Ultrasonic Determination of the Superconducting Energy Gap in Tantalum*†‡

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Ultrasonic measurements have been performed on two single crystals of tantalum axially oriented on ⟨110⟩. The temperature dependence of the attenuation coefficient of longitudinal waves propagating in this direction was used to compute the temperature dependence of the superconducting energy gap of tantalum. It was found to be closely predicted by the Bardeen-Cooper-Schrieffer theory. The zero-temperature energy gaps of the two were $(3.4\pm0.2)kT_c$ and $(3.5+0.2)kT_c$, respectively, which are compatible with BCS result, $2\epsilon_0(0)=3.5\ kT_c$. In the frequency range of these experiments, 45 to 340 Mc/sec ql was smaller than one.

INTRODUCTION

THE temperature dependence of the superconducting energy gap was measured in two samples of tantalum by making a detailed investigation of the ultrasonic-attenuation coefficient in the normal and superconducting state. The sample chamber, cryogenic apparatus, and ultrasonic electronic equipment, together with the pulse-echo technique employed, are described elsewhere.[1]

All the following measurements were performed using longitudinal waves propagating along ⟨110⟩, which was parallel to the cylindrical axis of the samples.

Tsuneto[2] and Levy[3] have investigated ultrasonic attenuation of longitudinal waves in the superconducting state to cover the range where the product of the ultrasonic wave vector q times the mean free path l is smaller than one. They find that the same result holds as the one obtained by Bardeen, Cooper, and Schrieffer[4] (BCS) for $ql\gg1$.

$$\frac{\alpha_s}{\alpha_n}=\frac{2}{e^{\epsilon_0(T)/kT}+1},$$

where α is the attenuation coefficient, s refers to the superconducting state, n to the normal state, and $2\epsilon_0(T)$ is the superconducting energy gap. $\epsilon_0(T)/\epsilon_0(0)$ is a universal function of the reduced temperature, $T_R=T/T_c$, where T_c is the critical temperature.

Some of the properties of the two tantalum single crystals are tabulated in Table I.

EXPERIMENTAL RESULTS

Measurements were performed at four frequencies, 157.5, 97.5, 70, and 43.2 Mc/sec in Ta No. 1. Except for the data at 43.2 Mc/sec, the results are shown in Figs. 1, 2, and 3. The 43.2-Mc/sec data are not shown since the total measurable ultrasonic attenuation change was about 7 dB, and, the nature of the measurements is such, that this amount of attenuation does not yield a reliable value for the superconducting energy gap. The solid line in Fig. 1 is plotted according to Eq. (1) for a zero-temperature energy gap $2\epsilon_0(0)$ of $3.5kT_c$. The dots indicate data obtained while the temperature of the sample was being increased in discrete steps and the crosses, while it was being decreased. L is the total length traveled by the particular pulse being measured, the fourth pulse in this case; therefore, α_nL is the total amount that the pulse is attenuated by electron-phonon processes in the normal state.

The first measurements were performed at 97.5 Mc/sec and in all of these, attempts were made at measuring several return pulses at once. This procedure proved fruitless since the scatter of the data so obtained

TABLE I. Properties of the tantalum samples.

	No. 1	No. 2
Transition temperature[a]	4.36°K	4.42°K
Resistivity ratio[b]	35	40
Diamond pyramid hardness	100	86
Purity[c]	99.9%	99.9%
Size (diameter and length)[d]	0.25 in.×1.0546 in.	0.25 in.×1.0963 in.
Axial orientation[e]	⟨110⟩	⟨110⟩
Method of growth[f]	Electron beam, zone refined	Electron beam, zone refined
Source[g]	M.R.C.	M.R.C.

[a] The transition temperature was determined acoustically.
[b] The residual resistivity ratio was measured by an eddy-current technique. [C. P. Bean, R. W. DuBlois, and L. B. Nesbitt, J. Appl. Phys. 30, 1976 (1959).]
[c] The purity was obtained from Material Research Corporation, New York (M.R.C.).
[d] The ends of the cylinder were optically polished and ground parallel to 0.1 mil.
[e] The crystals were grown along ⟨110⟩. The axial orientation was within 2° of ⟨110⟩.
[f] Quarter-inch cylinders were grown, which were then cut to the proper length.
[g] The authors are indebted to Dr. J. R. Neighbours, U. S. Naval Postgraduate School, Monterey, California, for supplying Ta No. 1.

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‡ Parts of this work are based on a thesis submitted by M. Levy in partial fulfillment of the requirements for the Ph.D. at the University of California, Los Angeles.
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[1] J. L. Brewster, M. Levy, and I. Rudnick, preceding article, Phys. Rev. **132**, 1062 (1963)
[2] T. Tsuneto, Phys. Rev. **121**, 402 (1961).
[3] M. Levy, Phys. Rev. **131**, 1497 (1963).
[4] J. Bardeen L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

