Correlation between Superconducting Carrier Density and Transition Temperature in NbB$_{2+x}$

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We report on the magnetic penetration depth, $\lambda$, in a type II superconductor NbB$_{2+x}$ determined by muon spin rotation method. We show in the sample with $x = 0.1$ that $\lambda$ at 2.0 K is independent of an applied magnetic field. This suggests that the superconducting order parameter in NbB$_{2+x}$ is isotropic, as expected for conventional BCS superconductors. Meanwhile, the superconducting carrier density ($\propto \lambda^{-2}$) exhibits an interesting tendency of increase with increasing $T_c$ (where $T_c$ varies with $x$). Possible origin of such behavior is discussed in comparison with the case of exotic superconductors.

KEYWORDS: NbB$_{2+x}$, superconductivity, $\mu$SR, magnetic penetration depth, carrier density

The recent revelation of superconductivity in MgB$_2$ with high transition temperature ($T_c = 39$K)$^1$ has revived much interest in hexagonal diborides which were once subjected to active studies from 1950’s through 70’s.$^2$−$^4$ The discovery of MgB$_2$ prompted various theoretical and experimental investigations to clarify the origin of the high $T_c$ seemingly exceeding the so-called ‘BCS-barrier’ ($\sim 30$ K). These compounds have a simple layered structure along $c$-axis, consisting of an alternative stack of metal ion layers forming a triangular lattice and boron atom layers in a honeycomb network. In MgB$_2$, both theoretical and experimental studies suggested that the strong electron-phonon interaction in accordance with the light mass of the organized atoms and two-dimensional character of boron atom network are closely related to the relatively high-$T_c$ superconductivity. Moreover, it turned out that some of the unconventional properties in the superconducting phase can be attributed to the multiband superconductivity, where the presence of two energy gaps corresponding to $p_\pi$ and $p_\sigma$ orbits of boron atoms have been confirmed by experimental$^5$ and theoretical studies.$^6$

Among various diborides, NbB$_2$ is intriguing as it exhibits strong sensitivity of superconducting transition temperature to the stoichiometric imperfection; Cooper et al. reported $T_c = 3.87$ K for boron-rich NbB$_2$,$^3$ while Leyarovska et al. reported much lower $T_c$ ($\sim 0.62$ K)

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for a stoichiometric NbB$_2$.

Schirber et al. showed $T_c = 9.4$ K for single-crystalline sample of NbB$_x$ ($x \sim 2$).

Recently, Yamamoto et al. reported that $T_c$ changes between 2 K and 9.2 K in the samples prepared under high pressure, probably because of the shift in the composition ratio between Nb and boron.

It is noticeable that Escamilla et al. found a maximum $T_c = 9.8$ K, which is slightly higher than that of elemental Nb (=9.23 K). Thus, it might be possible to obtain a guide for ever higher $T_c$ in hexagonal diborides by studying the relationship between $T_c$ and various parameters including chemical composition and crystal structure in NbB$_{2+x}$.

In this paper, we report on the magnetic penetration depth, $\lambda$, in the mixed state of NbB$_{2+x}$ studied by muon spin rotation and relaxation method ($\mu$SR). The magnetic penetration depth, which reflects superconducting carrier density, $n_s (\propto \lambda^{-2})$, is determined microscopically by $\mu$SR signals due to the inhomogeneity of magnetic field distribution in the flux line lattice (FLL). We show that $\lambda$ is independent of the applied field, strongly suggesting that NbB$_{2+x}$ has an isotropic superconducting order parameter. More interestingly, a quasi-linear relationship has been observed between the muon spin relaxation rate $\sigma$ ($T = 0$ K, which is proportional to $n_s$) and $T_c$ as it varies with $x$. This result suggests that the change of $T_c$ in NbB$_{2+x}$ depends on the superconducting carrier density.

