

Ultrasonic Measurements in Normal and Superconducting Niobium

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Phonon attenuation versus temperature measurements have been made on single-crystal niobium from 1.3 to 10°K for longitudinal phonon frequencies of 30 and 220 Mc/sec using the echo technique. In addition, the frequency dependence of the normal attenuation at 1.42°K has been determined from 30 Mc/sec to approximately 450 Mc/sec. Finally, time-of-flight shear and longitudinal measurements have been made at 4.2°K and 30 Mc/sec. By averaging numerous experimental points it has been calculated that the superconducting energy gap is $(3.63 \pm 0.06)kT_c$ for sound propagation along the [100], [110], and [111] crystallographic axes; that the normalized gap varies more strongly with the reduced temperature near T_c than is predicted by the BCS theory; that the Debye temperature at 4.2°K is $(271 \pm 5)^\circ\text{K}$, as calculated from the computed elastic constants; and that the ratio of superconducting-to-normal attenuation falls below the value predicted by BCS as the temperature is increased towards T_c for the 30-Mc/sec phonons. The attenuation varied as the square of the frequency below 110 Mc/sec, while for the higher frequencies the dependence on frequency decreased. Thus, at 220 Mc/sec, $ql \sim 1$. The samples were grown by an electron beam zone refining technique; and from well-oriented samples, experimental crystals were selected on the basis of mass spectrographic analyses and by measurements of T_c by the ultrasonic method. A typical acceptable sample was at least 99.8% pure and had $T_c = (9.15 \pm 0.02)^\circ\text{K}$. Other typical values were a resistivity ratio of 520 ± 50 and upper critical magnetic fields of 1710 ± 20 Oe and 2020 ± 20 Oe at 4.2 and 1.4°K, respectively. The results are briefly discussed in terms of several models and calculations which have been reported in the literature.

INTRODUCTION

THE experimentally determined temperature dependence of the increase in the attenuation of longitudinal acoustic waves in a superconductor, as the temperature is increased through the critical temperature, is explained satisfactorily by the Bardeen, Cooper, and Schrieffer (BCS) theory¹ for many nontransition series elements when the wavelength of the externally introduced elastic wave is comparable with the electronic mean-free-path; that is, when $ql \sim 1$, where q is the phonon wave vector and l is the electronic mean-free-path.² Measurements on some of the same elements for the case when $ql < 1$ ^{2,3} show discrepancy not only with the BCS result but also with the more recent treatment of ultrasonic attenuation in superconductors by Tsuneto.⁴

For the case of superconducting elements in the transition series, the situation is even less definite because of the imprecise phonon attenuation data which have been available—no doubt a reflection of the difficulty in obtaining reasonably pure samples, especially of niobium. Nevertheless, since niobium has the highest zero-field transition temperature, the highest zero-degree critical magnetic field, and is the hardest of the known superconducting elements, it was deemed worthwhile to spend considerable time in securing useful single-crystal specimens of niobium in order to determine if its behavior deviates from the BCS predictions;

and if deviations should occur, to see how well they can be explained by the various modified models of the superconducting state, using electron-electron matrix elements which have been modified in form and strength, that have been developed since the BCS theory.

EXPERIMENTAL

The ultrasonic pulse-echo technique is well known²; therefore, it will be discussed briefly in terms of the actual experiment. Radio frequency pulses of the desired ultrasonic frequency (30 Mc/sec to 500 Mc/sec), of 1.0- μ sec duration, with a repetition rate of 60 cps are impressed across a quartz transducer (X cut except for one velocity measurement) bonded to the flat end-face of a cylindrical niobium sample. The rf electric field pulse, with the oscillator tuned to the fundamental or odd harmonic frequency of the piezoelectric transducer causes it to produce a pulse of ultrasound that passes into the specimen. This pulse, repeatedly reflected from the far end of the specimen, returns after each reflection to the transducer to produce a voltage across the same electrodes which impressed the initial rf pulse across the quartz. A radar receiver picks up this small voltage, amplifies and video detects it. The detected signal is displayed on the screen of an accurately calibrated oscilloscope as a spectrum of almost exponentially decaying echoes. The change in height of the echoes with time is a measure of the total attenuation of the phonons in the sample, bonding-material, and transducer system; the spacing between echoes is a measure of the velocity of propagation of the sound wave packet. Fortunately, attenuation effects other than the attenuation due to the conduction electrons in the specimen can be subtracted off in this experi-

* Operated with support from the U. S. Air Force.