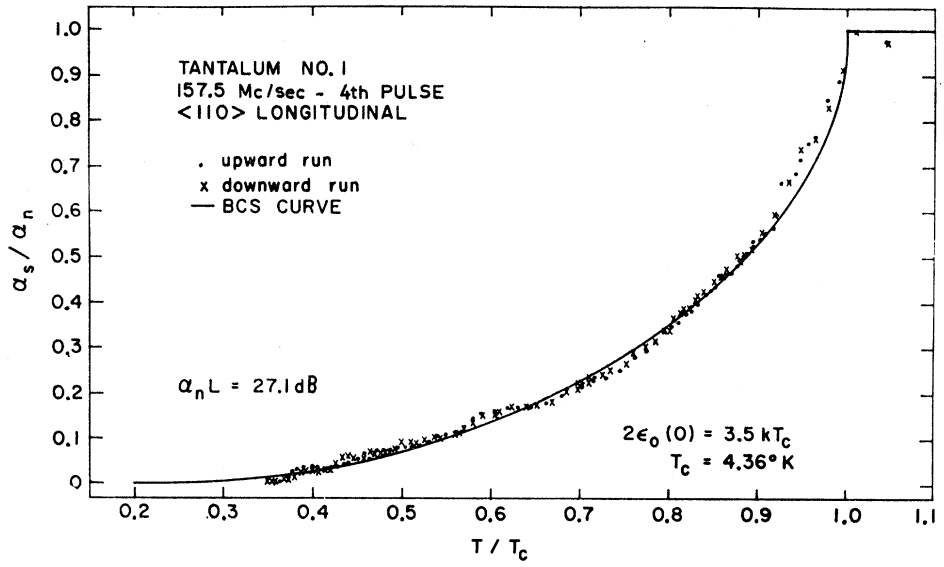

FIG. 1. Normalized attenuation as a function of reduced temperature in Ta No. 1 at 157.5 Mc/sec.

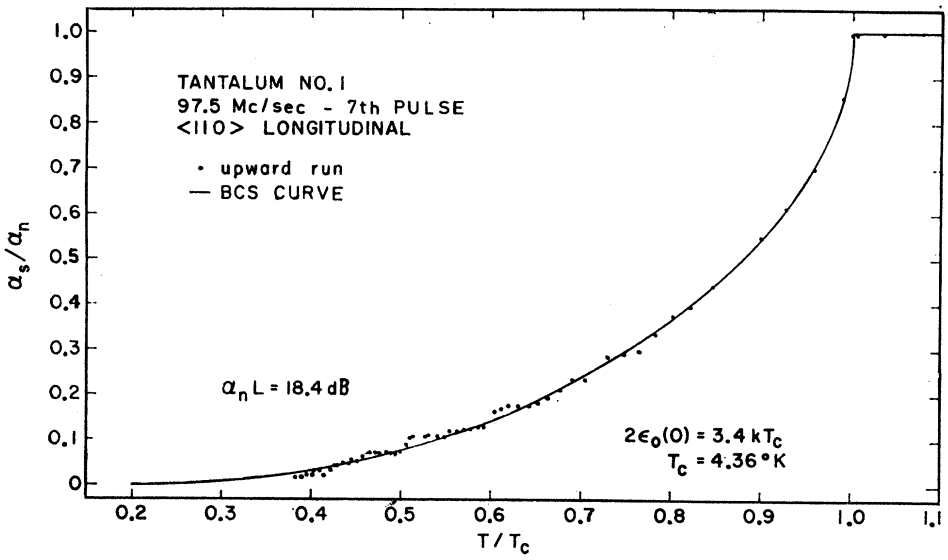

FIG. 2. Normalized attenuation as a function of reduced temperature in Ta No. 1 at 97.5 Mc/sec.

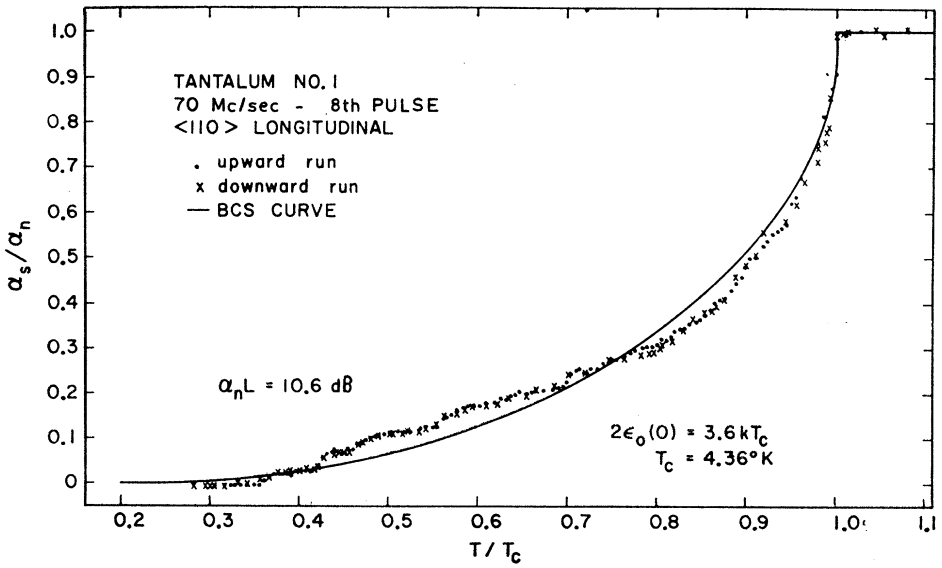

FIG. 3. Normalized attenuation as a function of reduced temperature in Ta No. 1 at 70 Mc/sec. This set of data clearly shows the small oscillations which are believed to be produced by acoustic interference.