Polycrystalline samples of NbB$_{2+x}$ ($x = 0, 0.03, 0.1$ where $x$ is a nominal value) used in this experiment were synthesized from Nb powder (99.96 %) and boron crystalline powder (99 %). The pellets of these mixtures were sealed by quartz tube at vacuum pressure (< $3.0 \times 10^{-5}$ Torr) and heated at 1000 °C for 30 hours. These samples were confirmed to be single phase, and to decrease $a$-axis and increase $c$-axis with increasing $x$ by the X-ray powder diffraction pattern using the conventional X-ray powder spectrometer (RAD-C; RIGAKU). The magnetic susceptibility and electrical resistivity were measured with the SQUID magnetometer (MPMS2; Quantum Design Co., Ltd.) and the PPMS system (Quantum Design Co., Ltd.).

Figure 1 shows the temperature dependence of magnetic susceptibility upon field cooling at 10 Oe, where one can observe significant reduction of the susceptibility at a well-defined temperature, $T_c$, for respective compositions. This is obviously due to the Meissener diamagnetism associated with the superconducting transition. It is also clear in Fig. 1 that $T_c$ increases with increasing $x$. The superconducting volume fraction at 1.8 K is estimated to be approximately 44, 34 and 29 % for NbB$_2$, NbB$_{2.03}$ and NbB$_{2.1}$. The corresponding upper critical field ($H_{c2}(0)$) are 6.4, 7.6 and 10.5 kOe respectively, which were estimated from the results of electrical resistivity measurements under an applied magnetic field.

The $\mu$SR experiment was performed on the M15 and M20 beamlines at TRIUMF which provides a muon beam with the momentum of 29 MeV/c. The polycrystalline samples were mounted on sample holders having a dimension of 7 × 7 mm$^2$ (M15) or 25 × 25 mm$^2$ (M20). The $\mu$SR spectra were obtained at $H = 1$ kOe and at $T = 2$ K to map out the temperature
and magnetic field dependence, respectively. Care was taken to cool down the sample in the field-cooled condition at each applied field to avoid the effect of flux pinning.

Since the muons stop randomly on the FLL, the muon spin precession signal $\hat{P}(t)$ provides a random sampling of the internal field distribution $B(\hat{r})$,

$$
\hat{P}(t) \equiv P_x(t) + iP_y(t) = \int_{-\infty}^{\infty} n(B) \exp(i\gamma_{\mu}Bt) dB;
$$

$$
n(B) = \langle \delta(B(\hat{r}) - B) \rangle_r,
$$

where $\gamma_{\mu}$ is the muon gyromagnetic ratio ($= 2\pi \times 13.553$ MHz/kOe), and $n(B)$ is the spectral density for muon precession determined by the local field distribution. These equations indicate that the real amplitude of the Fourier transformed muon precession signal corresponds to the local field distribution $n(B)$. The London penetration depth in the FLL state is related to the second moment $\langle (\Delta B)^2 \rangle = \langle (B(\hat{r}) - H)^2 \rangle$ of the field distribution reflected in the $\mu$SR line shape. In polycrystalline samples, a Gaussian distribution of local fields is a good approximation,

$$
\hat{P}(t) \simeq \exp(-\sigma_j^2 t^2 / 2) \exp(i\gamma_{\mu}B_j t),
$$

$$
\sigma_j = \gamma_{\mu} \sqrt{\langle (\Delta B)^2 \rangle},
$$

For the ideal triangular FLL with isotropic effective carrier mass $m^*$, $\lambda$ is given by the relation,

$$
\sigma [\mu s^{-1}] = 4.83 \times 10^4 (1 - h)(1 + 3.9(1 - h)^2)^{1/2} \lambda^{-2} [\text{nm}],
$$

where $h = H/H_{c2}$, and $\lambda$ is related to the superconducting carrier density,

$$
\lambda^2 = \frac{m^* c^2}{4\pi \varepsilon_0 \mu_0 e^2},
$$

indicating that $\lambda$ is enhanced upon the reduction of $n_s$ due to the quasiparticle excitations.

