Electronic stiffness of a superconducting niobium nitride single crystal under pressure

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We report a quantitative study of pressure effects on the superconducting transition temperature \( T_c \) and the electronic stiffness of niobium nitride. It is found that \( T_c \) increases initially with pressure and then saturates up to 42 GPa. Combining phonon and structural information on the samples obtained from the same single crystal, we derive a nonmonotonic pressure dependence of the electronic stiffness, rising moderately at low pressure while dropping slightly at high pressure. The theory of Gaspari and Gyorffy is found to reproduce the observed low-pressure results qualitatively but fails to predict the high-pressure data. The observed pressure effect on \( T_c \) is attributed to the pressure-induced interplay of the electronic stiffness and phonon frequencies.

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I. INTRODUCTION

High-pressure studies have been crucial for tuning the superconducting transition temperatures \( T_c \)'s of materials, pursuing new classes of superconductors and shedding light on the theory of superconductivity. Over many decades, there has been no agreement regarding which of the quantities—the electronic stiffness \( N(E_F)/(\hbar^2) \) or the lattice stiffness \( M(\omega^2) \)—determines the pressure dependence of \( T_c \) in a narrow-band superconductor to a greater degree [\( N(E_F) \) is the density of states per cell at the Fermi energy \( E_F \), \( \langle \hbar^2 \rangle \) is the mean-square electron-ion interaction matrix element, \( M \) is the atomic mass, and \( \langle \omega^2 \rangle \) is a weighted mean square of the phonon frequency].

The importance of \( N(E_F)/(\hbar^2) \) was first addressed by Hopfield in the theoretical study of the pressure effect in lanthanum, where the drastic increase in \( T_c \) under pressure is primarily attributed to the pressure-induced increase of \( N(E_F)/(\hbar^2) \). The determination of \( N(E_F)/(\hbar^2) \) strongly depends on accurate measurements of both \( T_c \) and the phonon spectra. The theory of Gaspari and Gyorffy has been proven to be very powerful in predicting \( N(E_F)/(\hbar^2) \) for many transition metals and compounds. However, the absence of experimental determination of \( N(E_F)/(\hbar^2) \) at high pressure makes a comparison between the theory and experiments difficult. Experimental attempts in this direction are therefore highly desirable not only for understanding the pressure effect on \( T_c \) itself but also for examining whether the theory applies to high-pressure conditions.

When investigating the pressure dependence of \( N(E_F)/(\hbar^2) \), one needs to determine the pressure-induced phonon frequency shift and the pressure dependence of \( T_c \), and assumes that the Coulomb pseudopotential \( \mu^* \) depends weakly on pressure. A direct experimental determination of phonon frequency can be made by measuring the electron-phonon coupling strength \( \alpha^2(\omega)F(\omega) \) at different pressures by tunneling. Unfortunately, such measurements are exceedingly difficult for transition metals and their alloys and compounds, even at atmospheric pressure, and they have not yet been attempted at high pressure. The measurement of the pressure dependence of the phonon density of states \( F(\omega) \) by inelastic neutron scattering is also capable of providing good values of phonon frequencies. However, few neutron studies of the pressure dependence of phonon frequencies have been reported.

On the other hand, experimental studies of some transition metals have shown that higher pressures sometimes give rise to a more complicated dependence of \( T_c \) than that at low pressure. The presence of such a nonmonotonic dependence of \( T_c \) calls for experiments in the region of high pressures to see how \( N(E_F)/(\hbar^2) \) and/or \( M(\omega^2) \) determine the pressure behavior of \( T_c \).

In this paper we address these issues by investigating pressure effects on niobium nitride. We report measurements of the pressure dependence of \( T_c \) in a single crystal up to 42 GPa. Combining the determined phonon and structural information on the samples that were separated from the same single crystal, we are able to obtain direct information on the pressure dependence of the electronic stiffness. We also calculate the electronic stiffness as a function of pressure up to 30 GPa based on the theory of Gaspari and Gyorffy. There is a qualitative agreement between the experiment and theory at low pressures but a large discrepancy for high-pressure data. We show that the pressure-induced interplay of the electronic stiffness and phonon frequencies is responsible for the pressure dependence of \( T_c \) in this material.

II. EXPERIMENT

Single crystals of NbN were grown from sintered rods using a zone-melting and zone-annealing technique, as described in detail elsewhere. Plate-shaped crystals were separated mechanically from the bar. X-ray diffraction confirmed that NbN has the sodium chloride (B1) structure with a lattice constant \( a_B \) of 4.379 Å at ambient condition. The composition was determined to be NbN\(_{0.99(1)}\) from gravimetric chemical analysis. The measurements of \( T_c \) under pres-
sure were performed using a highly sensitive magnetic susceptibility technique. Hydrostatic pressure was generated in a Mao-Bell diamond anvil cell. Neon was loaded into the gasket to serve as the pressure medium. Pressure at low temperatures was determined by the $R_1$ fluorescence line of ruby.