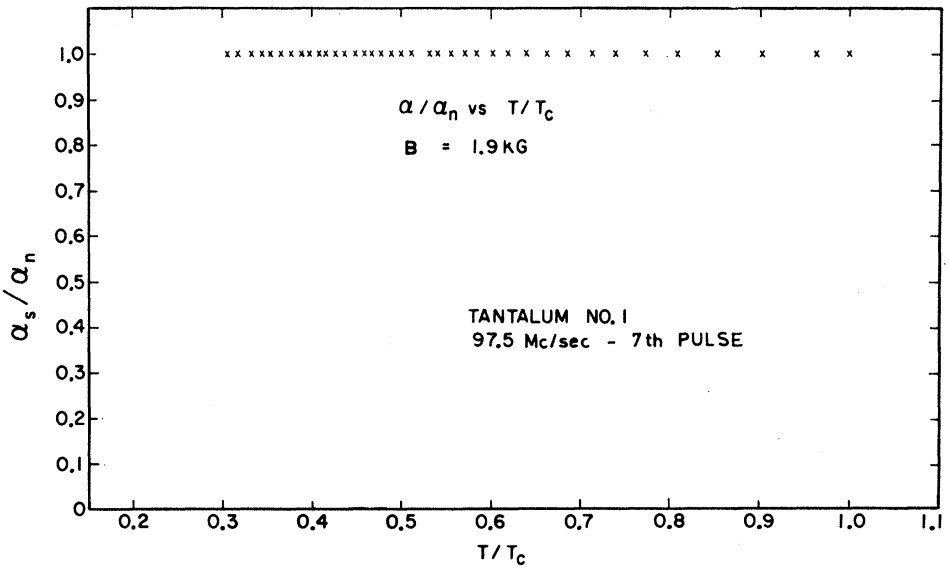

FIG. 4. Attenuation coefficient in the normal state at temperatures below T_c in Ta No. 1.

was too large to be acceptable and we were not able to obtain reproducible data for both upward and downward runs in temperature; therefore, we have selected, for this frequency, data taken during a single upward run which seemed most reliable, Fig. 2.

The presence of small oscillations about the theoretical curve is quite noticeable in the data obtained at 70 Mc/sec, Fig. 3, where $\alpha_n L = 10.6$ dB. The oscillations are not quite as pronounced in the higher-frequency data where $\alpha_n L = 18.4$ and 27.1 dB. These oscillations were first observed by Brewster[5,1] on an impure sample of vanadium where the total measured change in attenuation was 8.3 dB. It is evident from the reproducibility of the data that the oscillations are not being produced either by a temperature lag between the thermometer and the sample or by power changes in the transmitter. The response of the receiving equipment showed no indications of oscillations to an accuracy of 0.15 dB. Furthermore, the attenuation in the normal state is a constant throughout the temperature range; see Fig. 4. In Ref. 1 it was shown that these oscillations have an acoustic origin and it was postulated there that they were produced by interference of the high-order elastic modes which comprise the longitudinal wave pulses. Measurements made on the 3rd and 9th pulse at 95.5 Mc/sec on the second tantalum sample, Figs. 5 and 6, are in agreement

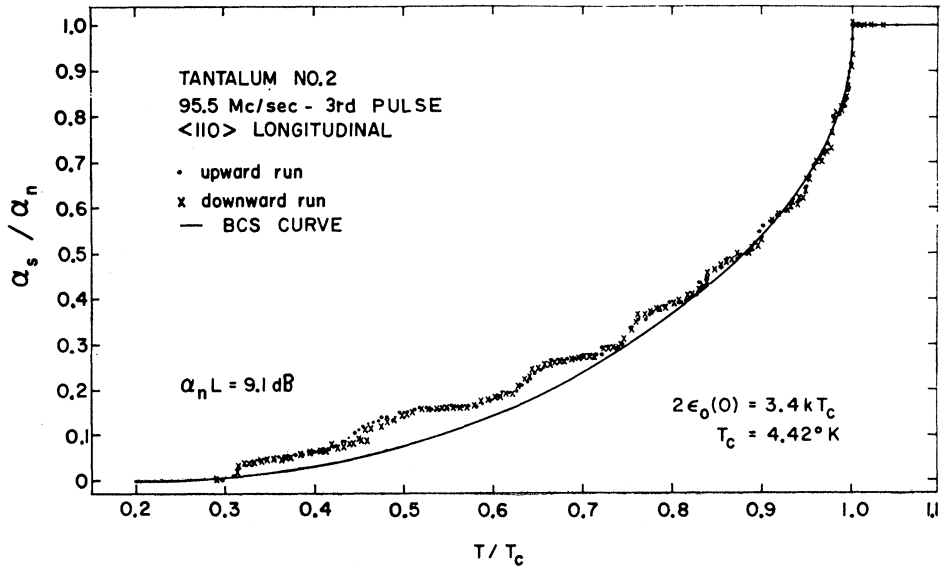

FIG. 5. Normalized attenuation versus reduced temperature for Ta No. 2 at 95.5 Mc/sec. The measurements were performed on the 3rd pulse. The small oscillations are clearly present here, however, they are absent for measurements on the 9th pulse at the same frequency (see Fig. 6).

