

## Study of the Attenuation of Ultrasonic Shear Waves in Superconducting Aluminum<sup>†</sup>

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Measurements were made of the ultrasonic shear wave attenuation in superconducting aluminum, using 99.999% pure single crystals with parallel faces in the [100], the [110], and the [111] directions. It was found that the temperature dependence of the attenuation could be separated into two parts: a sharp decrease in attenuation very close to the transition temperature and a residual attenuation having a temperature dependence similar to that for the longitudinal waves. The method of adiabatic demagnetization was used to lower the temperature to 0.3°K, and an extrapolated plot of the residual attenuation in this range could be used to determine an effective BCS energy gap. The fraction of the total attenuation represented by the residual attenuation was found to be strongly temperature-dependent. Application of a magnetic field was found to lower the transition temperature as would be expected. In fact, it was found that the method of ultrasonic attenuation could be used to determine the critical fields accurately near the zero-field value, where permeability measurements are difficult. A theory was developed to explain the behavior of the shear-wave attenuation as a function of temperature. The formulation began with approximations which should be valid in the London region and employed a self-consistent method for determining the dissipative forces on the lattice. Suitable modification extended the theory to cover the entire superconducting temperature range. Using the theoretical results, it is possible to determine the parameters  $\tau$  and  $l$ , the electron relaxation time and mean free path, for one orientation and frequency and then predict the correct results for other frequencies at the same orientation. One thus obtains the correct frequency dependence for the total electronic attenuation. Some correlation was made between results for different orientations.

### INTRODUCTION

FROM the very first observations of ultrasonic attenuation in superconductors, it was recognized that the decrease in attenuation as a function of temperature must in some way reflect the decrease in the number of "normal" electrons. However, the observed drop is so abrupt that it could not be reconciled with any other estimate of the temperature dependence of the normal component of a two-fluid model. According to the thermodynamic theory of Gorter and Casimir, for instance, the density of normal electrons is proportional to  $(T/T_c)^4$ , while the observed decrease in attenuation seemed to be nearly exponential. In 1957 when the Bardeen, Cooper, Schrieffer<sup>1</sup> theory of superconductivity (designated BCS) was presented, the superconducting attenuation for compressional waves with propagation vector  $q \gg l^{-1}$  found an immediate explanation. In this case the energy loss can be calculated on the basis of electron-phonon scattering and the result is

$$\alpha_s/\alpha_n = 2f(\epsilon) = 2\{\exp(\epsilon(T)/kT) + 1\}^{-1}, \quad (1)$$

where  $\epsilon(T)$  is the temperature-dependent energy gap of the BCS theory. Tsuneto<sup>2</sup> has shown that for impurity-limited scattering the same functional form of  $\alpha_s/\alpha_n$  as in Eq. (1) is valid for all wavelengths less than those for which  $h\nu \simeq 2\epsilon(T)$ .

Morse *et al.*<sup>3,4</sup> found that the shear-wave attenuation in superconductors could not be fit quite so easily by the BCS function  $2f(\epsilon)$ . In polycrystalline tin at 27.5 Mc/sec the attenuation was found to drop extremely rapidly just below the transition temperature to about 50% of its initial value. This rapid fall was followed by a more gradual decrease on lowering the temperature which had the same temperature dependence as the compressional attenuation [and hence agreed with the BCS function  $2f(\epsilon)$ ]. The motivation for the work reported here was the need for a study of the relative size of the discontinuity in aluminum as a possible function of direction of propagation, direction of polarization, and of  $ql$ , where  $\mathbf{q}$  is the propagation vector for the sound wave and  $l$  is the electron mean free path.

This observed discontinuous behavior in the shear-wave attenuation has led many people to assume that there are two distinct types of interaction involved. In 1956 Holstein<sup>5</sup> attempted to explain the result in terms of the shorting out of roughly that fraction of the attenuation which is due to the thermal relaxation of the electrons. In a private communication to Morse in 1958, Holstein further pointed out that if, in addition to a potential  $V_1$  which is electromagnetic in origin, there is a second potential  $V_2$  which depends on the local electron and ion configurations, then the latter would be unaffected by the appearance of super-

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<sup>1</sup> J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957).

<sup>2</sup> T. Tsuneto, *Phys. Rev.* **121**, 402 (1961).

<sup>3</sup> R. W. Morse, *Progress in Cryogenics* (Heywood and Company, Ltd., London, England, 1959), Vol. I.

<sup>4</sup> R. W. Morse and H. V. Bohm, *J. Acoust. Soc. Am.* **31**, 1523 (1959).

<sup>5</sup> T. Holstein, Research Memo 60-94698-3-M17, Westinghouse Research Laboratories, Pittsburgh, Pennsylvania, 1956 (unpublished).

conductivity and would give a contribution to the total attenuation which would depend only on the effective density of normal electrons. This is similar to the suggestion of Morse that perhaps the residual attenuation is due to a shear-strain term which arises in a real metal because of the complicated Fermi surface.

Recently, Pippard<sup>6</sup> has given a derivation of the attenuation in a real metal. In addition to the electromagnetic forces, he considers the deformations of the Fermi surface caused by strain, as well as the force due to a relative velocity effect arising when an electron travels between regions which move at different speeds. Since Pippard's results are quite complicated, a more simplified theoretical approach is indicated here. The authors were led to consider the electromagnetic attenuation close to the transition temperature and to make certain reasonable approximations in this region. Using a self-consistent dissipative force which includes the reaction on the lattice of the momentum exchange between the electrons and the impurities, a  $ql$  dependence was derived for the residual attenuation which agrees remarkably well with experiment.

Morse<sup>7</sup> has reported on some of the results of this study elsewhere. However, the detailed results and theoretical calculations herein have not been previously published. Some recent work by others on this problem will be discussed below.

#### EXPERIMENTAL TECHNIQUE

The attenuation of the ultrasonic wave as it passed through the sample was measured by a standard pulse technique such as has been discussed in many places.<sup>8-11</sup> The electronic apparatus used in the course of these experiments for the purpose of generating and displaying ultrasonic pulses was developed by Truell and his collaborators at the Metals Research Laboratory at Brown University.<sup>12</sup> AC-cut quartz transducers with fundamental frequencies of 5 and 10 Mc/sec were used (supplied by Valpey Crystal Corporation, Holliston, Massachusetts). The material used in these experiments for making bonds was a high-viscosity (1 500 000 centistoke) Dow Corning silicon fluid.

Three single crystals of aluminum were used in these studies. Most of the measurements were made in a crystal grown by the Bridgman method from 99.999% pure aluminum. It was shaped as a right cylinder with axis along the [100] direction; another set of parallel faces were cut on the sides perpendicular to an equiv-

alent [110] direction. Other measurements were taken in a less pure crystal with [100] faces and in a 99.999% pure crystal with [111] faces.

The low temperatures required for the experiment were obtained both by the evaporation of liquid helium and by adiabatic demagnetization of a paramagnetic salt. The transition temperature of aluminum was measured to be 1.192°K. The lowest temperature obtainable by pumping on the vapor phase of the liquid helium was 1.120°K. This temperature was enough below the transition temperature to allow a study of the rapid-fall region of the attenuation, plus a part of the temperature region where the attenuation falls gradually. However, this information tells nothing about the total superconducting fall off of electronic attenuation, nor does it tell much about a possible BCS energy gap. For these purposes the temperature must be reduced to at least  $0.3T_c$ . A single shot demagnetization system was used to reach this temperature.

Because the complete system necessary for demagnetization cooling is rather large and cumbersome, and because a great deal of helium is wasted in cooling the apparatus, it was decided to design a simple, efficient Dewar system for the highly controlled measurements close to the transition temperature. Thus the entire temperature range was covered in two stages with some overlap measurements made on the demagnetization runs. The pumping system was capable of lowering the vapor pressure of the liquid helium to about  $300 \mu$ . The temperature of the sample in the region about the transition temperature was measured in two ways. While the system was maintained in equilibrium at some temperature by controlling the

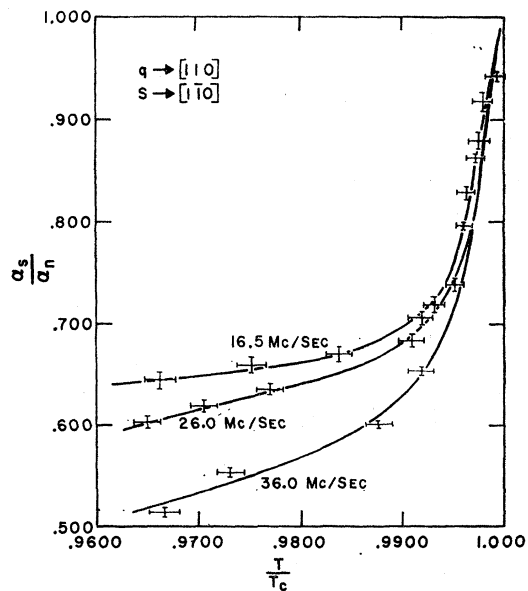


FIG. 1. A plot of experimental values for the ratios of superconducting to normal attenuation versus the reduced temperature ( $T/T_c$ ). The orientation is [110, 110].