¹ J. Bardeen, L. Cooper, and J. Schrieffer, *Phys. Rev.* **108**, 1175 (1957).

² R. W. Morse, in *Progress in Cryogenics* (Heywood and Company Ltd., London, 1959), Vol. 1.

³ R. Morse, H. Bohm, and J. Gavenda, *Bull. Am. Phys. Soc.* **3**, 44, 203 (1958).

⁴ T. Tsuneto, *Phys. Rev.* **121**, 402 (1961).

ment, as will become clear when the treatment of the data is discussed.

Approximately 120 dB of isolation, eliminating receiver saturation, was achieved between the initial rf excitation pulse and the input to the radar receiver by the use of adequate shielding, a directional coupler, and a tandem arrangement of switching diodes before the input to the receiving system.

The load represented by the specimen-transducer system was matched to the system to give the maximum number of echoes for a given pulse input voltage (of the order of 1 V, peak to peak) by the use of a quarter wavelength stub and adjustable coaxial line. At the higher frequencies, i.e., above about 100 Mc/sec, improved matching was obtained by the use of a small (0–20 mmF) piston-type capacitor directly across the transducer electrodes (the specimen and a metallic coating on one side of the transducer).

The system was calibrated by feeding pulses of the proper frequency through the entire receiving system and attenuating them in a known fashion. This procedure was carried out for all combinations of frequency range and gain settings of the receiver and oscilloscope which were employed, and was repeated periodically.

For a rough check of the sample geometry, the transducer flatness, and the bond, an adjustable exponential decay pattern was displayed on the screen of the viewing oscilloscope. Once reasonable concurrence between the tips of the echoes and a decay pattern was obtained, more careful measurements were performed taking into account the calibration of the system. No data were recorded for any group of echoes that was not closely exponential over its lifetime.

The quartz transducers used for the attenuation measurements were X cut, gold-plated on one side, clear-polished, 0.1 in. in diameter, and of nominal fundamental frequencies ranging from 15 to 67 Mc/sec. Satisfactory transducers were selected according to their response to overtone excitation and according to their effect on the shape of the echo spectrum. From one to another, they varied considerably in both regards.

Temperature control of at least $\pm 0.02^\circ\text{K}$ for periods of 5 min was realized over the range from 1.3 to 11°K by the use of an already described quadruple Dewar system⁵ and mechanical pump. The temperature was determined by carbon resistance thermometry, a McLeod gauge, and a gold-cobalt thermocouple junction referenced at the lowest temperature of the run ($\approx 1.3^\circ\text{K}$). Calibration points for the carbon resistance and thermocouple were obtained below 4.2°K by the McLeod gauge, at 4.2°K by the helium bath, and above 4.2°K by comparison with an accurately calibrated germanium resistor. The carbon resistance and the thermocouple junction were fastened directly to the wall of the cylindrical specimen which was placed with

the axis of the cylinder perpendicular to the wall of the Dewar. Whenever there was inconsistency among the various methods for temperature determination, the data were discarded.

A complete attenuation run consisted of increasing the temperature from 1.3°K to above 10°K in approximately 0.1°K steps. At each step, once temperature stability was attained, an attenuation reading was taken using the maximum number of echoes possible (approximately 12 in the superconducting state at 1.3°K). This procedure was repeated up through 10 or 11°K . Then, the temperature was reduced to 1.3°K by pumping on the helium bath. Once temperature equilibrium was reached, a transverse dc magnetic field of greater than 7000 Oe was applied to the specimen. This made the sample normal and an attenuation versus temperature run was made once again, but in steps of approximately 0.5°K , up to 10 to 11°K . For this situation, especially at the higher phonon frequencies, there were few echoes (two or three) available for measurement purposes. Fortunately, over this same range the attenuation was approximately constant.