[5] J. L. Brewster, J. Acoust. Soc. Am. 32, 151 (1960).

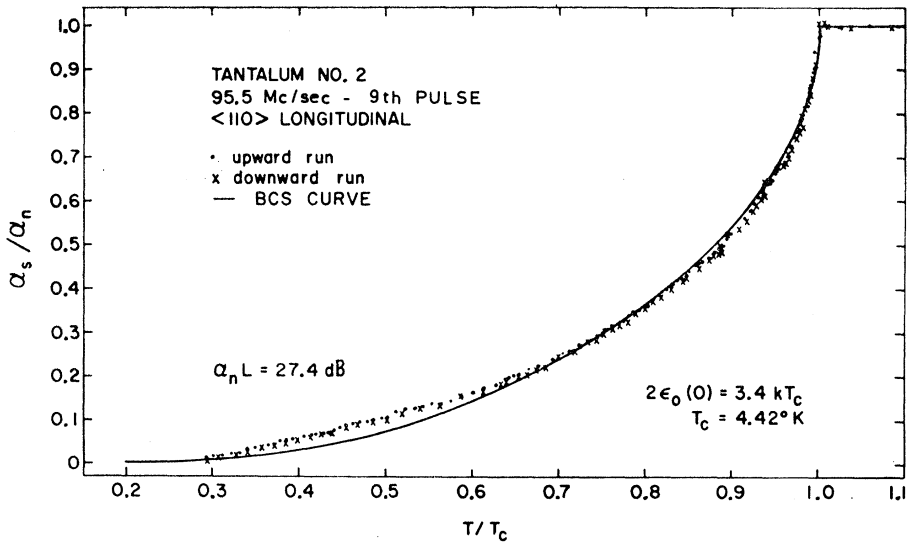

FIG. 6. Attenuation measurements on the 9th pulse at 95.5 Mc/sec on Ta No. 2. The oscillations are not very apparent in this graph. Since their magnitude and number seems to depend on the total change in attenuation $\alpha_n L$ (see Fig. 5), it is assumed that they are produced by acoustic interference.

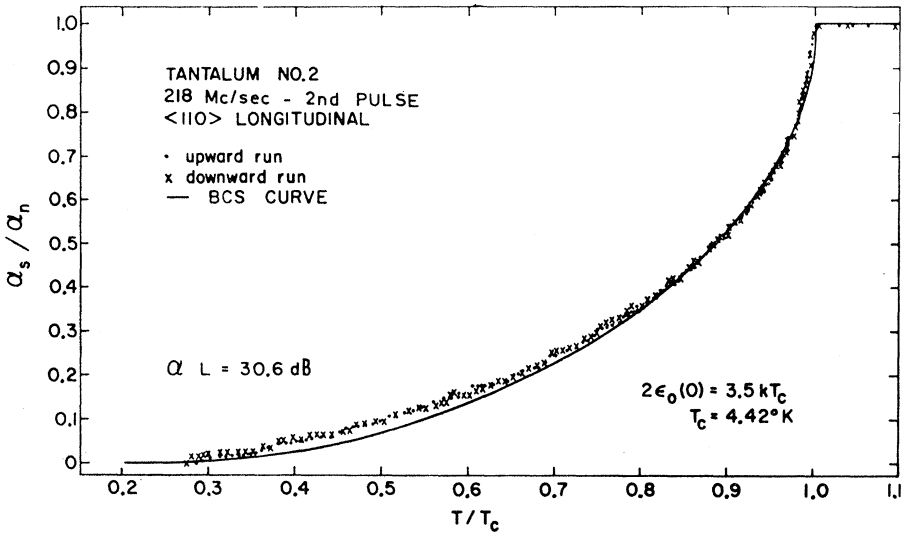

FIG. 7. Normalized attenuation versus reduced temperature for Ta No. 2 at 218 Mc/sec.