<sup>6</sup> A. B. Pippard, in *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons Inc., New York, 1960), p. 224.

<sup>7</sup> R. W. Morse, IBM J. Res. Develop. **6**, 58 (1962).

<sup>8</sup> W. P. Mason and H. J. McSkimin, J. Acoust. Soc. Am. **19**, 469 (1947).

<sup>9</sup> W. P. Mason and H. J. McSkimin, J. Appl. Phys. **19**, 940 (1948).

<sup>10</sup> W. Roth, J. Appl. Phys. **19**, 901 (1948).

<sup>11</sup> H. J. McSkimin, J. Acoust. Soc. Am. **28**, 484 (1956).

<sup>12</sup> B. B. Chick, G. P. Anderson and R. Truell, J. Acoust. Soc. Am. **32**, 186 (1960).

pumping rate, the vapor pressure was read with a Stokes portable McLeon gauge with the Flosdorf modification. The temperature could be obtained from the tables of liquid-helium vapor pressure versus temperature which were compiled by J. R. Clement at the Naval Research Laboratory, Washington, D. C. At the same time that the vapor pressure was read the resistance of a Speer carbon resistor was measured (this had a room temperature resistance of 470Ω). The resistance was calibrated as a function of temperature, and further resistance measurements were useful for accurate measurement of very small temperature changes.

Since it was desired to eliminate the magnetic field of the earth at the sample, it was necessary to design a pair of Helmholtz coils which could be mounted about the Dewars and rotated to the proper angle. In order to apply a controlled magnetic field on the sample and observe its effect on the transition as seen by the attenuation technique, a solenoid was designed which could be slipped directly over the nitrogen Dewar and held in place by a ring stand.

**SUMMARY OF EXPERIMENTAL RESULTS**

Since Morse and Bohm<sup>4</sup> had observed what appeared to be a discontinuity in the shear-wave attenuation in aluminum at the superconducting transition, the first studies undertook to examine this discontinuity as a function of such parameters as direction of propagation, polarization, frequency, and sample purity. The earlier measurements had been with a sample of relatively short mean free path. Therefore, the first of this series of measurements were made in a Bridgman

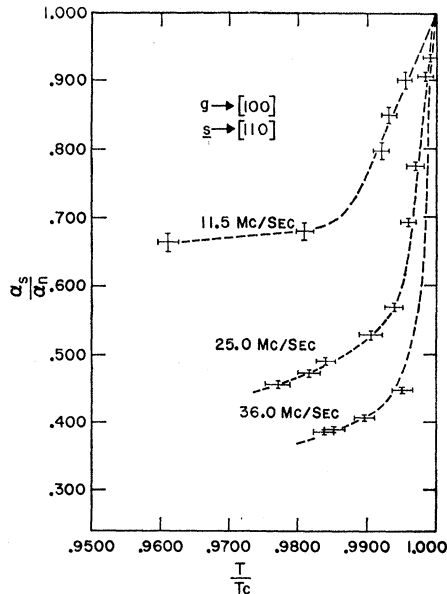


FIG. 2. A plot of experimental  $(\alpha_s/\alpha_n)$  versus  $(T/T_c)$  for the orientation  $[100, 110]$ .

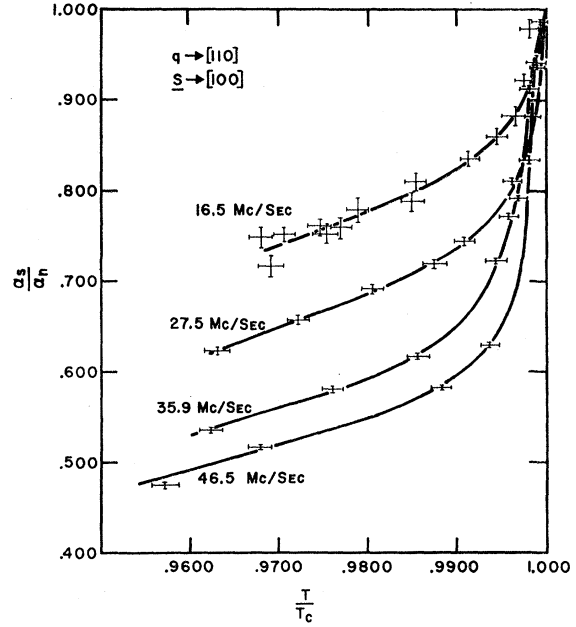


FIG. 3. A plot of experimental  $(\alpha_s/\alpha_n)$  versus  $(T/T_c)$  for the orientation  $[110, 100]$ .

$[100]$  crystal grown from aluminum of 99.999% purity. It was hoped that this sample might prove to have a significantly longer mean free path than the one used by Morse and Bohm and that any  $ql$  dependence of the discontinuity could be determined.

The first observation was for directions of propagation and polarization the same as those of Morse and Bohm. It was soon found that there was no discontinuity if the magnetic field of the earth were canceled. Although there was a rapid fall in attenuation in the temperature range close to the transition point, the slope was finite and the variation could be followed point by point. At a few thousandths of a degree below the transition there was a rapid change in slope and the remaining change in attenuation with temperature was much more gradual. For example, at 25 Mc/sec there was a decrease of 5 dB between 1.190 and 1.185°K, but there was a decrease of only 2 dB between 1.185 and 1.155°K. A summary of such measurements is contained in Figs. 1 through 3, where the fractional attenuation is plotted versus the reduced temperature. (The determination of the total attenuation used in making such plots is discussed below.) When the attenuation was measured without canceling the magnetic field of the earth, the transition temperature was shifted downward. Since this narrowed the temperature range of the rapid-fall region, the change in attenuation necessary to drop to the original curve was increased. The net effect was to make the change appear more like a discontinuity. Nevertheless, the change could still be followed point by point if care was taken to allow the sample to come to equilibrium with the bath.

The most striking difference between these data and that obtained by Morse and Bohm (for short  $ql$ ) is the strong frequency dependence of the curves for a given propagation and polarization orientation. They found very little dependence of  $\alpha_s/\alpha_n$  on frequency for the short  $ql$  case. In the present case  $\alpha_s/\alpha_n$  changes from 0.750 to 0.520 at  $T/T_c=0.9700$  as the frequency is increased from 16 to 46 Mc/sec for the case, where  $\mathbf{q}$  is in the  $[110]$  direction and  $\mathbf{s}$  is in the  $[100]$  direction. We also find a difference in the frequency variation of  $\alpha_s/\alpha_n$  for different propagation and polarization directions. The frequency dependence seems to be strongest in the case for  $\mathbf{q}$  in the  $[100]$  and  $\mathbf{s}$  in the  $[110]$  directions, while the dependence seems to be weakest for  $\mathbf{q}$  in the  $[110]$  and  $\mathbf{s}$  in the  $[1\bar{1}0]$  directions. This latter case was the one examined by Morse and Bohm.

A discussion of these data in the light of theoretical work is given in a later section and so further discussion of these aspects of the data will be deferred to that section.

The dependence of shear-wave attenuation on temperature was obtained below  $1.1^\circ\text{K}$  by the adiabatic-demagnetization technique mentioned above. For each orientation of propagation vector and polarization several demagnetization runs were made in order to increase the density of experimental points. A typical plot of the temperature variation of attenuation is given in Fig. 4. It is evident from Fig. 4 that the lowest temperatures reached for these data were about  $0.35^\circ\text{K}$ . On some of the runs it was possible to go to slightly lower temperatures, the lowest value being  $0.29^\circ\text{K}$ . The points near  $T_c$  in Fig. 4 are from the studies made in the smaller cryostat.

The temperatures determined experimentally below  $1^\circ\text{K}$  were found by extrapolating the susceptibility of the paramagnetic salt and by an extrapolation of the resistance of the Speer resistor.

Deviations of the real temperature from the extrapolated one can significantly alter the apparent temperature variation of the attenuation. Since this problem only arose at the lowest temperatures and because

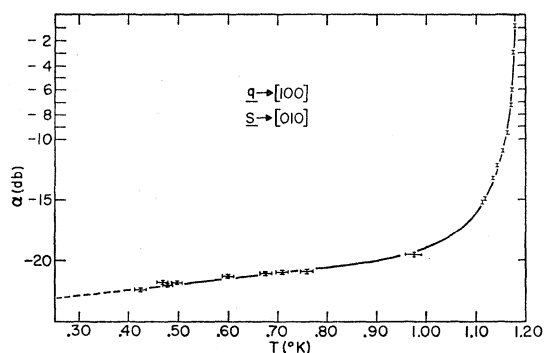


FIG. 4. A plot of experimental  $(\alpha_s/\alpha_n)$  versus  $(T/T_c)$  over the total range for the orientation  $[100, 010]$ .

attenuation changes below  $0.5^\circ\text{K}$  are small, it is not expected that the total decrease in attenuation from the normal state should be seriously in error by temperature errors. However, if one attempts to compare the data with the BCS temperature variation, inaccuracy in temperature compounds a problem which is difficult at best. The usual procedure is to make a plot of  $\ln(\alpha_s/\alpha_n)$  versus  $T_c/T$ . Below  $T=0.5T_c$  the BCS energy gap is approximately constant and the above plot should be a straight line with slope  $-\epsilon_0(0)/kT_c$ . Inaccuracies in attenuation measurements of 0.1 dB become quite significant as  $T \rightarrow 0$  and the energy gap is determined by a fitting process. When systematic errors in temperature are introduced, it is seen at once that the apparent slope will be quite different and the empirical energy gap in error.