With the above data, it was possible to determine a zero-field transition temperature as given by the coincidence of the normal attenuation α_n and the superconducting attenuation α_s .

The time-of-transit measurements were made by superposing a sinusoidal reference trace on the echo spectrum display so that there was an integral number of cycles between the "first" and the "last" echo. The frequency and number of cycles of the sinusoidal voltage in conjunction with the effective length of the sample (twice the length of the sample multiplied by one less than the number of echoes used) determines the velocity of propagation of the phonons. With this simple scheme, accuracies of the order of 0.2% can be obtained in the velocity measurements which is adequate for calculating the elastic constants from which the Debye temperature θ_D can be computed.

The single-crystal niobium samples were grown by a floating-zone electron beam technique.⁶ As received, the specimens were right circular rods, 2 in. in length and $\frac{1}{4}$ in. in diam. They were oriented with either the [100], [110], or [111] crystallographic axes along the cylindrical axes of the rods. The nominal error in orientation was of the order of $\pm 2^\circ$ or $\pm 3^\circ$. The relative zero-field transition temperatures T_c of the various specimens were determined by inserting them in the core of an inductor in a tank circuit which resonated at 100 kc/sec, and noting the sharp change in its Q as the temperature was reduced to 4.2°K . Those samples with definitely lower T_c were eliminated from further consideration.

From among the remaining samples, one more selection was made based on mass spectrographic analyses

⁵ R. Weber and P. E. Tannenwald, Phys. Chem. Solids (to be published).

⁶ Specimens were obtained from Materials Research Corporation, Orangeburg, New York.

of small pieces cut from each rod. These analyses varied by as much as a factor of 20 in the ppm of Ta and W but were fairly uniform in the ppm of the other detectable impurities. The analyses were accurate to within a factor of 2 or 3. A typical analysis in ppm atomic read as follows: Na, 20; Si, 100; Cl, 10; K, 7; Fe, 20; Zn, 5; Ge, 5; Zr, 20; Pd, 5; Sn, 25; Hf, 6; Ta, 40; W, 70; Bi, 3; Al, 1; Hg, 30; Te, 10; Ti, 10; and Ca, 10. Nothing could be said about the presence of C, O, H, N, or S. If present, all other elements were in concentrations of less than 1 ppm.

Lengths of the order of 1.5 cm were then cut from each rod, oriented to within $\pm\frac{1}{2}^\circ$, and slowly ground so that the end faces were flat and parallel. The cutting and grinding was performed with the specimen kept at approximately 10°C . To remove any work hardening, each specimen was etched and x rayed until a clean Laue pattern was obtained. By trying combinations of transducers, bonds, and specimens, and by slightly roughening the sides of the specimens, it was possible to obtain exponentially decaying phonon attenuation behavior from at least one single crystal of each crystallographic orientation.

The echo technique itself provided the means by which a final selection was made. Since the attenuation in the normal state at 4.2°K and 200 Mc/sec was approximately the same from sample to sample, that sample within each group with the highest T_c was chosen to be used in subsequent experiments.

It was found that annealing the samples at 1400°C under a vacuum of 10^{-7} mm Hg for eighteen hours with six-hour warmups and cool-downs between 800 and 1400°C increased T_c by 0.05 to 0.10°K . T_c for the [111] sample was increased the maximum amount.

RESULTS

Figure 1 shows the attenuation of 220-Mc/sec longitudinal phonons propagating along the [100] axis as a function of temperature for several complete runs over both superconducting and normal phases of the specimen. The residual attenuation α_r , i.e., that which remains at 0°K in the superconducting state and is considered to be nonelectronic in origin, has been subtracted off. It was possible to determine accurately the value of α_r because the attenuation in the superconducting state from 2.2 to 1.3°K was found to be constant within an equipment sensitivity to changes of attenuation of 0.01 dB per phonon trip through the sample.