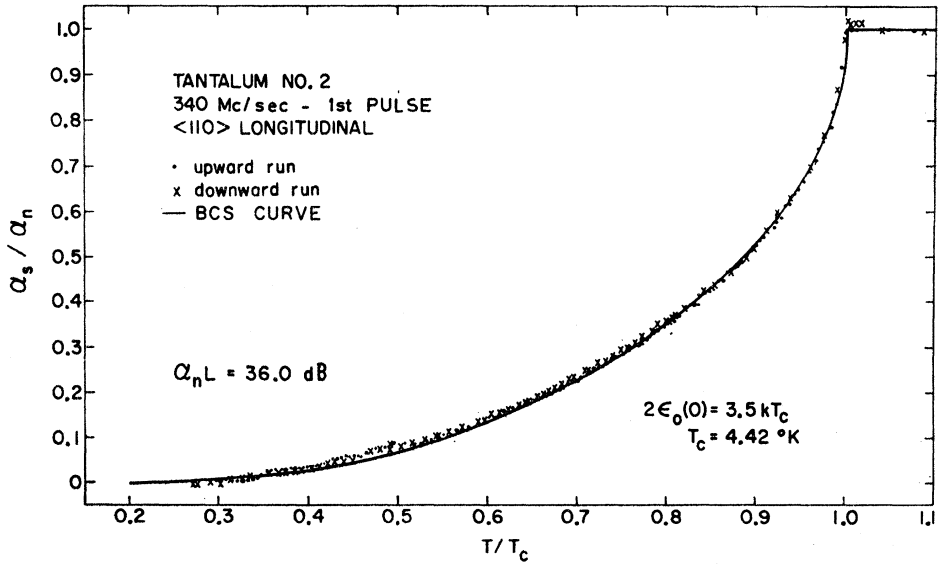

FIG. 8. Normalized attenuation versus reduced temperature for Ta No. 2 at 340 Mc/sec.

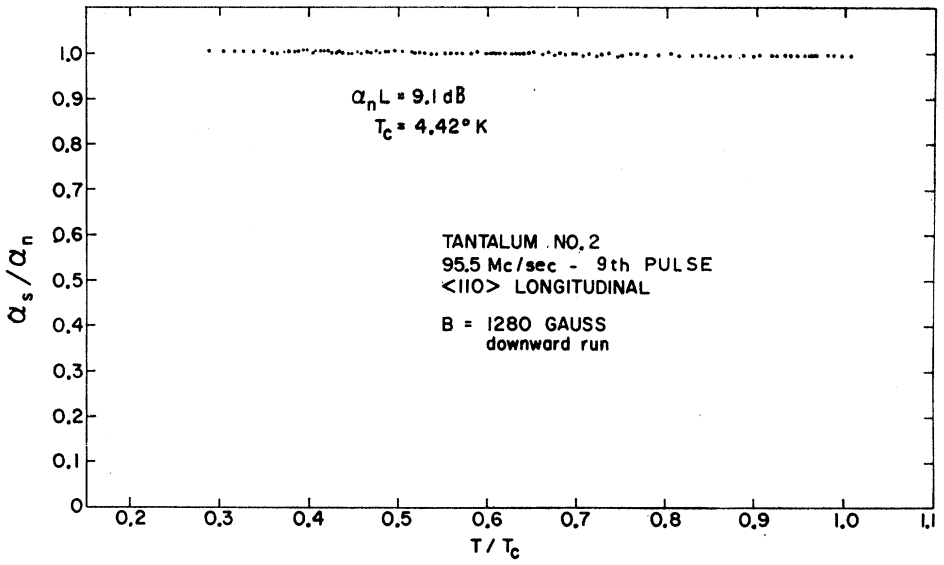

FIG. 9. Attenuation coefficient in the normal state at temperatures below T_c in Ta No. 2.

with the above interpretation of the origin of the small oscillations.

Figures 7 and 8 show our results on Ta No. 2 at 218 and 340 Mc/sec. Both sets of data are fit by BCS curves with $2\epsilon_0(0)=3.5kT_c$.

The attenuation in the normal state for both samples was checked by quenching them with a magnetic field produced by a superconducting solenoid.[6] It was found that the ultrasonic attenuation coefficient in the normal state was a constant for the two crystals throughout the temperature range covered, Figs. 4 and 9.

A detailed examination of α_s/α_n was made on the second tantalum sample in the presence of a magnetic field large enough to shift the transition temperature by one tenth of its value. Figure 10 shows these results. As the temperature is lowered the ultrasonic attenuation remains constant until the new transition temperature is obtained, then it drops sharply until it approaches the theoretical curve for the superconducting metal in the absence of the magnetic field. The BCS curve is plotted for $2\epsilon_0(0)=3.4kT_c$, which is the value that was used for the other measurements at 95.5 Mc/sec. These results are similar to those obtained by David, Van der Laan, and Poulis[7] on aluminum. As would be

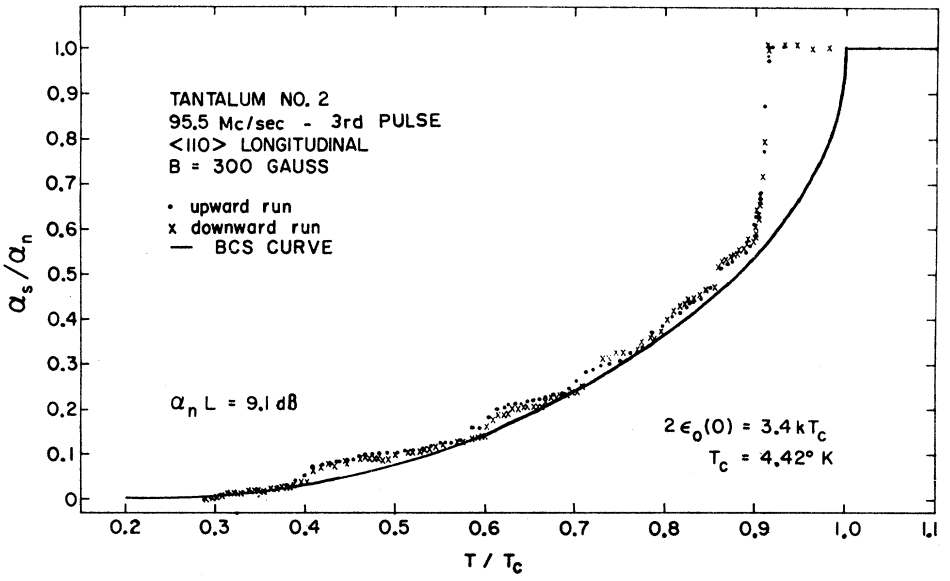

FIG. 10. Effect of a magnetic field on the attenuation curve of Ta No. 2 at 95.5 Mc/sec.