III. RESULTS AND ANALYSIS

Figure 1 shows representative temperature scans at different applied pressures for a NbN$_{0.90(1)}$ single crystal. The superconducting transition is identified as the temperature where the signal goes to zero on the high-temperature side which is the point at which magnetic flux completely enters the sample. The superconducting transition of 12.4 K is obtained at ambient pressure, which is in good agreement with previously reported values of samples with similar compositions. The transition temperature weakly depends on the applied pressure. At high pressures the shape of the signal does not change.

Figure 2 shows the experimental transition temperature as a function of pressure. There is a roughly linear dependence of the transition with applied pressure up to 4 GPa. The initial pressure derivative of $T_c$, $dT_c/dP$ ($\sim$0.03 K/GPa) is in good agreement with the value of 0.04 K/GPa reported previously for NbN$_{0.92}$ (Ref. 18). Measurements at higher pressures are of special interest as the transition temperature is observed to level off from 4 to 42 GPa. This behavior is very similar to observations of Nb, where the $T_c$ is nearly constant from 10 to 70 GPa. This similarity suggests that $d$ states dominate superconductivity at high pressure in such transition metals and their compounds. There are no reports of anomalies in compressibility and elastic constants of NbN over a wide pressure range. Until now, exact information about the phonon spectrum of niobium nitride under high pressure from neutron scattering or tunneling experiments has not been available. However, we have found that the pressure-induced phonon frequency shifts can be well determined from Raman scattering measurements because of a good agreement between the phonon density of states obtained from neutron scattering and the Raman response. The phonon frequency determined from Raman scattering for NbN was found to decrease with increasing pressure after passing through a maximum at around 20 GPa. It is indicated that the variation of $\langle \omega^2 \rangle$ with pressure alone is not adequate for a complete description of the observed pressure effect on $T_c$ in this material. One should also note that the pressure behavior in NbN appears to agree with the chemical trends in structural properties proposed by Phillips. Since pressure drives the crystal towards short-wavelength instabilities, $T_c$ is expected to increase until reaching saturation, although $\langle \omega^2 \rangle$ may not necessarily increase under pressure.

The primary determinant of $T_c$ is the electron-phonon coupling constant $\lambda$. The direct dependence of $\lambda$ on the electronic characteristics can be taken into account by the electronic stiffness $N(E_F)\langle \bar{F}^2 \rangle$. We have performed first-principles calculations using the all-electron linearized augmented plane-wave (LAPW) method within the local density approximation (LDA). The $k$-point mesh is of $16 \times 16 \times 16$, and the convergence parameter $RK_{\text{max}}=8.0$. The calculated zero-pressure equilibrium lattice constant $a_0$ is 4.360 Å. The theoretical pressure is thus rescaled to fit the experimental value of $a_0$. The density of states $N(E)$ derived from the tetrahedral method at three selected pressures for stoichiometric NbN is shown in Fig. 3. The general shape and relative magnitude of the peaks agree quite well with previous theoretical calculations. The Fermi energy $E_F$ is about 4 eV above $\Gamma_{15}$ and occurs within the $\bar{t}_{2g}$ manifold of the niobium 4$d$ bands. The peak of the density of states for the higher bands is at 2.0 eV above $E_F$. The dominant effect of pressure on $N(E)$ is a broadening of the bands and the resulting decrease of $N(E)$ in most energy regions. The density of states at $E_F$, $N(E_F)$, decreases from 0.85 eV$^{-1}$ cell$^{-1}$ at ambient pressure to 0.72 eV$^{-1}$ cell$^{-1}$ at 50 GPa (inset of Fig. 3). We have estimated the contributions of states of different symmetry to the density of states at the Fermi level. It turns out that for NbN the contribution of $d$-type states to $N(E_F)$ substantially exceeds those of the $s$ and $p$ states. This shows that mainly $d$ states are responsible for the superconductivity

FIG. 1. Magnetic susceptibility signal vs temperature for a NbN$_{0.90(1)}$ single crystal at various pressures. The superconducting transition temperature $T_c$ is marked by an arrow.