The residual attenuation, of the order of 10% of the normal attenuation for $t < 1.0$, is thought to be due to impurity scattering, sample-end effects, beam spreading, losses in the bond, and losses in the quartz transducer. The assumption that α_r is constant from 0 to 9.2°K is reasonable since the normal attenuation is constant over the same temperature range for 220-Mc/sec phonons. If one should imagine α_r to be an increasing function of increasing temperature, the calculated value

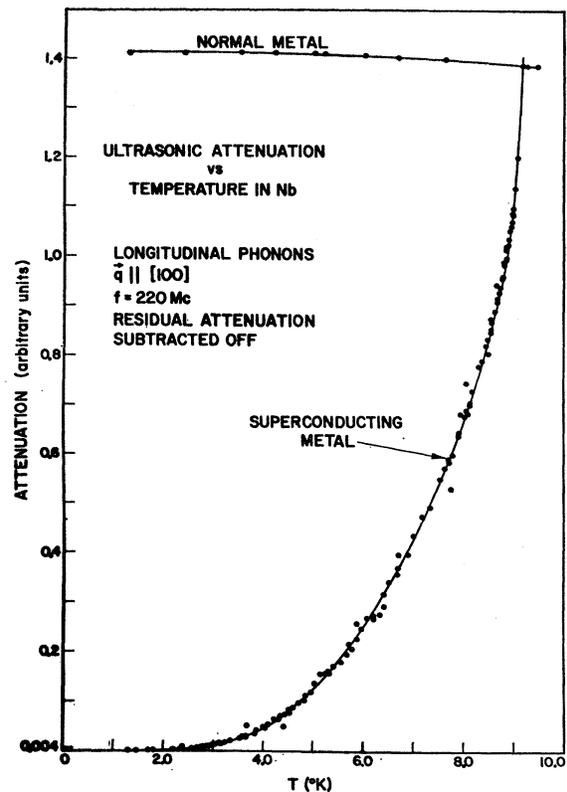


FIG. 1. Ultrasonic attenuation of 220-Mc/sec longitudinal phonons along the [100] crystallographic axis in normal and superconducting niobium metal as a function of temperature.

of the zero-degree superconducting energy gap would be larger than that found by assuming α_r to be constant. Of course, if some of the conduction electrons in niobium remain normal to 0°K , the entire subtraction procedure is invalid. However, since the same situation prevails in experiments on 'soft' superconductors,² the latter possibility seems to be remote. For the phonon wave vector \mathbf{q} along the [110] and [111] axes, similar results were obtained. From these data, it was determined that $T_c[100] = 9.16 \pm 0.02^\circ\text{K}$, $T_c[110] = 9.17 \pm 0.02^\circ\text{K}$, and $T_c[111] = 9.08 \pm 0.02^\circ\text{K}$.

Using the procedure just outlined, it was possible to measure the attenuation of longitudinal phonons propagating through niobium in the normal state as a function of frequency from 30.2 Mc/sec to 448.1 Mc/sec at 1.42°K . The results are shown in a log-log plot in Fig. 2 in terms of the attenuation normalized to 30 Mc/sec. The data shown are from the [100] sample. The [110] and [111] samples gave similar results ($\pm 1\%$). It is clear that the normal attenuation α_n is proportional to the phonon frequency squared, f^2 , up to about 130 Mc/sec. For the higher frequencies, the dependence of α_n on f is not as strong. This fact, coupled with the results of a complete attenuation run at 30.2 Mc/sec which exhibited a strong temperature dependence of α_n at the lower frequencies and little above about 150 Mc/sec,

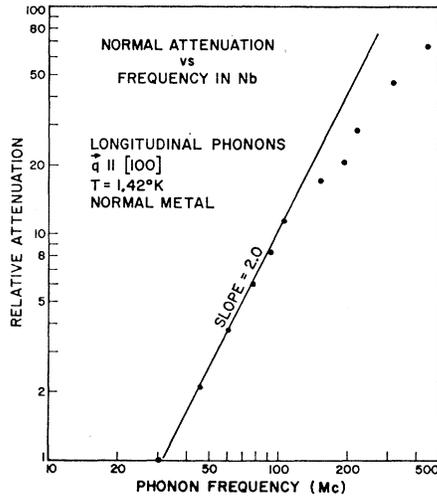


FIG. 2. Ultrasonic attenuation of longitudinal phonons in normal niobium metal at 4.2°K as a function of phonon frequency, normalized to 30.2 Mc/sec.