Bearing these difficulties in mind we carried out the procedure for determining the energy gap. Since it was hoped that errors in temperature would be systematic and would also be consistent from one run to the next, it was felt that any large differences in energy gap with direction would show up even though the actual values might not be very reliable. The following is a table of the results:

$\mathbf{q}$	$\mathbf{s}$	$\epsilon_0$
$[100]$	$[110]$	$(1.2 \pm 0.2)kT_c$
$[110]$	$[010]$	$(1.7 \pm 0.2)kT_c$
$[110]$	$[1\bar{1}0]$	$(1.2 \pm 0.2)kT_c$

Because of the difficulties in absolute measurement outlined above, the values of  $\epsilon_0$  must be regarded as only suggestive. It is felt that the probable error of  $\pm 0.2kT_c$  is realistic.

Steinberg<sup>13,14</sup> has demonstrated by two methods that if a magnetic field is applied perpendicular to both the direction of propagation and the direction of polarization of an ultrasonic shear wave in a metal with  $ql \ll 1$  the attenuation should decrease with increasing field strength according to

$$\alpha(H)/\alpha(0) = \{1 + (2\omega_c\tau)^2\}^{-1}, \quad (2)$$

where  $\omega_c = eH/m^*c$  is the cyclotron frequency. Thus, an estimate of the total electronic attenuation could be obtained by fitting the experimental variation of attenuation versus magnetic field strength. A comparison of the results for the total electronic attenuation obtained from the magnetic data with those from the superconducting data shows that they are consistent within about 3%. In each case the value from the magnetic variation was larger than that from the superconducting variation. This fact is interpreted to stem from a systematic error in the temperature calibration as discussed above. In later analysis, the values used for the total electronic attenuation will be those obtained from the magnetic data. Their close

<sup>13</sup> M. S. Steinberg, Phys. Rev. **110**, 772 (1958).

<sup>14</sup> M. S. Steinberg, Phys. Rev. **111**, 425 (1958).

agreement with the temperature data suggests that errors would not be more than a few percent and so would not change significantly the results of the analysis which will follow.

The transition temperature, as viewed by ultrasonic attenuation, is shifted to lower values when a magnetic field is applied. This effect should reflect the usual dependence on temperature of the critical field,<sup>15</sup> i.e.,

$$H_c(T) = H_0[1 - (T/T_c)^2], \quad (3)$$

where  $H_0$  is the critical field at absolute zero. In Fig. 5 the current in the solenoid (described in Sec. 1) is plotted versus the square of the observed transition temperature for  $\mathbf{q}$  in the [110] direction,  $\mathbf{s}$  in the [100] direction, and  $\mathbf{H}$  parallel to  $\mathbf{q}$ . The magnetic field was linear in the current and for the current range from 0.1 to 1.0 A the observed field agreed with the calculated value of 13.9 G/A. Assuming Eq. (3) to be valid, the extrapolated value of  $H_c$  is 114 G. Chanin and Caplan<sup>16</sup> have recently studied the temperature dependence of the critical field in aluminum in the temperature range 0.28°K to a measured transition temperature of  $1.175 \pm 0.001^\circ\text{K}$ . The extrapolated critical field at absolute zero was  $104.0 \pm 0.5$  G. While it is not surprising that the extrapolation of the parabolic temperature dependence from the small field limit gives a different result, refinements on the use of the ultrasonic technique might result in an improved method for studying the critical field near  $T_c$ . Cochran *et al.*<sup>17</sup> measured the temperature dependence of  $H_c$  and found a  $T_c$  of  $1.196^\circ\text{K}$  and extrapolated a zero temperature of  $H_c$  of  $99 \pm 1$  G. The measured values of  $T_c$  in the ultrasonic experiments ranged from 1.187 to  $1.192^\circ\text{K}$ , lying between the values of  $T_c$  quoted above. It should be emphasized that the measurement of small changes

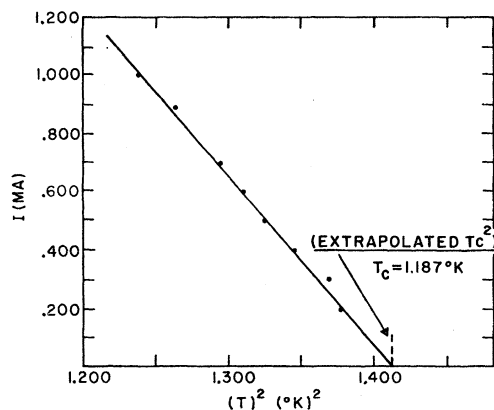


FIG. 5. A plot of critical field versus the square of the transition temperature for [110, 100].

<sup>15</sup> F. London, *Superfluids* (Dover Publications, Inc., New York, 1961), Vol. I.

<sup>16</sup> G. Chanin and S. Caplan, *Bull. Am. Phys. Soc.* **9**, 30 (1964).

<sup>17</sup> J. F. Cochran and D. E. Mapother, *Phys. Rev.* **111**, 132 (1958).

in temperature by means of the resistance thermometer are much more accurate than the absolute determination of  $T_c$ . It is estimated that the values of  $T/T_c$  plotted in Figs. 1, 2, and 3 are accurate to  $\pm 0.0002$ .

#### ATTENUATION IN THE NORMAL STATE

Before attempting a theoretical explanation of the experimental results discussed above, it will be necessary to consider the methods for calculating the ultrasonic attenuation in both normal and superconducting metals. The usual procedure is to start with the Boltzmann transport equation and solve for the distribution function  $f$  in configuration space in the presence of a plane sound wave with propagation vector  $\mathbf{q}$  and frequency  $\omega$ . The collision drag mechanism causes the electrons to relax to a Fermi distribution centered about a local lattice velocity (see Holstein<sup>5</sup>). A velocity and coordinate independent relaxation time is assumed for simplicity. At this point the electron current can be calculated in terms of local fields,  $\boldsymbol{\varepsilon}$ , from the integral relation

$$\mathbf{j}_e = -e \int \mathbf{v} \phi d\mathbf{v}, \quad (4)$$

where  $\mathbf{v}$  is the electron velocity,  $\phi = f - f_0$ , and  $f_0$  is the equilibrium electron distribution. An additional relation between current and fields is obtained from Maxwell's equations and the condition of quasineutrality (see Bardeen<sup>18</sup>). Both  $\mathbf{j}_e$  and  $\boldsymbol{\varepsilon}$  are uniquely determined in terms of the fundamental parameters of the electron distribution and the sound field. In the case of normal metals and compressional waves in superconductors the reaction of the collision drag mechanism on the lattice, through the strong coupling of the scattering centers to the lattice, is found to be a negligible effect in calculating the attenuation. In this case the attenuation  $\alpha$  is just the ratio of the dissipated power,  $\frac{1}{2} \text{Re}(\mathbf{j}_e^* \cdot \boldsymbol{\varepsilon})$  to the product of the energy density of the sound field and the sound velocity. The normal metal, electronic attenuation for a compressional wave is

$$\alpha_L = \frac{Nm2^{-1}}{c_{s1}\rho\tau} \left\{ \frac{(ql)^2}{3} \left[ \frac{\tan^{-1}(ql)}{(ql) - \tan^{-1}(ql)} - 1 \right] \right\}, \quad (5)$$

and a shear wave is

$$\alpha_T = \frac{Nm2^{-1}}{c_{s2}\rho\tau} \left[ \frac{1 - g(ql)}{g(ql)} \right], \quad (6)$$

where

$$g(ql) = \frac{3}{2(ql)^2} \{ [(ql)^2 + 1](ql)^{-1} \tan^{-1}(ql) - 1 \},$$

$l$  is the electron mean free path,  $Nm$  is the electron mass density,  $\rho$  is the lattice mass density,  $c_{s1}$  and  $c_{s2}$  are the respective sound velocities, and  $\tau$  is the relaxa-

<sup>18</sup> J. Bardeen, *Phys. Rev.* **52**, 688 (1937).

tion time. These results are in agreement with the one-electron calculation of Pippard.<sup>19</sup>

#### ATTENUATION IN THE SUPERCONDUCTING STATE

The first observations of the superconducting state showed that it is unique in its electrical and magnetic properties. It was found that the dc resistance<sup>20</sup> within a superconductor is zero and that the magnetic flux<sup>21</sup> is zero. In order to account for the electromagnetic properties London *et al.*<sup>22</sup> proposed a phenomenological theory in which it was postulated that the superconductor contained two types of electrons. There would be a density of superconducting electrons which would satisfy

$$\mathbf{\varepsilon} = \Lambda(d\mathbf{j}_s/dt) \quad (7)$$

with  $\Lambda \equiv m/Ne^2$ , to account for zero resistance, and

$$\text{curl}\Lambda\mathbf{j}_s = -(1/c)\mathbf{H} \quad (8)$$

to account for the exclusion of the magnetic field. The normal electrons were assumed to have a Fermi energy distribution and obey the Maxwell equations as in the normal metal. In order to explain penetration phenomena, Pippard<sup>23</sup> proposed a nonlocal modification to the London equations in which the fields are effective over a coherence distance. There is a limiting case of the BCS theory in which the London equations are valid; however, in general the energy-gap formulation leads to a Pippard type coherence.