FIG. 2. Dependence of the superconducting transition temperature $T_c$ on pressure in a NbN$_{0.90(1)}$ single crystal. The error bars give the transition onset uncertainty. The solid curve is a fit to the experimental data.
over the pressure range studied. Similar behavior has also been reported previously by Palanivel et al.\textsuperscript{23} from band structure calculations. Their predicted $T_c$ behavior under pressure is in contrast with our measurements. Therefore neglected.\textsuperscript{2} However, an analysis of magnetostriction data\textsuperscript{25} reveals that $\mu^*$ does change with volume (pressure), usually in the sense of decreasing $\mu^*$ with decreasing volume. The pressure enters $\mu^*$ as $\mu^*(P)=\mu(0)/[1+\mu(0)\ln(\beta(0))]$ through the screened Coulomb interaction $\mu=0.5\ln[(1+\alpha^2)/\alpha^2]$ and $\beta=E_F/\omega_{pb}$ with $a^2=\pi e^2\hbar^2N(E_F)/k_F^2$ and $\omega_{pb}$ a characteristic phonon frequency.\textsuperscript{26}

Considering that $k_F=[3\pi^2/2\Omega]^{1/3}$ and $E_F=\hbar^2k_F^2/2M$ with $\Omega$ the atomic volume and $Z$ the valence, one can write $\beta(E_F)=\beta(0)\omega_{pb}(0)/\omega_{pb}(E_F)\Omega(0)/\Omega(P)^{1/3}$ and $a^2(E_F)\Omega(0)/\Omega(P)^{1/3}$.

Geballe et al.\textsuperscript{27} reported a value of $\Theta_D=331$ K from low-temperature heat capacity measurements of a NbN\textsubscript{0.86}. This value is similar to the reported $\Theta_D=320(25)$ K for a NbN\textsubscript{0.90(1)} single crystal.\textsuperscript{13} Therefore, we believe that a choice of 331 K for $\Theta_D$ is reasonable for the present investigation. Substituting this value along with the experimentally determined $T_c(0)$ into Eq. (1), we obtain $\lambda(0)=0.87$.

\begin{figure}
\centering
\includegraphics[width=0.45\textwidth]{Figure3}
\caption{(Color online) Plot of the calculated density of states vs energy of NbN at different pressures. Inset: density of states at the Fermi level $N(E_F)$ as a function of pressure in NbN. The solid line is a fit to the calculated data.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=0.45\textwidth]{Figure4}
\caption{Pressure dependence of the phonon frequency of the acoustic branch ($\omega_{ac}^2$) in a NbN\textsubscript{0.90(1)} single crystal deduced from high-pressure Raman data (Ref. 19). The solid curve is a fit to the data points.}
\end{figure}

Taking a typical value of 0.4 for $a^2(0)$ (Ref. 26), one then obtains $\beta(0)$ of 448 for the material studied. These parameters determined at ambient condition will be used to determine the high-pressure behavior of $N(E_F)(F^2)$.

In NbN, the mass of the metal $M_{Nb}$ is apparently larger than that of the nitrogen $M_N$. The ratio between them is equal to the ratio between the average square of phonon frequencies in the optical branch $\langle \omega_{op}^2 \rangle$ and in the acoustic branch $\langle \omega_{ac}^2 \rangle$ expected from nearest-neighbor forces.\textsuperscript{28} Thus, the information on the change in $\langle \omega^2 \rangle$ can be obtained from the shift in phonon frequency $\omega_{ac}$ or $\omega_{op}$ due to the relation $\langle \omega_{ac}^2 \rangle \approx (2M_{Nb}/M)^{1/2}\langle \omega_{ac}^2 \rangle \approx (2M_{N}/M)^{1/2}\langle \omega_{op}^2 \rangle^{1/2}$ (Refs. 27, 19, 28, and 29). Our Raman studies of NbN\textsubscript{0.90(1)} single crystal\textsuperscript{19} showed that the low-frequency acoustic branch is more pronounced and broadened compared to the optical branch. Such a feature leads us to conclude that the frequency of the acoustic phonon branch would provide more accurate information than that of the optical branch. Using the approximation calculation of $\langle \omega^2 \rangle = \int \omega F(\omega) d\omega / \int \omega^{-1} F(\omega) d\omega$ (Ref. 29), we deduce the values of $\langle \omega_{ac}^2 \rangle^{1/2}$ under various pressures based on the Raman scattering data corrected for background contribution in the wave number range of 50–400 cm\textsuperscript{-1} (Ref. 19). The pressure behavior of $\langle \omega_{ac}^2 \rangle^{1/2}$ is shown in Fig. 4.

