting temperature for the tantalum monocarbide TaC is quite similar to \( T_c \) found for our sample (9-11.4 K \(^{[4]}\)), the reported \( H_{c2} \) is only 4.6 kOe \(^{[4]}\).

Alternatively, the apparent discrepancy in the properties of our specimen of TaB\(_2\) and that studied in Ref. \(^{[5]}\) could be attributed to some difference in the stoichiometry of these two samples. The hexagonal phase TaB\(_2\) is known to form within a rather broad homogeneity range \(^{[13]}\) giving sub- and superstoichiometric compositions. It seems conceivable that the effect of superconductivity is restricted to a particular nonstoichiometric composition TaB\(_{2+x}\) and is governed by existing defects in the AlB\(_2\)-type unit cell, which can play similar role as oxygen in high-\(T_c\) superconductors.

ACKNOWLEDGMENTS

The authors are indebted to Dr. P. Peshev for providing the sample of TaB\(_2\) and Dr. Z. Bukowski for synthesizing the samples of TaB and Ta\(_3\)B\(_4\).

* also at the International Laboratory of High Magnetic Fields and Low Temperatures, ul. Gajowicka 95, 53-421 Wroclaw, Poland

[1] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zanitani, and J. Akimitsu, Nature 410, 63 (2001).
[2] J. S. Slusky, N. Rogado, K.A. Regan, M. A. Hayward, P. Khalifah, T. He, K. Inumaru, S. Loureiro, M. K. Hass, H. W. Zandbergen, and R. J. Cava, cond-mat/0102262 (2001).
[3] I. Felner, cond-mat/0102508 (2001).
[4] Y. G. Zhao, X. P. Zhang, F. Y. Qiao, H. T. Zhang, S. L. Jia, B. S. Cao, M. H. Zhu, Z. H. Han, X. L. Wang, and B. L. Gu, cond-mat/0103077 (2001).
[5] L. Leyarovska, and E. Leyarovski, J. Less Common Met. 67, 249 (1979).
[6] H. Kawanowa, R. Souda, S. Otani, and Y. Gotoh, Phys. Rev. Lett. 81, 2264 (1998).
[7] H. Kawanowa, R. Souda, K. Yamamoto, S. Otani, and Y. Gotoh, Phys. Rev. B 60, 2855 (1999).
[8] G. Satta, G. Profeta, F. Bernardini, A. Continenza, and S. Massida, cond-mat/0102538 (2001).
[9] N. I. Medvedeva, A. L. Ivanovskii, J. E. Medvedeva, and A. J. Freeman, cond-mat/0103157 (2001).
[10] J. E. Hirsch, cond-mat/0102211 (2001).
[11] P. Peshev, L. Leyarovska, and G. Bliznakov, J. Less Common Met. 15, 259 (1968).
[12] J. Freudenberger, S. L. Drechsler, G. Fuchs, A. Kreyssig, K. Nenkov, S. V. Shulga, K. H. Müller, Physica C 306, 1 (1998).
[13] M. Wells, M. Pickus, K. Kennedy, and V. Zackay, Phys.
Rev. Lett. 12, 536 (1964).
[14] H. J. Fink, A. C. Thorsen, E. Parker, V. F. Zackay, and L. Toth, Phys. Rev. 138, A1170 (1965).
[15] Binary Alloy Phase Diagrams, 2nd Edition, T. B. Massalski (Editor-in-Chief), Vol. 1, ASM International, 1990.

A. Figure captions

Fig. 1. Powder X-ray diffraction pattern (CuKα1 radiation) for TaB2 at room temperature. Arrows mark the reflections from possible TaB impurity.

Fig. 2. Low-temperature dependence of the magnetization in TaB2, taken at H = 50 Oe in the ZFC and FC regimes.

Fig. 3. Field variation of the magnetization in TaB2, measured at T = 1.7 K with increasing and decreasing field.

Fig. 4. Temperature dependence of the in-phase and out-of-phase magnetic susceptibility components for TaB2, measured in the AC field H = 10 Oe with the frequency f = 1 kHz.

Fig. 5. Temperature variation of the upper critical field $H_{c2}$ in TaB2. The solid line is a fit of the experimental data to the function $H_{c2} = H_{c2}(0)[1-T/T_c]^{-\beta}$ with the parameters: $H_{c2}(0) = 23.6$ kOe and $\beta = 2.2$. 
This figure "fig1.JPG" is available in "JPG" format from:

http://arxiv.org/ps/cond-mat/0103571v2
This figure "fig2.JPG" is available in "JPG" format from:

http://arxiv.org/ps/cond-mat/0103571v2
This figure "fig3.JPG" is available in "JPG" format from:

http://arxiv.org/ps/cond-mat/0103571v2
This figure "fig4.JPG" is available in "JPG" format from:

http://arxiv.org/ps/cond-mat/0103571v2
This figure "fig5.JPG" is available in "JPG" format from:

http://arxiv.org/ps/cond-mat/0103571v2