NMR and Seebeck coefficient studies of the electronic band structure in Nb$_{1-x}$B$_2$

T. H. Su,$^{1}$ C. S. Lue,$^{1,2}$a) and Y. K. Kue$^{2, b}$

$^1$Department of Physics, National Cheng Kung University, Tainan 70101, Taiwan
$^2$Department of Physics, National Dong Hwa University, Hualien 97401, Taiwan

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With the aim of providing experimental information for the Nb deficiency enhanced superconducting temperature ($T_c$) in the Nb$_{1-x}$B$_2$ samples, we carried out a study on Nb$_{1-x}$B$_2$ ($x=0, 0.13, 0.20, \text{and} 0.26$) by means of nuclear magnetic resonance (NMR) and Seebeck coefficient ($S$) measurements. From the $^{93}$Nb NMR spin-lattice relaxation rates, we can deduce the Nb 4$d$ partial Fermi level density of states (DOS) $N_d(E_F)$ for each individual composition. The result indicates that Nb$_{0.74}$B$_2$ and Nb$_{0.80}$B$_2$ possess large $N_d(E_F)$ while the lowest one appears in Nb$_{0.87}$B$_2$. The Seebeck coefficient also shows smaller absolute values in Nb$_{0.74}$B$_2$ and Nb$_{0.80}$B$_2$, associated with higher Fermi level DOS in both compounds. Interestingly, the temperature variation in $S$ exhibits a broad minimum in Nb$_{0.87}$B$_2$, which is attributed to the presence of a pseudogap near the Fermi level. These observations were found to be in good agreement with the prediction from band structure calculations based on the appearance of the Nb vacancies in Nb$_{1-x}$B$_2$. In addition, the present study clearly reveals that the observed $T_c$ enhancement by Nb deficiency has no direct relevance to their electronic Fermi level DOS. © 2008 American Institute of Physics. [DOI: 10.1063/1.3006439]

I. INTRODUCTION

The discovery of superconductivity at 39 K in MgB$_2$ stimulated a large number of investigations, particularly focusing on the search for new superconductors with hexagonal graphitelike structure. Transition metal based diborides, isostructural to the AlB$_2$-type structure (space group $P6/mmm$), have thus refocused interest. Among these diborides, some have been observed to exhibit superconducting behavior with very low transition temperature ($T_c$), while a substantial $T_c$ enhancement has been achieved as deviating from ideal stoichiometry. The titled compound NbB$_2$ is a material of this prototype. Early studies indicated the absence of superconductivity or having a moderate $T_c$ of NbB$_2$ samples. To elucidate the possible origin for the observed $T_c$ enhancement, many efforts have been made to establish correlations between $T_c$ and Nb deficiency, especially on their electronic density of states (DOS), according to the Bardeen-Cooper-Schrieffer (BCS) framework. Theoretical calculations indicated that the electronic Fermi level ($E_F$) DOS, $N(E_F)$, is reduced by introducing Nb vacancies in Nb$_{1-x}$B$_2$. On the other hand, Farrell et al. proposed that the formation of the substitutional B dimers at the Nb sites instead of the Nb vacancies would cause an increase in $N(E_F)$. Hence, the atomic picture of the Nb-deficient compositions Nb$_{1-x}$B$_2$ remains debatable. Nevertheless, there is little experimental work associated with their local electronic band structures, essential to provide identification for both scenarios.

Nuclear magnetic resonance (NMR) is an atomic probe in metallic alloys yielding microscopic information on the Fermi surfaces. The Seebeck coefficient ($S$) measurement is also known as a sensitive probe of energy relative to the Fermi surface, providing a qualitative insight into the Fermi level band features. In this paper, we present the $^{93}$Nb NMR and the Seebeck coefficient data of Nb$_{1-x}$B$_2$ ($x=0, 0.13, 0.20, \text{and} 0.26$) as connected to their local electronic characteristics. Both results consistently indicated that $N(E_F)$ decreases for small $x$ values and then become larger with further increase in the Nb-deficient level. Such a tendency is in good agreement with those predicted from band structure calculations based on the presence of the Nb vacancies in Nb$_{1-x}$B$_2$. It thus tends to reinforce the conclusion that the observed $T_c$ enhancement by Nb deficiency is strongly related to the appearance of the Nb vacancies in these samples.