Figure 2 shows typical muon spin precession signals in NbB$_2$ at various temperatures under a transverse field of 1 kOe, where one can observe the change in the lineshape due to FLL formation as the temperature passes through $T_c$. The damping of precession amplitude above $T_c$ is mainly due to static random local fields from $^{93}$Nb and $^{10,11}$B nuclear magnetic moments. Upon cooling below $T_c$, the spectrum exhibits enhanced depolarization, which indicates that magnetic field distribution becomes inhomogeneous due to the formation of magnetic vortices. In analyzing these spectra, we adopted the following fitting function,

$$
A\hat{P}(t) = \sum_{j=1}^{2} A_j \exp \left(-\frac{\sigma_j^2 t^2}{2}\right) \cos(-\gamma_{\mu}B_j t + \phi_j),
$$

where the index $j$ denotes the components of normal ($j = 1$) and superconducting ($j = 2$) domains, $A$ is the total positron decay asymmetry, $A_j$ is the partial asymmetry, $\sigma_j$ is the muon spin relaxation rate, $B_j$ is the central frequency and $\phi_j$ is the initial phase for
respective components. We define $\sigma_1$ to reflect the spin relaxation in the normal state where it is dominated by the nuclear magnetic moments, $\sigma_n$, and $\sigma_2$ in the superconducting state where $\sigma_2^2 = \sigma_n^2 + \sigma_v^2$ with $\sigma_v$ being due to the formation of FLL. The temperature dependence of $\sigma_v$ in NbB$_{2.1}$ at $H = 1$ kOe is shown in Fig. 3. In the FLL state, $\sigma_v$ increases with decreasing temperature below $T_c(1$ kOe) $\sim 5$ K. According to the empirical two-fluid model, which is supposed to be a good approximation for the BCS theory, the following relation is expected,

$$\lambda(T) = \lambda(0) \frac{1}{\sqrt{1 - \tau^4}},$$  

(8)

which leads to

$$\sigma_v(T) = \sigma_v(0)(1 - \tau^4),$$  

(9)

where $\tau \equiv T/T_c(1$ kOe). As clearly seen in Fig. 3, the agreement between the above relation and our data is far from satisfactory. A better agreement is attained when we perform the fitting analysis by a similar formula,

$$\sigma_v(T) = \sigma_v(0)(1 - \tau^2).$$  

(10)

It yields $T_c = 5.3(1)$ K when $T_c$ is a free parameter, which is in good agreement with the value estimated from the electrical resistivity measurement under the same field ($\sim 5.0$ K). We also performed fitting analysis by a weak-coupling BCS model (w-BCS),$^{13}$ which turned out to reproduce the experimental data very well. Thus, these analyses indicate the difficulty to assess the structure of order parameter in NbB$_{2+x}$ based solely on the temperature dependence of $\sigma_v$ with the data above 2 K.

The situation is much improved by looking into the magnetic field dependence of $\sigma_v$. As shown in Fig. 4(a) $\sigma_v$ in NbB$_{2.1}$ decreases with increasing external field, where the solid line represents the fitting result by eq.(5) with $H_{c2} = 6.7$ kOe determined by electrical resistivity measurements. The corresponding field dependence of $\lambda$ is shown in Fig. 4(b), where $\lambda$ is mostly independent of applied magnetic field. For a quantitative evaluation on the strength of the pair-breaking effect by external field, we performed a fitting analysis by the following simple linear relation,

$$\lambda(h) = \lambda(0)[1 + \eta h],$$  

(11)

where $\eta$ is a dimension-less parameter which represents the strength of pair breaking effect, and $h \equiv H/H_{c2}(2$ K) with $H_{c2}(2$ K) = 6.7 kOe. From the fitting analysis for the data by eq.(11), we obtain $\eta = 0.02(2)$ with $\lambda(0) = 233(2)$ nm, where the result is shown as a solid line in Fig. 4(b). It has been established experimentally that the parameter $\eta$ represents the degree of anisotropy in the superconducting order parameter,$^{14}$ since the pair-breaking mechanism due to the quasi-classical Doppler shift has come to wide recognition.$^{15}$ For example, in Y(Ni$_{0.8}$Pt$_{0.2}$)B$_2$C,$^{16}$ Cd$_2$Re$_2$O$_7$$^{17}$ and V$_3$Si ($h < 0.5$),$^{18}$ which behave as conventional BCS superconductors with isotropic s-wave pairing, $\eta$ is reported to be nearly zero. On the other hand, $\eta = 5 - 6.6$
in a high-$T_c$ cuprate YBa$_2$Cu$_3$O$_{7-\delta}$ which has a $d$-wave pairing. In the case of YNi$_2$B$_2$C which turned out to be an anisotropic $s$-wave superconductor, $\eta \simeq 1$ is reported. From the comparison of these results with our result, it is strongly suggested that NbB$_{2+x}$ has an isotropic $s$-wave order parameter.