[6] The superconducting magnet was obtained from S. H. Autler, Lincoln Laboratories, MIT.
[7] R. David, H. R. Van der Laan, and N. J. Poulis, Physica 28, 330 (1962).

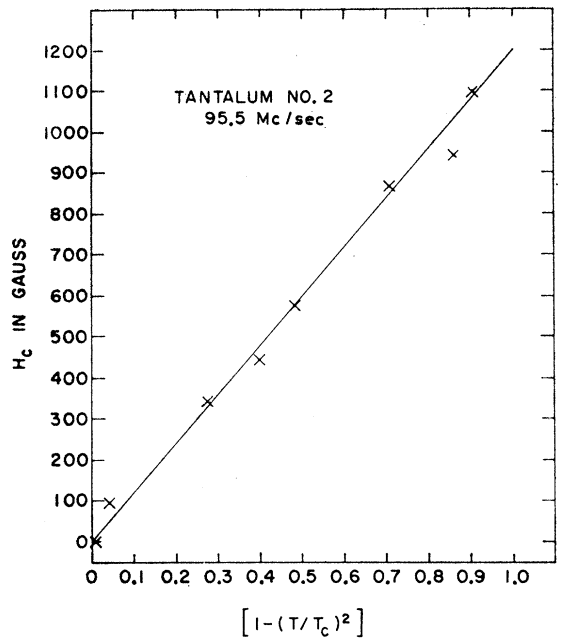

FIG. 11. Parabolic fit of the critical magnetic field for Ta No. 2.

expected, the magnetic field has no noticeable effect on the bulk energy gap, once the sample becomes superconducting, since it is excluded from the interior of the sample by surface currents.

The magnetic-field dependence of the transition temperature was also checked for this sample. Figure 11 shows a parabolic fit of the data. The accuracy of measurements of the magnetic field was such that the deviation predicted by BCS could not be detected. Extrapolation of the line shows that the critical field, H_0, is 1200 G as compared to 840 G reported by Budnick.[8] The difference is probably due to the fact that our sample was less pure; its transition temperature, 4.42°K, is lower than Budnick's value of 4.48°K.

Pippard[9] has shown that $\alpha_n \simeq f^2$ for $ql<0.7$; for values of ql from 0.7 to about 8, the square-law dependence gradually shifts to a linear frequency dependence, and for $ql>8$, $\alpha_n \simeq f$.[10] As may be seen in Fig. 12, $\alpha_n \simeq f^2$ for both samples, therefore $ql<1$, in the frequency range employed.

DISCUSSION AND CONCLUSION

The detailed temperature dependence of the energy gap as computed from the data of the temperature dependence of α_s/α_n for the most reliable data for Ta No. 1 and No. 2 are shown in Figs. 13 and 14, respectively. These figures also include the average value of the zero-temperature energy gap and its root mean square deviation as computed from all the points in each graph by a method described in Ref. 1.

The points are scattered for small values of T_R since in this range the normalized attenuation has dropped to a value sufficiently low so that a small deviation of the experimental points from the smooth α_s/α_n curve produces a large deviation from the energy gap curve.

Values for the zero-temperature energy gap for the two tantalum samples are shown in the first two rows of Table II. The first row gives the average of the best fit curves to the α_s/α_n points for the different frequencies. The second row, the average as computed from the points on the energy gap graphs. The latter

TABLE II. Zero-temperature superconducting energy gap in tantalum in units of kT_c.

	No. 1	No. 2
I	3.5±0.1	3.45±0.05
II	3.4±0.2	3.5 ±0.2
Infrared absorption	3.0	
Electron heat capacity	3.6	
Tunneling	3.5	
Thermal conductivity	3.5	

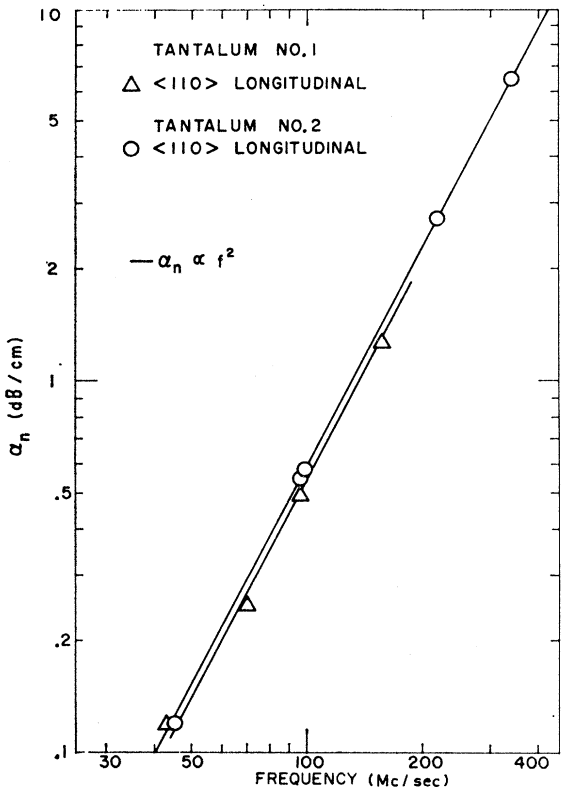

FIG. 12. Frequency dependence of the ultrasonic attenuation in the normal state for Ta No. 1 and Ta No. 2.