II. EXPERIMENTAL RESULTS AND DISCUSSION

Nonstoichiometric Nb$_{1-x}$B$_2$ samples were prepared by an ordinary solid state reaction technique, using commercial NbB$_2$ and amorphous boron powders as starting materials. Briefly, a mixture of an appropriate molar ratio of powders was pressed into pellets, placed in a sealed quartz tube under Ar atmosphere, and sintered at 800 °C for two days. This is a typical process to form in a single-phase AlB$_2$-type structure without employing high-pressure synthesis. A room-temperature x-ray diffraction taken with Cu Kα radiation on powder Nb$_{1-x}$B$_2$ samples is shown in Fig. 1(a). It is seen that the diffraction spectra in these materials were identical to the expected AlB$_2$-type structure. Two small faint peaks have been identified to arise from the impurities of Nb$_2$O$_5$ and B$_2$O. However, both have little effect on the present NMR and Seebeck coefficient measurements. In a more detailed analysis of the x-ray data, the $P6/mmm$ phase

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*a)Electronic mail: cslue@mail.ncku.edu.tw.
b)Electronic mail: ykkuo@mail.nbudhu.edu.tw.
was refined with the Rietveld method. We thus obtained the lattice parameters $a$ and $c$ for each individual composition with the variation as a function of $x$ illustrated in Fig. 1. It clearly exhibits an increase in $c$ but a reduction in $a$ as $x \geq 0.2$ of $\text{Nb}_1-x\text{B}_2$. Such an observation is consistent with that reported in the literature, suggesting a similar quality of these samples.

$\text{dc}$ magnetization $M$ measurements were carried out in a superconducting quantum interference device (SQUID) magnetometer under an applied field of 10 Oe in the zero-field cooling process. The temperature dependence of $M$ for $\text{Nb}_1-x\text{B}_2$ ($x > 0$) is displayed in Fig. 2(a). The inset shows the result for the nominal $\text{NbB}_2$ sample, indicating superconducting behavior below 2.5 K. In Fig. 2(b), we plotted the variation in $T_c$ with the Nb-deficient level of $\text{Nb}_1-x\text{B}_2$. Here $T_c$ was defined as the onset of the diamagnetic response in the magnetization data. The corresponding $T_c$ gradually increases with $x$ and tends to saturate as $x \geq 0.2$, being consistent with the previous observations.

NMR measurements were performed using a Varian 300 spectrometer, with a constant field of 7.05 T. Each specimen was put in a plastic vial that showed no observable $^{93}\text{Nb}$ NMR signal. Since the $^{93}\text{Nb}$ NMR resonance line is extremely quadrupolar broadened, the wide-line spectra were mapped out by integrating the spin echo signal of various excitations. Within the $\text{AlB}_2$-type crystal structure, there is a single crystallographic Nb site, which is axially symmetric, leading to a symmetric one-site $^{93}\text{Nb}$ NMR spectrum in $\text{Nb}_1-x\text{B}_2$. Due to electric quadrupole coupling, the $^{93}\text{Nb}$ NMR spectrum ($I=\frac{9}{2}$) consists of nine transition lines. Here we only showed the central transition $|m|=-\frac{9}{2} \leftrightarrow +\frac{9}{2}$ and first

![Figure 1](image1.png)

**FIG. 1.** (Color online) (a) X-ray diffraction patterns in the series of $\text{Nb}_1-x\text{B}_2$. Impurity peaks marked by asterisks arise from $\text{Nb}_2\text{O}_5$ and $\text{B}_2\text{O}_3$. (b) Variation in lattice parameters vs Nb deficiency in $\text{Nb}_1-x\text{B}_2$.

![Figure 2a](image2a.png)

**FIG. 2.** (Color online) (a) Temperature dependence of the magnetization $M$ measured at 10 Oe under a zero-field-cooled condition for $\text{Nb}_1-x\text{B}_2$ with $x > 0$. Inset indicates the superconducting behavior for the nominal $\text{NbB}_2$ sample. (b) Plot of transition temperature $T_c$ as a function of the Nb-deficient level in $\text{Nb}_1-x\text{B}_2$. 