We made additional measurements for NbB$_{2+x}$ with $x = 0$ and 0.03 to clarify the relation between the bulk $T_c$ and microscopic parameters such as $\lambda$. The relation between $T_c$ and $\sigma_v(0)$, which is extrapolated from the temperature dependence of $\sigma_v(T)$, is shown in Fig. 5. By the comparison between eqs.(5) and (6), the following relation is derived:

$$\sigma_v \propto \frac{1}{\lambda^2} \propto \frac{n_s}{m^*}.$$  

It is inferred from Fig. 5 that $T_c$ increases with increasing $n_s/m^*$ with a quasi-linear relation ($T_c \propto n_s/m^*$). This strongly suggests that the change of $T_c$ is associated with that of the superconducting carrier density. It is interesting to note that this behavior has a certain similarity with the case of exotic (e.g. high-$T_c$ cuprate, organic, heavy-fermion) superconductors. According to the MEM/Rietveld analysis on the synchrotron radiation X-ray measurements, this corresponds to the change in the number of electrons at Nb- and B-sites. It is generally expected from the BCS theory that

$$T_c \propto \exp(-1/N(0)V),$$  

where $N(0)$ is the density of state at the Fermi surface and $V$ is the electron-phonon coupling constant. Assuming that $V$ is independent of the slight change in the chemical composition, our result suggests that $N(0)$ is strongly dependent of the boron content $x$ in NbB$_{2+x}$. This might suggest that a similar effect may have to be considered in understanding the Uemura-plot for exotic superconductors. However, we note that the possibility of $x$-dependent electron-phonon coupling cannot be ruled out solely based on the present result, considering the possible modulation of lattice structure by non-stoichiometric boron contents.

In summary, we have investigated the magnetic penetration depth in the FLL state of NbB$_{2+x}$ using $\mu$SR method. The field dependence of $\lambda$ strongly suggests that the superconducting order parameter in NbB$_{2+x}$ is isotropic and thereby described by the BCS $s$-wave pairing. The composition dependence of $T_c$ in this compound suggests that the superconducting carrier density is a limiting factor in determining $T_c$ as inferred from the relationship between $T_c$ and $\sigma_v$.

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Fig. 1. Temperature dependence of the magnetic susceptibility at 10 Oe measured under field-cooling condition.
Fig. 2. Typical muon spin precession signals in NbB$_{2.1}$ ($T_c = 5.0$ K) under a transverse field of 1 kOe at temperatures of (a) 10 K (above $T_c$), (b) 4 K and (c) 2 K (below $T_c$).
Fig. 3. Temperature dependence of the muon spin relaxation rate $\sigma_v$ due to flux line lattice formation at $H = 1$ kOe. The curves are results of fitting by a relation $\sigma_v(T) = \sigma(0)[1 - (T/T_c)^\beta]$ and weak-coupling BCS model (dot-dashed curve). The solid curve is for $\beta = 2$ and the dotted curve is for $\beta = 4$. 
Fig. 4. Magnetic field dependence of (a) the muon spin relaxation rate $\sigma_v$ and (b) the magnetic penetration depth $\lambda$ in NbB$_{2.1}$ at 2 K. The curves in (a) and (b) are results of fitting by eqs.(5) with $\lambda$ proportional to $\lambda(0)[1 + \eta h]$ and (11).
Fig. 5. The correlation between $T_c$ at $H = 1$ kOe and $\sigma_v(T = 0 \text{ K})$ in NbB$_{2+x}$, where the latter is estimated from the temperature dependence of $\sigma_v$. 

$H = 1$ kOe

$T_c (1 \text{ kOe}) \text{ [K]}$

$\sigma_v (0 \text{ K}) \text{ [}\mu\text{s}^{-1}\text{]}$