indicates⁷ that $ql \approx 1$ at 220 Mc/sec. Complete data were not collected for frequencies higher than 220 Mc/sec (where ql would have been larger) because it would have meant going to another technique or shortening the sample in order to circumvent the difficulties caused by the rather large, increasing attenuation.

Figure 3 presents a plot of the ratio of the superconducting attenuation to the normal attenuation, $\alpha' \equiv \alpha_s/\alpha_n$, versus the reduced temperature, $t \equiv T/T_c$. This information was taken from Fig. 2 for the [100] sample.

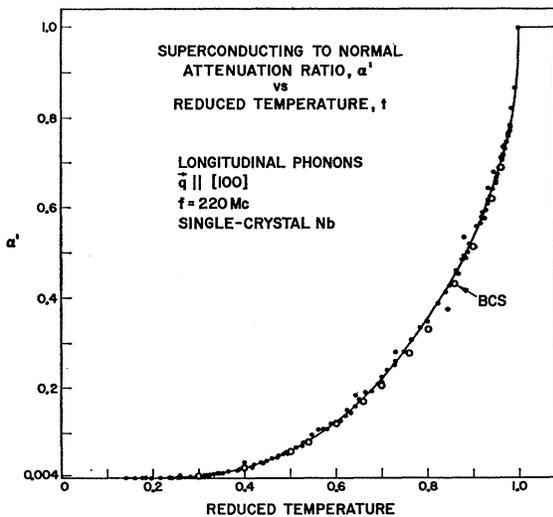


FIG. 3. Ratio of superconducting to normal longitudinal phonon attenuation in single-crystal niobium metal versus the reduced temperature for $T_c = 9.16^\circ\text{K}$. Open circles represent the BCS prediction for $\epsilon_0(0) = 3.63 kT_c$. Phonon propagation along the [100] crystallographic axis.

⁷ A. B. Pippard, *Phil. Mag.* 46, 1104 (1955).

BCS gives an expression for the variation of α' for longitudinal attenuation with t , which is a function of the temperature-dependent energy gap, $\epsilon_0(T)$:

$$\alpha' = \frac{2}{1 + \exp[\epsilon_0(T)/2kT]}, \quad (1)$$

where k is the Boltzmann constant.

Expression (1) may be rearranged to yield

$$t = \frac{\epsilon_0(T)}{4.606kT_c} \left[\frac{1}{\log((2/\alpha') - 1)} \right]. \quad (2)$$

With the experimentally determined $\alpha'(t)$, a plot of the bracketed factor versus t is given in Fig. 4. From this graph, knowing that the curve must pass through the origin, the slope of the curve as determined by the lower values of t yields the zero-degree superconducting energy gap. On the basis of several runs on each sample, the following results were obtained: $\epsilon_0(0) = 3.63 \pm 0.06 kT_c$ for each of the three directions of phonon propagation. Thus, within the limits of experimental accuracy, the gap is the same in all directions for 220-Mc/sec longitudinal phonons.