![Figure 2b](image2b.png)
satellite lines \( (m = \pm \frac{1}{2} \rightarrow \pm \frac{3}{2}) \) in Fig. 3. For powdered samples, as in our experiment, these lines appear as typical powder patterns, with distinctive edge structures corresponding to the quadrupole parameters. Since the first order quadrupole shift is the main effect shaping the satellite lines, the quadrupole frequency, \( \nu_q = 1.4 \pm 0.1 \) MHz, was determined directly from the separation of these lines. This value is consistent with the previous value for NbB\(_2\) reported by Kote-gawa et al.\(^{27}\)

\(^{93}\)Nb Knight shift (\(^{93}\)K) here was estimated from the position of the maximum of each spectrum with respect to an aqueous KNbCl\(_6\) solution reference.\(^{28}\) For these materials, the obtained \(^{93}\)K values are negative (\(-0.39\)%), indicative of a significant contribution from 4d states on the frequency shift since the hyperfine field associated with the core polarization via 4d electrons is negative.\(^{29–31}\) While associating the frequency shift with specific electronic changes is usually complicated by undistinguished quadrupole and orbital terms, the spin-lattice relaxation rate (1/T\(_1\)) is comparatively simple due to the domination by core polarization, thus providing a directly quantitative probe of Fermi surface changes.

The spin-lattice relaxation time measurements were carried out using the inversion recovery method. We recorded the signal strength by integrating the recovered spin echo signal. In these experiments, the relaxation process involves the adjacent pairs of spin levels, and the corresponding spin-lattice relaxation is a multiexponential expression.\(^{32}\) For the central transition with \( I = \frac{9}{2} \), the recovery of the nuclear magnetization \( M \) follows

\[
\frac{M(t) - M(\infty)}{M(\infty)} = -2\alpha(0.152e^{-t/T_1} + 0.14e^{-6t/T_1} + 0.153e^{-15t/T_1} + 0.192e^{-28t/T_1} + 0.363e^{-45t/T_1}),
\]

\(1\)

derived from the initial conditions used in our experiments. Here \( M(t) \) is the magnetization at the recovery time \( t \) and \( M(\infty) \) is the magnetization after long time recovery. The parameter \( \alpha \) is a fractional value derived from the initial conditions used in our experiments. The \( T_1 \) value was thus obtained by fitting into this multiexponential recovery curve. The observed temperature dependence of 1/T\(_1\) for Nb\(_{1-x}\)B\(_2\) is displayed in Fig. 4. For all studied compositions, the Korringa behavior (constant \( T_1/T \) (Ref. 33) is identified by straight lines, confirming that conduction electrons are responsible for the observed relaxation.

According to band structure calculations,\(^{21,23,34–36}\) the \( s \)-contact electrons have an insignificant contribution to \( T_1 \), and the orbital part is also negligible due to little orbital mixing. Therefore, the experimental 1/T\(_1\) is simply proportional to the square of the Nb 4d Fermi level DOS as

\[
\left( \frac{1}{T_1} \right) = 2\hbar \gamma_e H_{hf}^d N_d(E_F) T_1.
\]

\(2\)

Here \( \gamma_e \) is the Nb nuclear gyromagnetic ratio, \( H_{hf}^d \) is the hyperfine core-polarization field per Nb 4d electron at the Fermi level, and \( N_d(E_F) \) is the Nb 4d Fermi level DOS in units of states/eV spin. Taking \( H_{hf}^d \approx 2.1 \times 10^3 \) G in Nb-based metals,\(^{28}\) and experimental 1/T\(_1\) for each individual composition can be extracted from Eq. (2) with results summarized in Table I. For NbB\(_2\), the deduced \( N_d(E_F) = 0.75 \) states/eV f.u. is in good agreement with the values of 0.61–0.82 states/eV f.u. obtained from theoretical calculations.\(^{21,23,34,36}\) To have a clear view of the change in \( N_d(E_F) \) vs. \( x \) in Fig. 5, the result shows large \( N_d(E_F) \) values in Nb\(_{0.74}\)B\(_2\) and Nb\(_{0.80}\)B\(_2\) while the lowest one appears in Fig. 4. (Color online) Temperature-dependent \(^{93}\)Nb spin-lattice relaxation rate of Nb\(_{1-x}\)B\(_2\).