If the electron mean free path is sufficiently long ( $ql \gg 1$ ), then the compressional wave attenuation can be found by considering electron-phonon collisions. The result is that given in Eq. (1). To calculate the attenuation in an ideal metal for both compressional and shear waves with arbitrary mean free path, it is necessary to go to a density-matrix formulation. Bardeen and Mattis<sup>24</sup> used such a procedure to calculate the complex conductivity of a transverse electromagnetic field in a superconductor with scattering centers present. Tsuneto<sup>2</sup> calculated the conductivities for both longitudinal and transverse fields taking into account the fact that the scattering centers move with the lattice and the electrons are dragged along. For the longitudinal case with  $\hbar\omega \ll \epsilon(T)$ , but  $l$  arbitrary, Tsuneto found that when the scattering is impurity limited, the ratio of superconducting to normal attenuation for arbitrary mean free path is  $2f(\epsilon)$  just as in the limit of  $ql \gg 1$ .

Exact expressions for the transverse attenuation were found by Tsuneto in two limiting cases:  $\hbar\omega < 2\epsilon_0(T) \ll \hbar qV_0$ ; and  $\hbar qV_0 \ll \epsilon_0(T)$  with  $l = \infty$ . In both instances the attenuation is predicted to fall rapidly to zero near

the transition temperature. It should be emphasized that Tsuneto specifically notes that his expressions for the attenuation are derived by neglecting any dissipation arising from the collision-drag effect. In other words, the fact that there is a momentum change in the impurity system when the electrons are scattered preferentially has been neglected. In a later section it will be shown that the inclusion of collision drag is essential for the treatment of a shear wave in a superconductor, although it is of no importance for longitudinal waves.

#### THEORY OF SHEAR-WAVE ATTENUATION NEAR $T_c$

Even though we have seen that an approach using the Boltzmann transport equation is not fruitful for an exact solution of the attenuation in a superconductor, let us now consider what approximations to this treatment might be useful in a temperature range close to  $T_c$ . The importance of this region is suggested by the experimental fact that the rapid-fall region for transverse waves occurs within a relative temperature change  $\Delta T/T_c$  of about 0.005. Since the ratio of the energy gap to  $kT_c$  is, to first order in  $\Delta T/T_c$ ,

$$\frac{\epsilon_0(0)}{kT_c} = 3.06 \left[ \frac{\Delta T}{T_c} \right]^{1/2}, \quad (9)$$

we see that the energy gap is only about  $(0.2)kT$  when the rapid-fall portion of the attenuation is taken out.

For electromagnetic radiation on a superconductor the London region corresponds to approximately the same temperature range. For transverse sound waves in a superconductor a reasonable assumption for the criterion for the validity of the London equation would be  $\xi_0 \ll q^{-1}$ , where  $\xi_0$  is the coherence length. This condition is approximately realized for the frequencies considered here. It is interesting to note the results obtained using the Boltzmann transport equation and assuming the London two-fluid model suitably modified by the BCS theory.

Consequently, we shall follow the procedure of Holstein<sup>5</sup> in the London region, i.e.:

(1) Derive expressions for the longitudinal and transverse normal currents.

(2) Use the London equations to derive the supercurrents.

(3) Set up the dissipative force in terms not only of the irreversible scattering of the electrons, but also of the reaction of the scattering centers to electron-impurity collisions.

(4) Find that one is led to the prediction  $\alpha_s/\alpha_n = g[2f(\epsilon)]$  at temperatures for which the fields are effectively screened by the superconducting currents, where  $g = g(ql)$  is the function defined in Eq. (6).

The following is a list of the specific assumptions to be made initially: Rather than use the density

<sup>19</sup> A. B. Pippard, *Phil. Mag.* **46**, 1104 (1955).

<sup>20</sup> H. K. Onnes, *Comm. Phys. Lab. Univ. Leiden*, Nos. 119, 120, 122 (unpublished).

<sup>21</sup> W. Meissner and R. Ochsenfeld, *Naturwiss.* **21**, 787 (1933).

<sup>22</sup> H. London and F. London, *Proc. Roy. Soc. (London)* **A149**, 71 (1935).

<sup>23</sup> A. B. Pippard, *Proc. Roy. Soc. (London)* **A216**, 547 (1953).

<sup>24</sup> J. Bardeen and C. D. Mattis, *Phys. Rev.* **111**, 412 (1958).

matrix formulation, we shall follow an approach similar to the Boltzmann transport equation. Instead of using the excitation distribution function, we shall assume a Fermi distribution for normal electrons to be centered about the local lattice velocity. Rather than use the temperature and energy dependent relaxation time for excitations,

$$\tau' = \tau \frac{(\epsilon_0^2 + \epsilon_k^2)^{1/2}}{|\epsilon_k|}, \quad (10)$$

we shall assume the constant impurity scattering relaxation time for normal electrons  $\tau$ . Finally, rather than use the complete BCS equation for the superconducting currents, we shall assume that we are dealing with the London region.

The differential equation which will be used for the distribution function is simply that which was solved above for normal metals with the single modification that the density of electrons is now  $N_n$ , the density of normal electrons. The normal current is again obtained from Eq. (4).

In order to motivate our treatment of the attenuation in the superconducting state, let us consider the forces acting on the lattice. The sum of the real parts of these forces constitutes the dissipative force which gives rise to the attenuation. The contribution of the local electric field to the force density is equal to the force,  $e\mathcal{E}$ , acting on each ion multiplied by the ion density,  $N$ ; i.e.,

$$\mathbf{F}_1 = Ne\mathcal{E}. \quad (11)$$

$\mathbf{F}_1$  is the reaction on the lattice system to the time rate of change of electromagnetic momentum. Obviously, this is just the Lorentz force on the normal electrons. It follows that the real part of  $N_n e\mathcal{E}$  is the dissipative force on the lattice arising from the irreversible scattering of the electrons as they are dragged along with the local lattice current. It is obvious that the attenuation derived from this force alone is identical to that found by considering the energy dissipation term ( $\mathbf{j}^* \cdot \mathcal{E}$ ) mentioned previously. There is, however, an additional force on the lattice which must be included in the interest of self-consistency. The collision-drag assumption required that the electrons be scattered into a Fermi distribution centered about the local lattice velocity. Considering for the moment only impurity scattering, we see that as the electrons are given a change in mechanical momentum  $(d/dt)(N_n m v)$  the impurities suffer an equal but opposite change. Now due to the strong coupling between the lattice and impurity systems, this change in momentum should be included in the enumeration of forces on the lattice. If the electrons followed the lattice exactly their momentum at any time  $t$  would be  $N_n m \mathbf{u}$ . Actually they are scattered from the momentum

$$-(m/e)[\mathbf{j}_n(t)]$$

toward  $N_n m \mathbf{u}$  with the relaxation time  $\tau$ . (Note that  $\mathbf{u}$  and  $\mathbf{j}_n$  are both either longitudinal or transverse simultaneously.) Thus the average change in momentum per unit time evaluated at time  $t$  is

$$\tau^{-1}[N_n m \mathbf{u} + (m/e)\mathbf{j}_n]. \quad (12)$$

As a result the reaction experienced by the lattice is

$$\mathbf{F}_2 = -(m/e\tau)[\mathbf{j}_n + N_n e\mathbf{u}]. \quad (13)$$

The total force includes the electrical force and is

$$\mathbf{F}_d = \mathbf{F}_1 + \mathbf{F}_2 = Ne\mathcal{E} + (m/e\tau)(-\mathbf{j}_n - N_n e\mathbf{u}). \quad (14)$$

At this point it is convenient to show how one obtains the attenuation from the dissipative force. Below we show that

$$\text{Re}(\mathbf{F}_d) = -\mathbf{u} \cdot [\mathbf{K}(m, v_0, \tau, \omega, c_s)], \quad (15)$$

where  $\mathbf{K}$  is a function of the basic parameters of the problem, i.e., the electronic parameters, and the frequency and velocity of the sound wave. The equation for an acoustic wave in a medium with a dissipative force is

$$\frac{\partial^2 S_\zeta}{\partial t^2} = c_s^2 \frac{\partial S_\zeta}{\partial \zeta^2} + \frac{F_d}{\rho}, \quad (16)$$

where  $S_\zeta$  is the amplitude of the acoustic wave, and the  $\zeta$  is the direction of the displacement. From the plane-wave approximation

$$-\omega^2 S_\zeta = -c_s^2 S_\zeta - (k/\rho)(-i\omega)S_\zeta, \quad (17)$$

therefore,  $k^2 = k_0^2 - ik_0 K/c_s \rho$ , where  $k_0 = \omega/c_s$ . The amplitude attenuation is given by the imaginary part of  $k$ . By the very nature of the problem, the dispersive term is small in magnitude compared to  $k_0$ . Thus to first order in  $1/(k_0 K/c_s \rho)$ , the energy attenuation, which is twice the amplitude attenuation, is

$$\alpha = K/c_s \rho. \quad (18)$$

We now can write the attenuation given the reactive force on the lattice.