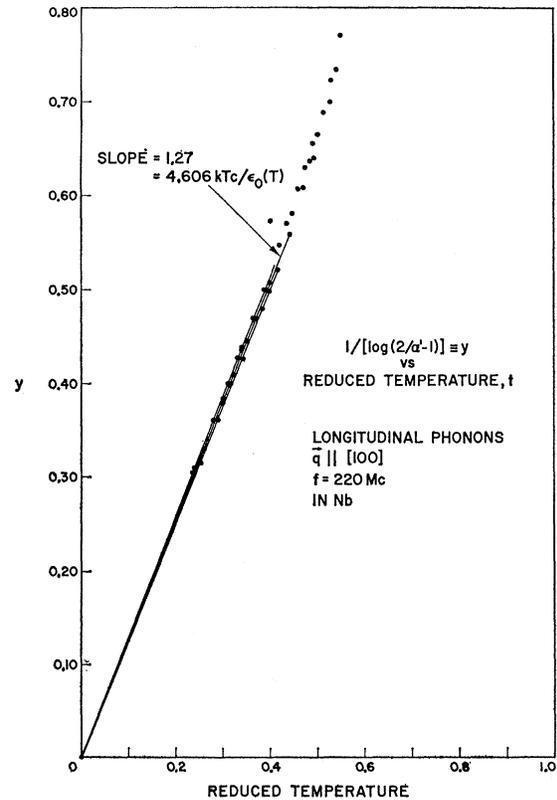


FIG. 4. Determination of the zero-degree superconducting energy gap, $\epsilon_0(0)$, for single-crystal niobium metal by plotting the BCS function $1/\log(2/\alpha' - 1) = (4.606 kT_c/\epsilon_0(t))t$ for small values of the reduced temperature, t .

With the determined $\mathcal{E}_0(0)$, a plot of the reduced energy gap, $\mathcal{E}_R \equiv \mathcal{E}_0(T)/\mathcal{E}_0(0)$ versus the reduced temperature t is presented as Fig. 5, along with the prediction of the BCS theory as to how the gap should open with decreasing t .

Returning to Fig. 3, the open points represent what one would expect from the BCS result for a zero-degree superconducting energy gap of $3.63 kT_c$. At 220 Mc/sec there is fair agreement between experiment and theory. However, at 30.2 Mc/sec, the α' versus t results fall below the BCS result from approximately $t=0.4$ to $t=1.0$.

The velocity of propagation measurements on the Nb samples yielded the following results at a nominal frequency of 30 Mc/sec.

For cubic crystals (Nb is bcc) there are well known⁸ relations for calculating the elastic constants in terms of the velocities v_1 , v_{31} , and v_{32} as presented in Table I. The results are, with a density of 8.44 ± 0.01 g/cm³ for Nb:

$$\begin{aligned} C_{11} &= (2.46 \pm 0.02)10^{12}, \\ C_{12} &= (1.34 \pm 0.04)10^{12}, \text{ and} \\ C_{44} &= (0.294 \pm 0.001)10^{12} \text{ dyn/cm}^2. \end{aligned} \quad (3)$$

With the results given in (3), v_2 was calculated to be $(4.98 \pm 0.04)10^5$ cm/sec, which compares favorably with the measured value of $(5.02 \pm 0.02)10^5$ cm/sec.

With the experimentally determined elastic constants of (3), the Debye temperature θ_D was calculated to be $271 \pm 5^\circ\text{K}$ by the method described by Anderson,⁹

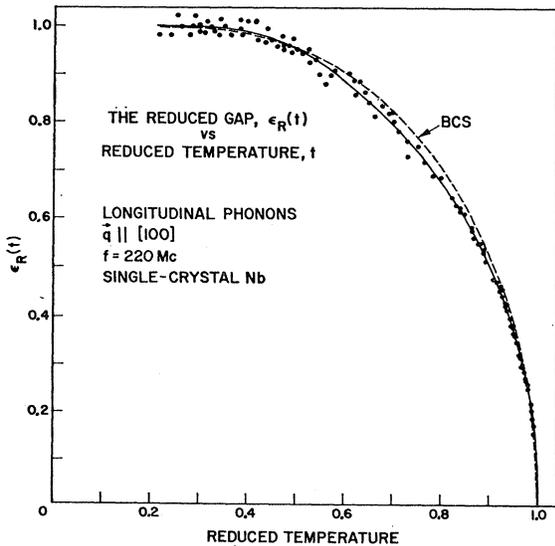


FIG. 5. Reduced energy gap in single-crystal niobium as a function of the reduced temperature as determined by longitudinal-phonon attenuation along the (100) direction for a phonon frequency of 220 Mc/sec. Dashed curve is the prediction of the BCS theory.