![Nb\(_{1-x}\)B\(_2\) NMR central transition and first satellite line shapes of Nb\(_{1-x}\)B\(_2\).](image-url)

![Temperature-dependent 93Nb spin-lattice relaxation rate of Nb\(_{1-x}\)B\(_2\).](image-url)

### Table I. Partial Nb 4d Fermi level DOS in units of states/eV f.u. for each studied composition of Nb\(_{1-x}\)B\(_2\).

<table>
<thead>
<tr>
<th>( x )</th>
<th>0</th>
<th>0.13</th>
<th>0.20</th>
<th>0.26</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N_d(E_F) )</td>
<td>0.75</td>
<td>0.51</td>
<td>0.86</td>
<td>0.85</td>
</tr>
</tbody>
</table>
Nb_{0.87}B_{2}. This observation is consistent with a substantial reduction in \( N_\delta(E_F) \) predicted for Nb_{0.87}B_{2} by Shein and Ivanovskii. It should be noted that such a tendency does not correlate with the \( T_c \) trend of Nb_{1-x}B_{2}, implying no direct relevance between the superconductivity and the electronic Fermi level DOS.

As mentioned, the Seebeck coefficient measurement can also qualitatively provide an insight into the electronic band feature around the Fermi level. Here the Seebeck coefficients were measured with a dc pulse technique. Seebeck voltages were detected using a pair of thin Cu wires electrically connected to the sample with silver paint at the same positions as the junction of differential thermocouple. The electrical lead contribution has been subtracted from the measured Seebeck coefficient and thus the data shown below are the absolute Seebeck coefficient. The stray thermal emfs are connected to the sample with silver paint at the same positions being consistent with the previous result for NbB_{2}. Upon heating, intrinsic electrons and holes are excited. If the holes have a slightly higher mobility than the electrons in these materials, the \( p \)-type carriers will eventually govern the thermal transport, leading to sign reversal in \( S \) at high temperatures. It is noted that a plateau was consistently observed around 30 K in these Nb_{1-x}B_{2} compounds, ascribed to the phonon-drag effect. The phonon-drag peak is commonly seen in metals and is generally active at low temperatures.

From the \( 1/T_1 \) analysis, we provided clear evidence that \( N_\delta(E_F) \) initially decreases with increasing Nb deficiency. After passing through a minimum value at \( x \approx 0.13 \), \( N_\delta(E_F) \) begins to increase with \( x \) in Nb_{1-x}B_{2}. Also the observed evolution of the Seebeck coefficient can be understood according to this tendency. Remarkably, such a feature is in good agreement with the prediction from band structure calculations based on the existence of the Nb vacancies in the Nb-deficient Nb_{1-x}B_{2} samples. These calculations indicated a notable pseudogap, about 1 eV below \( E_F \), which locates at the antibonding states for NbB_{2}. By removing Nb from stoichiometry, \( E_F \) will shift toward the low energy side accompanied by the decrease in \( N(E_F) \). With further reduction in Nb content, \( E_F \) falls into the pseudogap and then enters the bonding states with a larger \( N(E_F) \). In these respects, the band structure of Nb_{1-x}B_{2} can be qualitatively interpreted in terms of a rigid-band scenario without considering the detailed band-edge modification due to disorder-induced band broadening. Apparently, these facts are in contradiction with the picture of the formation of the B dimers at the Nb sites in Nb_{1-x}B_{2}.

\[
|S| \propto \frac{1}{N(E_F)} \left| \frac{\partial N(E)}{\partial E} \right|_{E=E_F}.
\]

Based on this relationship and DOS curves from calculated band structures of Nb_{1-x}B_{2}, very small \( |S| \) values in Nb_{0.74}B_{2} and Nb_{0.80}B_{2} can be connected to their large \( N(E_F) \) while a relative high \( |S| \) in NbB_{2} is attributed to its steep
the nonstoichiometric Nb$_{1-x}$B$_2$ samples where a systematic increase in the electronic Fermi level DOS with $x$ has been predicted.  

III. CONCLUSIONS

We have a concise picture of NMR features for Nb$_{1-x}$B$_2$, giving a viewpoint for their microscopically electronic properties. An analysis of the spin-lattice relaxation rate provides an estimate of the Nb $4d$ Fermi level DOS of each individual composition. Agreement is obtained for the deduced properties. An analysis of the spin-lattice relaxation rate provides

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