In view of the assumptions stated earlier, the total current  $\mathbf{J}$  at any point in the crystal will be given by the sum of the lattice current  $N_e \mathbf{u}$ , the normal electron currents  $+\mathbf{j}_n$  and the superconducting current  $+\mathbf{j}_s$ . Using the knowledge of  $\mathbf{j}_n$  and  $\mathbf{j}_s$ , along with Maxwell's equations, we shall show that it is possible to arrive at two equations in the variables  $\mathcal{E}_\zeta$  and  $\mathbf{j}_{n,\zeta}$  for both compressional and shear displacements. Thus, our procedure will be to solve for  $\mathcal{E}_\zeta$  in terms of the basic parameters and then determine  $\alpha_s$ .

We shall now specify the indices " $\zeta$ " and separate the two modes of vibration. Consider again a wave propagated along the  $x$  axis such that the time and space variation is  $e^{i(kx - \omega t)}$ , and take the  $y$  direction to be the direction of the transverse vibrations of the ions. We have exactly the same reduced Maxwell's equations

that we found in the section on Attenuation in the Normal State. From the London equations

$$j_{sy} = -\frac{N_s e^2 \mathcal{E}_y}{i\omega m}, \quad (19)$$

and

$$j_{sz} = -\frac{N_s e^2 \mathcal{E}_x}{i\omega m}. \quad (20)$$

Let us consider the attenuation of a transverse wave, where  $\mathbf{u} = u_y \hat{y}$ . In this case

$$\mathcal{E}_y = \frac{4\pi i}{\omega} \left(\frac{c_s}{c}\right)^2 \left[ N_e u_y - N_n e g \left( u_y - e \mathcal{E}_y \tau / m \right) - \frac{N_s e^2 \mathcal{E}_y}{i\omega m} \right], \quad (21)$$

and

$$j_{ny} = N_n e g \left( u_y - \frac{e \mathcal{E}_y \tau}{m} \right). \quad (22)$$

Let us drop the  $y$  subscripts for the moment. Then solving for  $N_n e \mathcal{E}$  we find

$$N_n e \mathcal{E} = - \left\{ \frac{N_n m u}{\tau} \left[ 1 - \frac{N_n}{N} g \right] \right. \\ \left. \times \left[ \frac{N_n}{N} g - \frac{N_s}{N} \frac{1}{i\omega \tau} - \left(\frac{c}{c_s}\right)^2 \frac{\omega m}{4\pi e^2 \tau N i} \right]^{-1} \right\}. \quad (23)$$

The term

$$\left(\frac{c}{c_s}\right)^2 \frac{\omega m}{4\pi e^2 \tau N i}$$

has been estimated in the discussions of the shear wave attenuation in a normal metal.<sup>5</sup> We now see that the condition of quasineutrality for transverse vibrations of the ions remains valid in the superconducting state with the same limits on frequency, i.e.,  $f < 10^9 \text{ sec}^{-1}$  and so the same approximation can be made. Thus we get:

$$N_n e \mathcal{E} = - \frac{N_n m u}{\tau} \left[ 1 - \left(\frac{N_n}{N}\right) g \right] \\ \times \left[ \left(\frac{N_n}{N}\right) g - \left(\frac{N_s}{N}\right) \frac{1}{i\omega \tau} \right]^{-1}. \quad (24)$$

The force  $F_2$  can be written

$$F_2 = \frac{m}{\tau} \left[ N_n g \left( u - e \frac{\mathcal{E} \tau}{m} \right) - N_n u \right], \quad (25)$$

and so

$$F_d = N_n e \mathcal{E} \left( 1 - \frac{N_n}{N} g \right) + \frac{N u m}{\tau} \left[ \frac{N_n}{N} g - \frac{N_n}{N} \right]. \quad (26)$$

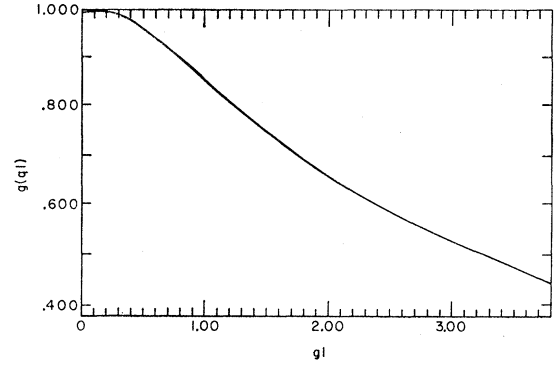


FIG. 6. The function  $g(ql)$  versus  $ql$ .

Finally

$$F_d = - \frac{N u m}{\tau} \left\{ \left[ 1 - \left(\frac{N_n}{N}\right) g \right]^2 \left(\frac{N_n}{N}\right) \right. \\ \left. \times \left[ \left(\frac{N_n}{N}\right) g - \frac{N_s}{N} \frac{1}{i\omega \tau} \right]^{-1} + (1-g) \left(\frac{N_n}{N}\right) \right\} \quad (27)$$

and

$$\text{Re}(F_d) = - \frac{N u m}{\tau} \frac{(1-g)}{g} \left\{ \frac{1}{(1-g)} \left( 1 - \frac{N_n}{N} g \right)^2 \left(\frac{N_n}{N}\right) g \right. \\ \left. \times \left[ \left(\frac{N_n}{N}\right) g + \left(\frac{N_s}{N}\right) \frac{1}{(\omega \tau)^2 g} \right]^{-1} + \left(\frac{N_n}{N}\right) g \right\}. \quad (28)$$

Consequently we find that the relative attenuation is given by

$$\frac{\alpha_s}{\alpha_n} = \frac{1}{(1-g)} \left( 1 - \frac{N_n}{N} g \right)^2 \left(\frac{N_n}{N}\right)^2 g \\ \times \left[ \left(\frac{N_n}{N}\right) g + \left(\frac{N_s}{N}\right) \frac{1}{(\omega \tau)^2 g} \right]^{-1} + \left(\frac{N_n}{N}\right) g, \quad (29)$$

where we have used the fact that

$$\alpha_n = \frac{N m}{2c_s \rho \tau} \frac{(1-g)}{g}. \quad (30)$$

For the temperature variation of the density of normal electrons close to the transition temperature we shall consider first that predicted by the BCS theory for the "London region," i.e.,<sup>25</sup>

$$\frac{N_s}{N} = 1 - \frac{N_n}{N} \sim 2 \left[ \frac{T_c - T}{T_c} \right]. \quad (31)$$

The function  $g(ql)$  is a monotonic decreasing function of  $ql$  over the domain  $(0, +\infty)$  with range  $(+1 \geq g \geq 0)$  as shown in Fig. 6. Therefore,  $0 \leq g N_n / N \leq 1$ . The term

<sup>25</sup>L. M. Khalatnikov and A. A. Abrikosov, *Advances in Physics* (Taylor & Francis, Ltd., London, 1959), Vol. 8, p. 45.



$[(N_s/N)(\omega\tau)^{-1}]^2$  will dominate the denominator when  $N_s/N$  becomes somewhat larger than  $\omega\tau$ . The angular frequency  $\omega$  is about  $10^8$  rad/sec for the experimental case, and  $\tau$  is expected to be on the order of  $10^{-11}$  sec; thus  $\omega\tau \approx 10^{-3}$ . If  $N_s/N \approx 10^{-2}$ , the first term of  $\alpha_s/\alpha_n$  is greatly reduced. This would occur for  $2(T_c - T)/T_c \approx 10^{-2}$  or  $T/T_c = 0.9950$ . A plot of the reduced attenuation versus temperature (Fig. 7) shows that in a very small increment in  $T/T_c$  the first term becomes insignificant compared to  $g(N_n/N)$ . We notice now that this quite simple approach with the inclusion of the collision-drag term has qualitatively reproduced the essential feature of our experimental data. Just below the transition temperature there is a region in which the attenuation drops quite rapidly down to some fraction of the normal-state value. Further decreasing of the temperature causes a much more gradual decrease in attenuation. We see also that the residual attenuation, or that fraction remaining after the rapid decrease, has a frequency dependence which is predominantly determined by the factor  $g(q\ell)$ . This behavior is consistent with the experimental work where it was noticed that increasing the frequency tended to decrease the residual attenuation.

