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Pressure dependence of the superconducting transition temperature in single-crystal NbB_x (x near 2) with $T_c = 9.4$ K

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We have measured the pressure dependence of the superconducting transition temperature (9.4 K) of NbB_x with x near 2 by direct comparison with elemental Nb. We find $dT_c/dP = 0.04\ (\pm 0.015)$ K/kbar.

INTRODUCTION

Niobium diboride,[1] NbB_x with x between ~ 1.9 and 2.5, crystallize in the AlB_2-type structure ($P6/mmm$). *Arc*-melted samples with $x \sim 2.5$ were reported[2] to be superconducting with transition temperatures as high as 6 K, while with x near 2 the transition was below 1 K. Superconductivity was also reported in niobium diborides prepared by borothermic reduction[3,4] where x values near 2.1 resulted in $T_c \sim 4$ K. Leyarovska and Leyarovski[3] reported $T_c = 0.62$ for NbB_2. It is apparent that T_c is a sensitive function of x and it is difficult both to control and measure accurately the magnitude of x. We report measurements of the pressure dependence of T_c of single-crystal NbB_x with x near 2 having a $T_c = 9.4$ K. These pressure studies were prompted in part by the unexpectedly high value of T_c and the need for characterization of superconducting properties to differentiate from Nb and other stoichiometries of NbB_x.

EXPERIMENTAL

Single crystals were grown by reaction of Nb and B in molten Al under an Ar atmosphere.[4] The crystals grew in several morphologies which nevertheless proved to be $P6/mmm$ with varying lattice parameters near $a \sim 3.11$ Å and $c \approx 3.31$ Å, presumably depending upon the exact stoichiometry of the particular crystal. Complementary powder studies[5] show linear behavior of the lattice parameters for x values from 2.5 to 1.9. The particular crystal used in our pressure study had $a = 3.1069(3)$ Å and $c = 3.3103(6)$ Å. Energy-dispersive spectroscopy disclosed no detectable impurities to the level of a percent. We were particularly concerned about Al (the flux from which the crystal was grown) because valence-three Y is known[2] to raise the T_c of $Nb_{0.9}Y_{0.1}B_2$ to over 9 K.

The static magnetic properties of one relatively large single crystal of NbB_x (approximately $1.2 \times 0.7 \times 0.03 \text{mm}^3$) were studied in a commerical SQUID magnetometer. X-ray diffraction showed that the crystal c axis was in the plane of this thin plate, parallel to the long dimension. Figure 1 shows Meissner-effect data (magnetization versus decreasing temperature) measured in a field of 0.5 mT applied normal to the plate. The onset temperature for superconductivity is near 9.6 K in this crystal, slightly above that for the smaller crystal used in the pressure study. Stoichiometry differences, identified by the varying lattice parameters for different crystals, would account for such small variations in T_c. The Meissner volume susceptibility at low temperatures is $-4.8/4\pi$, enhanced by the strong demagnetization effect for this field orientation. Low-temperature, low-field diamagnetic shielding data for the same orientation show a volume susceptibility of $-15/4\pi$ (i.e., an enhancement of 15), compared to a calculated demagnetization enhancement of 19 for an ellipsoid of revolution with the dimensions of the crystal plate. Hence, the single crystal is fully superconducting, eliminating the possibility of superconductivity due to Nb metal present as inclusions.

Pressures to 5 kbar were obtained by careful isobaric freezing[6] of He. The supercoducting transition temperature was detected in the pressure experiments by use of an rf impedance technique[7] which has been shown to give a signature for T_c corresponding to the onset of diamagnetism observed on the same samples in the SQUID magnetometer. Our usual thermometry is a carbon glass thermometer affixed to the exterior of the pressure vessel immediately adjacent to the sample. Temperatures are varied by positioning the pressure vessel above the liquid ^{4}He cryogenic bath.

In this study we expected small shifts in T_c with pressure because of the typically low compressibilities of refractory transition metal borides. Also, there was some

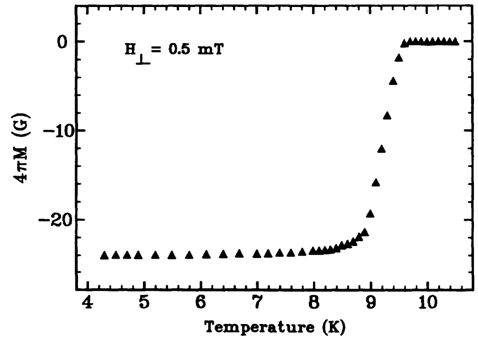

FIG. 1. Meissner data measured at 0.5 mT for NbB_x single crystal.

concern about the similarity of T_c value of our crystal to elemental Nb. Therefore, we placed a small chip of polycrystalline high-purity Nb next to the sample to serve as an internal thermometer. Nb is ideal for this role in a pressure experiment because the pressure derivative is, for our purposes, negligibly small. There is disagreement in the literature even as to the sign of the effect, but the magnitude in any case is of the order of 0.002 K/kbar.

RESULTS AND DISCUSSION

Direct measurement of the *difference* in T_c between the Nb internal thermomeer and our NbB_x single crystal at various pressures to 5 kbar give a value of $dT_c/dP=0.04(\pm 0.015)$ K/kbar. Here we have assumed that $dT_c/dP=0$ for Nb. Any error arising from the assumptions is well within our measurement uncertainties.

Applying a dc bias to our modulation coil of 100 G allows a semiquantitative measurement of dH_c/dT at T_c for both the sample and the Nb marker. An estimate of H_0, the critical field at absolute zero, can then be made assuming a parabolic $H_c(T)$ [that is $H_c/H_0=1-(T/T_c)^2$]. The results are shown in Table I. While this procedure is only approximate, the agreement of the Nb values[8] with the accepted values is quite satisfactory and makes it clear that the superconducting properties of this NbB_x crystal are quite distinct from those of Nb.

TABLE I. Comparison of the properties of Nb and single crystalline NbB_2.

	T_c (K)	dT_c/dP (K/kbar)	dH_c/dT (G/K at T_c)	H_0 (G)
Nb	9.20[a]	0[a]	440	2000
NbB_2	9.40	0.04($\pm$0.015)	330	1500

[a] Defined values for calibration.

CONCLUSIONS

We have measured the pressure dependence of the superconducting transition temperature of NbB_x with x near 2 by direct comparison with the behavior of elemental Nb. This measurement and the magnetic properties we obtained indicate that in spite of its unexpected high T_c, which is similar to that of Nb, NbB_x has distinctly different behavior from Nb as it is indeed a 9.4–9.6 K superconductor.

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