[8] J. Budnick, Phys. Rev. **119**, 1578 (1960).
[9] A. B. Pippard, Phil. Mag. **46**, 1104 (1955).
[10] R. W. Morse, *Progress in Cryogenics* (Heywood and Company Ltd., London, 1959), Vol. I, pp. 219 ff.
[11] P. L. Richards and M. Tinkham, Phys. Rev. **119**, 575 (1960).

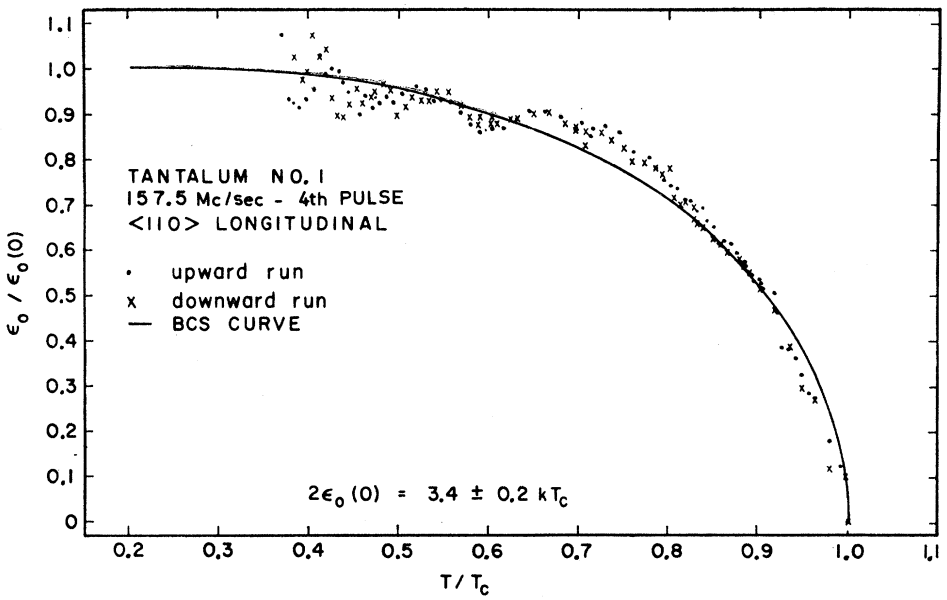

FIG. 13. Temperature dependence of the normalized superconducting energy gap in Ta No. 1.

values are probably more reliable. Also listed are the values obtained from infrared measurements by Richards and Tinkham,[11] from heat-capacity data by Goodman,[12] from tunneling experiments by Giaever,[13] and from thermal conductivity measurements by Connolly and Mendelssohn.[14] Except for the infrared absorption measurements, the values for $2\epsilon_0(0)$ are consistent. Richards and Tinkham suggest that their value of $2\epsilon_0(0)$ for Ta may be in error because the metal surfaces may have been gas contaminated.

In conclusion, the zero-temperature energy gap for Ta appears to be $3.5kT_c$, in agreement with the BCS theory; the temperature dependence of the energy gap is also predicted by the BCS theory. In the normal state, the attenuation is proportional to the square of the frequency; therefore, the mean free path for

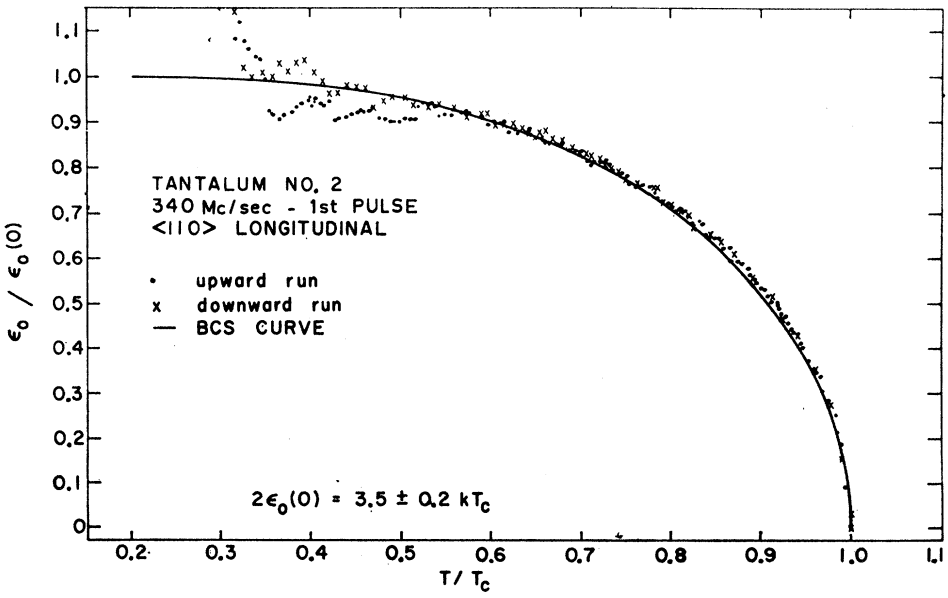

FIG. 14. Temperature dependence of the normalized superconducting energy gap in Ta No. 2.