Assuming that both $\Theta_D$ and $\omega_{pb}$ are proportional to $\langle \omega^2 \rangle^{1/2}$ and that $\langle \omega_{ac}^2 \rangle^{1/2} \approx \langle \omega_{ac}^2 \rangle^{1/2}$, we obtain the pressure dependence of these quantities through $\langle \omega_{ac}^2 \rangle^{1/2}$. Previously, we determined the pressure dependence of the lattice constant in a NbN\textsubscript{0.90(1)} single crystal.\textsuperscript{14} Using these high-pressure relations along with the determined $T_c(P)$ and $N(E_F)(P)$ data taken to 30 GPa, we can evaluate the pressure dependence of $N(E_F)(F^2)$ based on the equations developed above (Fig. 5). As can be seen, $N(E_F)(F^2)$ increases as expected to a maximum value at $\sim 20$ GPa where it is about 7% greater than its zero-pressure value and then begins to decrease slightly at higher pressure. This is the central result of the present work. The high-pressure behavior of $N(E_F)(F^2)$ is very similar to that of $\langle \omega_{ac}^2 \rangle^{1/2}$, with a maximum value at almost pres-
This monotonic pressure dependence of $N(E_F)(F^2)$ was also theoretically observed in lanthanum. The RMTA assumes that the $d$-wave function of the transition metal is strongly peaked and confined inside the muffin tin, so that the change in potential of the interstitial region has small effect on the $d$ electrons. With increasing pressure, the $d$-wave function extends more outside the muffin tin region, and therefore the RMTA becomes less accurate at high pressures. More accurate theoretical studies are necessary to bring theory into agreement with experiment at high pressure.

Our experimental data for NbN provide an estimate of the electronic stiffness, which agrees with the theory of Gaspari and Gyorffy over roughly half the pressure range studied. It should be emphasized that the experimental curve plotted in Fig. 5 does not include errors in measurements. Considering the errors of $T_c(P)$ within 2% and $\langle \omega^2 \rangle^{1/2}$ within 0.5%, we may have the $N(E_F)(F^2)$ errors less than 1.6%. Note that there exist systematic errors in Raman measurements. These errors may contribute to the pressure dependence of the phonon density of states. Since the same calculation procedure was used to derive $\langle \omega^2 \rangle$ after correcting for the background contribution over a wide wave number range, we believe that the pressure dependence of $\langle \omega^2 \rangle$ should not be altered due to systematic errors. An estimate of 0.5% scatter of $\langle \omega^2 \rangle^{1/2}$ would fully cover errors in Raman measurements. Although there exists a deviation of $N(E_F)(F^2)$ at individual pressure points, the deviatoric $N(E_F)(F^2)$ does not change the tendency of its pressure dependence. Good agreement between the experiment and theory still remains up to 15 GPa, even if the experimental errors would be taken into account.

Unlike previous theoretical treatments,2,30 we have already considered the pressure-dependent electron-electron interaction through the standard Coulomb pseudopotential approximation for $\mu'$. For a narrow-band superconductor, $\mu'$ may play an important role in determining $T_c$ only if the applied pressure is sufficiently high.31 NbN is generally considered to be a standard narrow-band superconductor. Thus, all assumptions made for the parameters entering the standard expression for $\mu'$ are believed to be sufficient for providing a reliable estimate of $N(E_F)(F^2)$ over the pressure range studied. Richardson and Ashcroft32 have determined the effective electron-electron interaction for monovalent and low-density alkali metals such as hydrogen and lithium by a method which treats electrons and phonons on an equivalent footing. This treatment is probably essential for providing a more accurate estimate of transition temperatures at high pressure in such lower-density systems, which waits for further experimental examination. The fact that $T_c$ depends weakly on $N(E_F)$ in NbN over a wide pressure range indicates that the standard Coulomb pseudopotential approximation for $\mu'$ is physically plausible. The inclusion of the effective Coulomb interaction on a completely equal footing with the phonon-mediated interaction may not greatly affect the behavior of $N(E_F)(F^2)$ for NbN under pressure.

V. CONCLUSION

We have measured the superconducting transition temperature of niobium nitride under pressure up to 42 GPa. We
observe that $T_c$ increases initially with pressure and then saturates at around 4 GPa. Combining the phonon and structural information determined previously by Raman scattering and x-ray diffraction, we obtain the pressure dependence of the electronic stiffness in terms of the McMillan theory. We find that the electronic stiffness rises moderately at low pressure but drops slightly at high pressure. Our low-pressure results are in qualitative agreement with predictions from the theory of Gaspari and Gyorffy, but the high-pressure data differ markedly from theory. Our results follow that the interplay of the counteracting changes in the electronic stiffness and phonon frequencies due to pressure is responsible for the observed pressure effect on $T_c$ in this material.

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