As pointed out earlier, the correct expression for the attenuation of a longitudinal wave in a BCS superconductor is  $\alpha_s/\alpha_n = 2f(\epsilon_0)$  no matter what  $ql$ . Comparing this fact with the result from the approximate treatment given above, it seems that  $2f(\epsilon)$  represents the temperature variation of the "normal" electron density of a superconductor insofar as ultrasonic attenuation is concerned. The experimental evidence cited for shear-wave attenuation in superconducting tin and the present work in aluminum both seem to indicate that the residual attenuation is proportional to the function  $2f(\epsilon)$ . If a plot is made of  $\ln(\alpha_s/\alpha_n)$  versus  $T_c/T$  a limiting value of  $\epsilon_0(T=0)$  can be determined. If, in addition, a plot of  $\ln[2f(\epsilon)]$  is made using the BCS prediction for the temperature variation of  $\epsilon(T)$ , it can be seen that the curve for the shear-wave attenuation lies below that for the BCS function by a constant amount, except for the region very close to the transition. According to our theory this constant should be  $\ln g$ . On the basis of the experimental observations and the equivalence of the terms  $N_n/N$  and  $2f(\epsilon)$  for longitudinal attenuation, we are led to make a plausible modification to the theory by substituting  $2f(\epsilon)$  for  $N_n/N$  in Eq. (29). This leads to the result

$$\frac{\alpha_s}{\alpha_n} = \left\{ \frac{(1-g)^{-1}(1-2f(\epsilon)g)^2(2f(\epsilon))^2g}{[2f(\epsilon)g]^2 + (1/g)[(N_s/N)(1/\omega\tau)]^2} + 2gf(\epsilon) \right\}. \tag{32}$$

The preceding modification has been chosen empirically and by analogy with the longitudinal wave. Theoretically, we expect some modification of the normal electron density from the simple two-fluid model because the distribution of excitations is not a

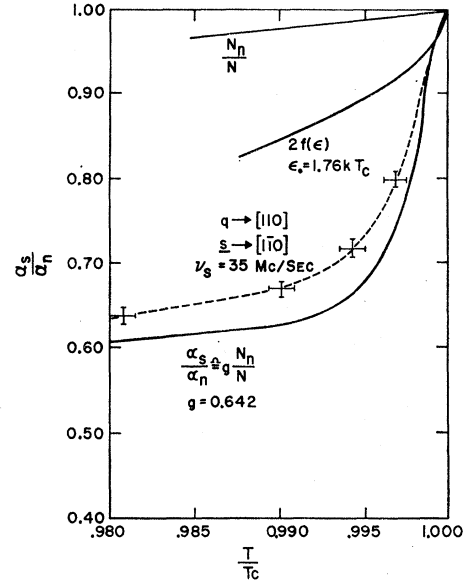


FIG. 7. A plot of functions associated with the approximate theory.

simple Fermi function and because the electromagnetic interaction is modified in the superconductor. In the London region of a BCS superconductor the form of the superconducting currents should not have to be modified from the London equations provided that the BCS prediction of  $N_s/N$  is used [i.e., in Eq. (32) we do not substitute  $1 - 2f(\epsilon)$  for  $N_s/N$ ]. In general the temperature range in which the London equations are valid varies from metal to metal. However, the range is limited on the higher temperature side by  $\hbar\omega \ll \epsilon_0(T)$  and on the lower temperature side by  $\epsilon_0(T) \ll kT$ .<sup>25</sup> Thus, for a metal in which this range coincides with the lower part of the rapid-fall region, Eq. (32) might be expected to be a good representation of the actual situation, and the width of the rapid-fall region should give a measure  $\omega\tau$ .

Recently Levy<sup>26</sup> has given a calculation of the shear-wave attenuation in a superconductor for the limit  $ql \ll 1$  or  $g \approx 1$ . He found that the collision-drag effect leads to an attenuation  $\alpha_s = \alpha_n[2f(\epsilon)]$ . Combining this result with the above calculation leads to a completely theoretical justification for the form of Eq. (32).

We shall now proceed to a more detailed comparison of Eq. (32) with the experimental results for aluminum.

#### COMPARISON OF DATA WITH THEORY

The principal results of the last section which we shall use in an analysis of the experimental data are as follows:

- (1) The width of the rapidly falling portion of the shear-wave attenuation is determined by the parameter  $\omega\tau$ .

<sup>26</sup> M. Levy, Phys. Rev. **131**, 1497 (1963).

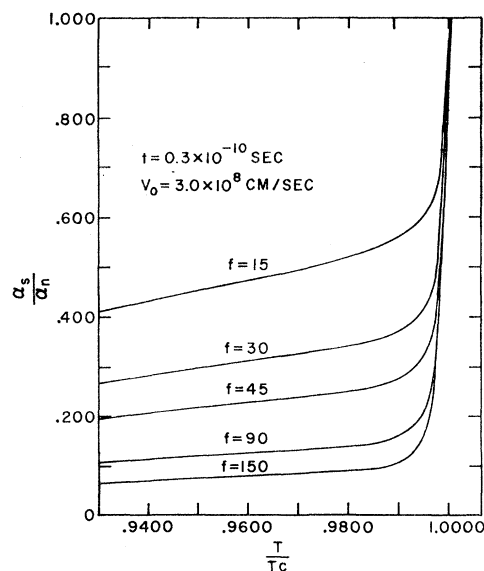


FIG. 8. A family of theoretical  $(\alpha_s/\alpha_n)$  versus  $(T/T_c)$  plots for fixed  $\tau$  and  $v_0$  but different frequencies.

(2) The residual attenuation has a  $ql$  dependence given by  $g(ql)$ .

(3) It has been inferred from data in other metals that after the initial rapid fall the temperature variation is the same as the BCS prediction, so we shall assume that the residual attenuation is given by  $g[2f(\epsilon)]$ .

The first two points will be used to determine whether or not the results are mutually consistent, and the third point will be checked insofar as possible.

In interpreting the data one needs to have some knowledge of the relationship between  $\tau$  and  $l$ . In the case of thermal scattering, for want of a better assumption, an isotropic  $\tau$  often is assumed. Since

$$\tau = lv_0^{-1}, \quad (33)$$

the assumption gives  $l$  the directional dependence of the Fermi velocity. In the case at hand, however, we are dealing with impurity limited scattering in a single crystal. For such a situation Wilson<sup>27</sup> has derived an expression for  $\tau$  as a limiting case of the relaxation time in an alloy. The result is

$$\tau^{-1} = [(2/m^*)E_f]^{1/2} l^{-1}(\mathbf{r}) \quad (34)$$

which can be written in exactly the same form as Eq. (33). Here  $\tau$  is not necessarily isotropic since  $l(\mathbf{r})$  and  $v_0(\mathbf{r})$  do not necessarily have the same directional dependence. Admittedly there will be no difference in the fitting of the experimental curves as to which of the above attitudes is adopted since Eqs. (33) and (34) are formally identical. However, it does simplify the discussion for us to make our analysis using the second viewpoint.

<sup>27</sup> A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, England, 1953), 2nd ed.

Before a detailed analysis of the data let us review exactly the theoretical predictions for the behavior of  $\alpha_s/\alpha_n$  as a function of frequency and the electron-lattice parameters. Figure 8 summarizes these for certain cases which reasonably could be expected to occur. The quantities  $ql$  and  $\omega\tau$  are fixed by any combination of three parameters such as  $\omega$ ,  $1/c_s$ , and  $\tau$ ; or  $\omega$ ,  $1/c_s$ , and  $1/v_0$ ; or, perhaps,  $\omega$ ,  $(v_0/c_s)$ , and  $\tau$ . The last combination was used in stipulating the conditions for each calculation. Fixing  $c_s$  at  $3 \times 10^5$  cm/sec,  $v_0$  was allowed to assume the values  $0.5 \times 10^8$  cm/sec,  $3 \times 10^8$  cm/sec and  $7 \times 10^8$  cm/sec;  $\tau$  was varied through the three orders of magnitude  $3 \times 10^{-12}$  sec,  $3 \times 10^{-11}$  sec, and  $3 \times 10^{-10}$  sec. The frequency was varied from 15 to 150 Mc/sec in steps of 15 Mc/sec. All of the results shown in Fig. 8 are for  $\epsilon_0(0) = 1.76kT_c$ , the standard BCS value. Different energy gaps give results which differ only in that the curves will lie uniformly above or below those for the standard gap.