⁸ American Institute of Physics Handbook (McGraw-Hill Book Company, Inc., New York, 1957), 1st ed.

⁹ O. L. Anderson, Phys. Chem. Solids 24, 909 (1963).

TABLE I. The longitudinal and shear velocities of 30-Mc/sec phonons in niobium.

Propagation direction	Particle direction	Transducer cut	Velocity $\times 10^5$ cm/sec	Velocity symbol
[100]	[100]	X	5.41 ± 0.01	v_1
[111]	[111]	X	5.02 ± 0.02	v_2
[110]	[110]	X	5.10 ± 0.02	v_{31}
[110]	[100]	AC	1.865 ± 0.002	v_{32}

which allows one to estimate accurately the average sound velocity from single-crystal elastic constants. The appreciable inaccuracy in the result for θ_D is a reflection of the fact that the extreme elastic anisotropy of Nb is detrimental to the accuracy of the method of calculation. The ratio of T_c/θ_D , using $T_c=9.14^\circ\text{K}$ and the calculated θ_D is approximately 0.03.

COMPARISONS

In the formulation of the BCS theory of superconductivity, an essentially attractive interaction V between pairs of electrons with opposite spins and momenta is responsible for superconductivity. It is a basic approximation that only two-body correlations are responsible for the qualitative features of superconductivity and that they have a strong tendency to form zero-momentum singlet pairs. The interaction matrix element consists of a term due to the virtual exchange of phonons and a term due to a screened Coulomb interaction. An approximation in the theory is that V is assumed constant over a small energy range near the Fermi surface and zero elsewhere (which implies that the Fermi surface is isotropic). This approximation was necessary in order to readily obtain an analytic expression for the energy-gap function from a nonlinear integral equation containing V in the integrand. The good qualitative results that have been obtained by comparing many superconductors with the theory have been interpreted as meaning that even though superconductors have different phonon spectra and band structures, the superconducting properties do not depend very strongly on the form of V .

In the BCS paper, $N(0)V$ is a parameter that is a measure of the strength of coupling between pair states of relative momentum \mathbf{k}' and \mathbf{k} . In the coupling parameter, $N(0)$ is the density per unit energy of electrons of one spin at the Fermi surface. BCS considered the weak coupling limit, i.e., $N(0)V \ll 1$ or $T_c/\theta_D \ll 1$ in detail. They predicted that for T_c/θ_D smaller than 0.01, $\mathcal{E}_0(0) = 3.5 kT_c$. From their work, the behavior of the square of the reduced gap near T_c , can be shown to be

$$\mathcal{E}_R^2 = (\mathcal{E}_0(t)/\mathcal{E}_0(0))^2 = a(1-t), \quad (4)$$

with a equal to approximately 3.0 for the limiting case as $t \rightarrow 1$.

Experimentally, it has been found that $T_c/\theta_D \approx 0.03$, $\mathcal{E}_0(0) \approx 3.63 kT_c$, and $a \approx 3.2$. Even though we are no

longer in the weak coupling limit (where T_c/θ_D is <0.01 and $N(0)V \ll 1$), Figs. 3 and 5 indicate that the qualitative agreement is reasonably good. However, the deviations are of interest.

Thouless¹⁰ has considered the BCS formulation in the strong coupling limit, $N(0)V \gg 1$ ($T_c/\theta_D \rightarrow \infty$). He found in this limit that $\mathcal{E}_0(0)_{\text{max}} = 4.0 kT_c$ and the ratio $a(\text{weak coupling})/a(\text{strong coupling}) = 0.93$. For the ratio we have the very approximate value 0.94. It would seem that we are not in the strong coupling limit of the BCS model, but perhaps in an intermediate region.