[12] B. B. Goodman, paper presented at Superconductivity Conference, Cambridge, 1959 (unpublished).

[13] I. Giaever, in *Proceedings of the Eighth International Congress on Low-Temperature Physics, London, 1962* (Butterworths Scientific Publications Ltd., London, 1962).

[14] A. Connolly and K. Mendelssohn, Proc. Roy. Soc. (London) **A366**, 429 (1962).

electron-phonon collisions is smaller than 1.4×10^{-4} cm. As would be expected, the zero-temperature energy gap of the bulk material is not affected by an external magnetic field which is much smaller than the critical field.

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Deformation Potentials in Silicon. III. Effects of a General Strain on Conduction and Valence Levels*

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Using a self-consistent perturbation theory developed in the first two papers of this series we have calculated the deformation potentials for a general strain for points of high symmetry (Γ, X, and L) in the conduction and valence bands of Si. We compare our calculated results with experimental values for (1) hydrostatic-pressure dependence of various energy gaps, (2) uniaxial-strain dependence of the splitting of the fourfold degenerate level at the top of the valence band, and (3) uniaxial strain dependence of the splitting of the degeneracy between equivalent valleys at the bottom of the conduction band. The agreement between theory and experiment ranges from fair to good.

I. INTRODUCTION

THE change in energy caused by an arbitrary strain is calculated here for states of high symmetry near the top of the valence band and the bottom of the conduction band in Si. The experimental studies of these effects can be grouped into three classes. (1) The fourfold degenerate $\Gamma_{25'}$ ($j=\frac{3}{2}$) level at the top of the valence band is split into two twofold levels by a general uniaxial strain. Hensel and Feher[1] have measured the cyclotron-resonance-effective masses of holes at the top of the valence band in Si as a function of strain and, thus, were able to calculate the strain-induced splitting of these levels. In the first paper of this series[2] (hereafter called I) the theory of the strain splitting of the top of the valence band is presented, and three other experiments performed on the holes to measure this splitting are briefly discussed. (2) Donor impurity electron wave functions in Si consist of linear combinations of conduction electron wave functions in the six valleys along the equivalent [100] directions in k space. Because of central cell corrections to the effective mass formalism[3] (chemical shifts), that combination of conduction-electron wave functions which adds in phase at the impurity site lies lowest in energy. When a uniaxial strain is applied along one of the valley directions, the intervalley degeneracy is destroyed and the lower lying valleys contribute a greater proportion to the impurity wave function. Thus, by measuring the amplitude of the wave function at the impurity site as a function of strain, Wilson and Feher[4] (by means of the hyperfine splitting of electron-spin-resonance lines in strained Si) measured the intervalley splitting. Similarly, a measurement of the strain dependence of the ionization energy of the donor electrons[5] leads to the intervalley strain splitting. (3) Paul and co-workers[6–8] have measured the shifts in the optical absorption peaks and, hence, in their associated energy gaps as a function of hydrostatic pressure. Unfortunately, most of the data is for Ge but the *pressure* dependence of any particular gap seems to be fairly constant among all the diamond and zinc-blende semiconductors.[9] Paul *et al.* have measured the pressure dependence of the indirect ($\Gamma_{25'}-\Delta_1$) gap in Si both by conductivity measurements and by direct observation of the shift of the indirect-transition edge. Philipp, Dash, and Ehrenreich[10] have attempted to map the motion of the band structure of Si under a bending type of strain which had both a hydrostatic and a uniaxial (either [100] or [111]) component. In view of the complexity of the behavior of the band structure under such a strain (see Sec. II) and the breadth of the re-

* Supported by the Advanced Research Projects Agency.
† National Science Foundation Cooperative Predoctoral Fellow during the time of this research.
[1] J. C. Hensel and G. Feher, Phys. Rev. **129**, 1041 (1963).
[2] L. Kleinman, Phys. Rev. **128**, 2614 (1962).
[3] W. Kohn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5, p. 258.
[4] D. K. Wilson and G. Feher, Phys. Rev. **124**, 1068 (1961).
[5] H. Fritzsche, Phys. Rev. **115**, 336 (1959).
[6] W. Paul, J. Phys. Chem. Solids **8**, 196 (1959).
[7] W. Paul and D. M. Warschauer, J. Phys. Chem. Solids **5**, 89 and 102 (1958).
[8] M. Cardona and W. Paul. J. Phys. Chem. Solids **17**, 138 (1960).
[9] W. Paul. J. Appl. Phys. **32**, 2082 (1961).
[10] H. R. Philipp, W. Dash, and E. Ehrenreich, Phys. Rev. **127**, 762, (1962).