The results can be summarized as follows: The effect of increasing the frequency is simply to decrease the residual attenuation. The effects of increasing  $\tau$  are twofold: The width of the rapidly falling region is increased; and because of the fact that  $ql$  can be written as  $(v_0/c_s)\omega\tau$ ,  $g$  decreases with increasing  $\tau$  and with it the residual attenuation. The effect of increasing  $v_0$  is to decrease the residual attenuation because it gives a larger  $ql$ .

Let us now compare the calculations with experiment. The first step is to select a particular direction of propagation and polarization and fit one frequency curve, obtaining  $g$  and  $\omega\tau$ . Using the fact that  $ql = \omega/c_s$ , we should then be able to predict what  $g$  should be for each of the other frequencies in that particular family of curves. Note that at temperatures sufficiently far

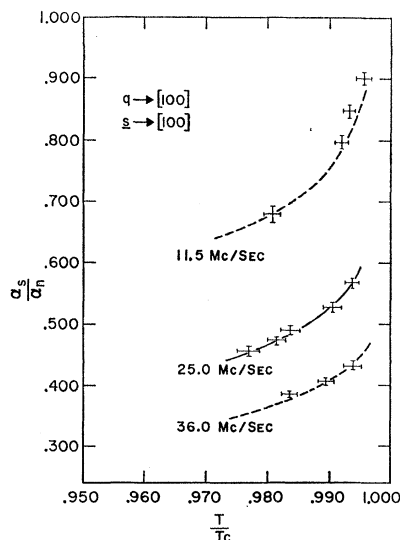


FIG. 9. A fit of the experimental data for  $(\alpha_s/\alpha_n)$  versus  $(T/T_c)$  in the  $[100, 100]$  orientation.  $g$  and  $2f(\epsilon)$  were selected for  $f = 26.5$  Mc/sec and the other  $g$ 's were predicted.

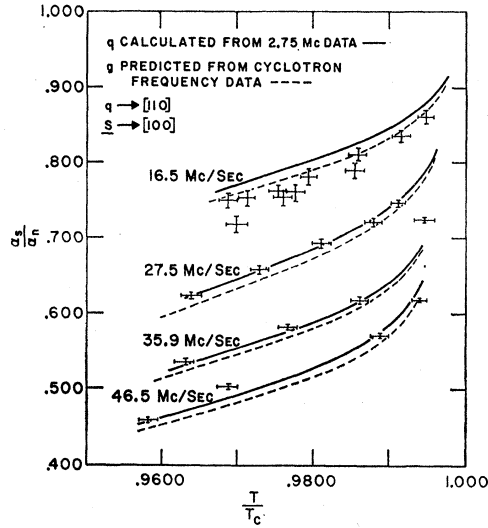


FIG. 10. A fit of the experimental data for  $(\alpha_s/\alpha_n)$  versus  $(T/T_c)$  in the  $[110, 100]$  direction.

below the transition temperature the attenuation is just  $g[2f(\epsilon)]$ . Thus the lower part of the curves can be matched by finding the combination of  $g$  and  $[2f(\epsilon)]$  which will correctly fit the other curves in the family at a given temperature. It might seem at first glance that two adjustable functions such as  $g$  and  $[2f(\epsilon)]$  would allow many combinations to give reasonable agreement with the data. However, we shall see that there is a unique  $[2f(\epsilon)]$  and only one  $(v_0/c_s)$  which will fit each family of curves. Furthermore, we shall see that the results for different orientations are quite consistent.

Consider the case  $[100, 110]$ , where the notation implies that the propagation is in the  $[100]$  direction and the polarization is in the  $[110]$  direction. We shall take the 25 Mc/sec curve and assume that  $T/T_c = 0.9750$  is sufficiently low so that  $\alpha_s/\alpha_n = g[2f(\epsilon)]$ . Let us first take  $[2f(\epsilon)]$  to be that for which the energy gap  $\epsilon(0) = 1.2kT_c$  is that obtained from the total superconducting fall-off data. In this case  $2f(\epsilon) = 0.850$  for  $T/T_c = 0.9750$ . Using this value we find  $g(25) = 0.529$ . This would predict that  $g(15) = 0.770$  and  $g(35) = 0.410$ . The notation  $g(15)$ ,  $\alpha(15)$ , etc., means that the quantity applies to the frequency (in Mc/sec) shown in the parentheses. These curves along with the experimental points are plotted in Fig. 9. It can be seen that the agreement is quite good. In view of the uncertainty of  $\epsilon(0)$  from our measurements we will consider this selection for  $[2f(\epsilon)]$  to be partly good luck.

Having now made a determination of the parameter  $g$  only from the residual attenuation viewpoint, one could argue reasonably that there are many functions of  $ql$  which would give approximately the same results in this range. Recall, however, that  $g$  also occurs in the total attenuation. Consequently, it would be reassuring if we could show that the  $g$  values derived above are

precisely those which give the correct frequency dependence of the total attenuation. We can write

$$\alpha = K[(1-g)/g], \tag{35}$$

where  $K$  is independent of the frequency. This means that if we solve for  $K$  in terms of  $\alpha(15)$  and  $g(15)$ , we can predict  $\alpha(25)$  and  $\alpha(35)$ . The results compare with the observed values as follows:

	$\alpha$ predicted	$\alpha$ observed	Error
$\alpha(25)$	17.6 dB/cm	17.8 dB/cm	-1.1%
$\alpha(35)$	28.3 dB/cm	28.0 dB/cm	+1.1%

This agreement seems to indicate that the  $g$  values are quite precisely determined.

Since all the empirical fittings of  $g$  seemed to be consistent for both the residual attenuation and the total fall-off, we were led to derive a relation which makes finding  $g$  from the data a great deal easier and which makes no assumptions about  $[2f(\epsilon)]$  except that it is frequency independent. For two frequencies in the same family we can write

$$\alpha_1 = K(1-g_1)/g_1; \quad \alpha_2 = K(1-g_2)/g_2. \tag{36}$$

Let  $a = \alpha_1/\alpha_2$  and  $g_2 = \chi g_1$ . Since at any sufficiently low temperature  $[(\alpha_s/\alpha_n)_1]/[(\alpha_s/\alpha_n)_2] = (g_1/g_2)$ ,

$$\chi = \frac{(\alpha_s/\alpha_n)_1}{(\alpha_s/\alpha_n)_2}, \tag{37}$$

it follows that

$$g_1 = \frac{\chi - a}{\chi(1-a)}. \tag{38}$$

Using Eq. (49) we see that there is a unique gap such that  $2f(\epsilon)$  fits the experimental family of curves. Curves predicted from Eq. (38) for  $[110, 100]$  are compared with data in Fig. 10 as indicated by the solid curves. The  $[2f(\epsilon)]$  value was found from the 25 Mc/sec curve.

Thus far we have been concerned with a family of curves for a single orientation at a time. If we could fit one member of a family and then predict not only the

TABLE I. Electronic and ultrasonic parameters estimated from data.

q	s	$\omega$ (Mc/sec)	$g$	$g$	$l$ $\times 10^{+3}$ (cm)	$\tau$ $\times 10^{+11}$ (sec)	$v_0$ $\times 10^{-8}$ (cm/sec)
[110]	[010]	16.5	1.03	0.850	3.88	2.8	1.38
		27.5	1.71	0.712			
		35.9	2.23	0.610			
		46.5	2.89	0.540			
[100]	[010]	11.5	1.38	0.770	6.50	7.0	0.93
		25.0	3.00	0.529			
		36.0	4.32	0.410			
[110]	[110]	15.0	0.71	0.917	2.56	2.0	1.28
		25.5	1.18	0.818			
		35.0	1.70	0.715			

other members of that particular family but also the  $g$  values for the other orientations, it would greatly strengthen the belief that  $g(ql)$  gives the correct  $ql$  dependence. There is one possibility for carrying out such a calculation. Steinberg's attenuation variation depends on the cyclotron frequency for an electron orbit in the plane defined by the propagation and polarization directions. The product of the cyclotron frequency and the relaxation time is

$$\omega_c \tau = \left( \frac{eH}{m^*c} \right) \frac{l}{v_0} = \frac{el}{(m^*v_0)c} H. \quad (39)$$

Let

$$b^2 \equiv \left[ \frac{el}{m^*v_0c} \right].$$

If the mean free path were a function of direction in the crystal rather than just energy, the collision-drag mechanism suggests that the relevant mean free path would be the one in the direction of polarization. Hence, if the  $m^*v_0$ 's of the electrons participating in the shear interaction for two orientations were precisely known, then the ratio of the mean free paths in the two different directions could be found from the ratio of  $b$ 's. In fact, for a spherical Fermi distribution

$$b_1/b_2 = l_1/l_2. \quad (40)$$

The actual Fermi surface in aluminum has been worked out in great detail by Heine<sup>28</sup> and Harrison<sup>29</sup> using a free electron model and then suitably modifying it to fit the results of the de Haas-van Alphen effect, cyclotron resonance and the anomalous skin effect. Roberts<sup>30</sup> has studied the surface further using the magnetoacoustic technique mentioned in the introduction. The results seem to indicate that the first zone is filled, the second zone has pockets of holes, and the third and fourth zones contain pockets of electrons. The shapes of these Fermi surface sheets are fairly well known.