More recently, Swihart¹¹ has attempted to determine if the results of the BCS theory are actually insensitive to the form of the interaction matrix V . By the use of a computer, the BCS integral equation was solved for $\mathcal{E}_0(0)$, the temperature dependence of the gap, and the electronic specific heat using a nonseparable square-well interaction that was a function of the energy difference between the electrons. For the intermediate coupling case, he computed $\mathcal{E}_0(0) = 3.63 kT_c$, $T_c/\theta_D = 0.023$, and $a = 3.18$. The agreement between these quantities and those found is interesting. It is of further interest to note that for indium, $T_c/\theta_D = 0.03$ and $\mathcal{E}_0(0) = 3.6 kT_c$.¹² Based on the electronic specific heat difference between the normal and superconducting states ΔC at $T = T_c$, given by¹¹

$$\frac{\Delta C}{\gamma T_c} = \frac{3}{4\pi^2} \left(\frac{2\mathcal{E}_0(0)}{kT_c} \right)^2 I a, \quad (5)$$

where γ is the heat capacity coefficient, and I is an integral over $\mathcal{E}_0(T)$, an additional check may be made. For the BCS approximation $I = 1/2$, while for Swihart's solutions $I < 1/2$. Using a value of $\Delta C/\gamma T_c \cong 1.8$ from Hirshfeld's data,¹³ and the experimental values of T_c and $\mathcal{E}_0(0)$, we calculate that $I \approx 0.53 \pm 0.05$, which is greater than the value 0.41 calculated for the intermediate coupling case.

The experimentally determined $\theta_D (271 \pm 5^\circ\text{K})$ for Nb compares with the value of 277°K found by Alers and Waldorf¹⁴ by ultrasonic measurements at 10 Mc/sec on specimens with unknown superconducting properties. Hirshfeld *et al.* found that $\theta_D \cong 245^\circ\text{K}$ from specific heat measurements on specimens of Nb which contained 0.2% atomic T_a , but were otherwise similar to ours in detectable impurities. No comparison can be made concerning the amount of oxygen and nitrogen present in the specimens since no pertinent analyses were performed.

¹⁰ D. J. Thouless, Phys. Rev. **117**, 1256 (1960).

¹¹ J. C. Swihart, IBM J. Res. Develop. **6**, 14 (1962).

¹² I. Giaever and K. Megerle, Phys. Rev. **122**, 1101 (1961).

¹³ A. T. Hirshfeld, H. A. Leupold, and H. A. Boorse, Phys. Rev. **127**, 1501 (1962).

¹⁴ G. A. Alers and D. L. Waldorf, Phys. Rev. Letters **6**, 677 (1961).

In the derivation by BCS of the temperature dependence of the longitudinal acoustic attenuation ratio α' [see Eq. (1)], the implicit assumption that $ql \gg 1$ was made. Tsuneto⁴ has carried out a treatment of ultrasonic attenuation of longitudinal waves in superconductors using the density-matrix formulation for arbitrary ql based on the BCS theory. He finds the attenuation to be approximately independent of ql and to be given by the BCS expression (1). It has been found here that the form of α' is not given by (1) for a phonon frequency of 30 Mc/sec assuming $\mathcal{E}_0(0) = 3.63 kT_c$ as obtained from the measurements at 220 Mc/sec. In fact, the 30 Mc/sec α' values lie sufficiently far below the BCS prediction except at small values of the reduced temperature ($t < 0.4$) that it is not valid to arrive at a value for the superconducting energy gap by fittings to the BCS expressions at this phonon frequency.

CONCLUSIONS

For $ql \sim 1$, the qualitative agreement of α' and \mathcal{E}_R with the BCS theoretical results is reasonably good. The quantitative derivations, however, indicate that the strength of coupling and the form of electron-electron interaction do play a role, but may require physically unrealizable values or forms to explain completely the differences. Perhaps, and especially so in relatively impure transition metal samples such as those used here, impurity scattering must be taken into account in expressing the Hamiltonian and wave functions of the problem. Regarding the isotropic results for $\mathcal{E}_0(0)$, any anisotropy of the gap may have been smeared out by the mixing of states due to impurity scattering.¹⁵

Since it has been found that α' does depend on ql , it would seem desirable to study the effects of the approximations and omissions for relatively impure materials in the treatment of Tsuneto. Measurements taken at much higher frequencies may be invaluable in directing the course of such a study.

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¹⁵ J. W. Garland, Phys. Rev. Letters **11**, 111 (1963).