However, at the present time it is not known exactly what group of electrons participates in the shear interaction, and so no exact statement can be made regarding the  $m^*v_0$  in Eq. (39). However, for small enough  $q$  one would expect that variations in  $m^*v_0$  will represent an average over the surface. If this is the case, then we should be able to calculate  $ql$  in any direction once all  $b$ 's are determined and  $ql$  is known for one orientation. It is realized that these assumptions must be highly doubtful, but it is interesting to note the results given below.

Taking the value of the mean free path for the orientation [100, 110] ( $l = 6.5 \times 10^{-3}$  cm), the mean free path for [110, 100] was calculated from Eq. (51) ( $l = 4.0 \times 10^{-3}$  cm) and the resulting values of  $g(ql)$  for the frequencies of the rapid-fall data were determined.

<sup>28</sup> V. Heine, Proc. Roy. Soc. (London) A240, 340 (1957).

<sup>29</sup> W. A. Harrison, G. E. Research Laboratory, Schenectady, New York (unpublished).

<sup>30</sup> B. W. Roberts, Phys. Rev. 119, 1889 (1960).

The ensuing theoretical curves for the superconducting attenuation are plotted in Fig. 10. It can be seen that the results are within a few percent of the values found by fitting the [110, 100] data.

The energy gap which would lead to a particular  $2f(\epsilon)$  at a given temperature can be found easily in the range close to  $T_c$ . Assuming  $\epsilon(T) \ll kT$  and using the  $\epsilon(T)$  approximation for first order in  $\Delta T/T_c$ , we can show that

$$\frac{\epsilon(0)}{kT_c} = \frac{1.16}{[1 - T/T_c]^{1/2}} \frac{T}{T_c} \{ [2f(\epsilon)]^{-1} - 1 \}. \quad (41)$$

For example, if  $(T/T_c) = 0.9750$  and  $2f(\epsilon) = 0.850$ , then  $\epsilon(0) = 1.25kT_c$ . That this is correct can be verified by substitution into the exact equation for  $2f(\epsilon)$ .

Thus far we have had nothing to say concerning the parameter  $\omega\tau$  in the region of rapid fall. We have used the London equations in order to determine the density of electrons or pairs which act to form the superconducting currents. For most metals the London region should occur in the temperature range which would coincide with the lower end of the region of rapid fall, and, hence, the London density as estimated from the BCS theory should give a rough estimate of the actual  $\omega\tau$ . As we have discussed in the last section, when  $(N_s/N) > \omega\tau$  the electric fields are reduced to a negligible value and the first term of Eq. (32) becomes negligible. In actual practice the data in the region of rapid fall are not sufficiently accurate to allow more than a rough estimate for  $\omega\tau$ . Bearing this fact in mind, attempts were made to determine  $\tau$ . For example, using the 45 Mc/sec data of the [110, 100] orientation it was found that  $\omega\tau = \omega\tau = 6.4 \times 10^{-8}$ , giving a  $\tau$  of  $2 \times 10^{-11}$ , which is not an unreasonable value (see Table I for a summary of evaluated parameters). The estimation of  $v_0$  from  $ql$  and  $\omega\tau$  can be accomplished as:

$$v_0 = \frac{qlc_s}{\omega\tau} = 1.38 \times 10^8 \text{ cm sec}^{-1},$$

where we have used the measured value of  $c_s$  for this orientation ( $c_s = 3.92 \times 10^5$  cm/sec). David *et al.*<sup>31</sup> have recently made shear wave attenuation measurements in aluminum at somewhat larger values of  $ql$ . They found a systematic deviation from the predicted residual attenuation according to the simplified theory. In fact the difference between the measured and predicted residual attenuation was found to be a monotonically increasing function of  $ql$ . One possible source of this deviation is the shear-wave deformation potential suggested by Pippard on the basis of the actual complicated electronic structure in real metals. Such a deformation potential would be expected to lead to a contribution to the residual attenuation which increases monotonically as a function of  $ql$ .

<sup>31</sup> R. David, H. R. Van Der Laan, and N. J. Poulis, Physica 29, 357 (1963).

One suggestion which is obvious from this consideration is to attempt a measurement of the shear-wave deformation by taking the difference between the experimental and predicted residual attenuation at large  $ql$  values.

### CONCLUSION

This article reports and interprets experiments which were conducted to determine the temperature dependence of shear-wave attenuation in superconducting aluminum. Some of the main results are:

(1) In contrast to the longitudinal-wave attenuation, the experiments showed a strong frequency dependence of the reduced attenuation ( $\alpha_s/\alpha_n$ ) as a function of temperature.

(2) The temperature variation of ( $\alpha_s/\alpha_n$ ) could be separated into two parts:

(a) a very sharp decrease with temperature very close to the transition temperature and

(b) a residual attenuation having a temperature dependence similar to that for longitudinal waves.

(3) A theoretical formulation was made which used approximations expected to be valid near the transition temperature. This theory employed a self-consistent treatment of the electron-impurity collisions and qualitatively reproduced the features of the experimental data.

(4) It was found that the specific details of the data could be predicted by this theory when the function  $2f(\epsilon)$  was used for the normal electron density.

(5) In particular the residual attenuation was shown to be  $g[2f(\epsilon)]$ , and the width of the region of rapid-falling attenuation was shown to be determined by  $\omega\tau$ .

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## Surface Integral Form for Three-Body Collision in the Boltzmann Equation

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A new form is given for the triple-collision term in the generalized Boltzmann equation which is more similar to the well-known binary-collision expression than those given heretofore. The form involved is a surface integral over a five-collision parameter space which is the generalization of the two-dimensional collision parameter space for binary collisions. For "soft" repulsive interactions, the expression involves both the asymptotic properties of three-body collisions before and after the collision, and the dynamics of binary collisions during the collision process. For hard spheres, the expression involves only the asymptotic properties of ternary and binary collisions.

### I. INTRODUCTION

IN recent years, several authors<sup>1-17</sup> have written on the structure of the asymptotic three-body collision term in a modified Boltzmann equation appropriate to

dense gases. At the present time, it appears that all methods of derivation lead to the same result, albeit in different mathematical forms.<sup>3,9,17</sup> In a form derived by the author,<sup>3</sup> this operator may be written

$$I_3 = \int \theta_{12} [S(123) - S(12)S(23) - S(12)S(13) + S(12)] \\ \times f(1)f(2)f(3)d(2)d(3), \quad (I)$$

where 1, 2, etc., are abbreviations for the momentum and configuration  $\mathbf{p}_1, \mathbf{x}_1; \mathbf{p}_2, \mathbf{x}_2$  of particles 1, 2, etc.,  $S(123), S(12)$  are the substitution operators which have been defined for instance in Ref. 10, and will be

<sup>1</sup> N. N. Bogolyubov, "Problems of a Dynamical Theory in Statistical Physics," translation by E. K. Gora from *Studies in Statistical Mechanics*, edited by J. deBoer and G. E. Uhlenbeck (North-Holland Publishing Company, Amsterdam, 1962), Vol. I.

<sup>2</sup> M. S. Green, *J. Chem. Phys.* **25**, 836 (1956).

<sup>3</sup> M. S. Green, unpublished letter to G. E. Uhlenbeck.

<sup>4</sup> M. S. Green, *Physica* **24**, 393 (1958).

<sup>5</sup> S. T. Choh and G. E. Uhlenbeck, thesis, University of Michigan, 1958 (unpublished).

<sup>6</sup> R. M. Lewis, *J. Math. Phys.* **2**, 222 (1961).

<sup>7</sup> S. Rice, J. Kirkwood, and R. Harris, *Physica* **27**, 717 (1961).

<sup>8</sup> E. G. D. Cohen, *Physica* **28**, 1025, 1045, 1060 (1962).

<sup>9</sup> E. G. D. Cohen, *Fundamental Problems in Statistical Mechanics* (North-Holland Publishing Company, Amsterdam, 1960).

<sup>10</sup> M. S. Green and R. A. Piccirelli, *Phys. Rev.* **132**, 1388 (1963).

<sup>11</sup> P. Resibois, *J. Math. Phys.* **4**, 166 (1963).

<sup>12</sup> E. G. D. Cohen, *J. Math. Phys.* **4**, 183 (1963).

<sup>13</sup> S. Ono and T. Shizume, *J. Phys. Soc. Japan* **18**, 29 (1963).

<sup>14</sup> R. Zwanzig, *Phys. Rev.* **129**, 486 (1963).

<sup>15</sup> J. Weinstock, *Phys. Rev.* **132**, 470 (1963).

<sup>16</sup> G. Sandri, *Ann. Phys. (N.Y.)* **24**, 332, 380 (1963).

<sup>17</sup> P. Resibois (private communication).