Orientation Dependence of Ultrasonic Attenuation in Copper*

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(Received 30 August 1967; revised manuscript received 26 June 1968)

The ultrasonic attenuation of longitudinal phonons in copper single crystals has been measured in a temperature range from 2 to 80°K, and in a frequency range from 8 to 72 Mc/sec; these measurements cover a range in ql from 0.07 to 4.0. Analysis of these results shows that for values of $ql \gg 1$, the attenuation associated with the electron-phonon interaction is a function of crystalline orientation. For values of $ql \ll 1$, the attenuation is found to be independent of crystalline orientation, and in good agreement with a free-electron model. The attenuation associated with the dislocation-phonon interaction is also found to be orientation-dependent. Calculations in which the deviations of the real Fermi surface from a free-electron sphere are considered do not account fully for the anisotropic behavior of the attenuation; hence one concludes that the deformation of the Fermi surface as a function of the direction and polarization of the imposed phonons must be the significant quantity.

INTRODUCTION

THE attenuation of ultrasonic waves at low temperatures in a metal such as copper is assumed to result from the interaction of the impressed ultrasonic wave with the conduction electrons of the metal and with the dislocation arrays in the metallic sample. Ultrasonic measurements on copper single crystals in temperature and frequency ranges such that the electron-phonon interaction dominates and for which the product of the phonon wave number q and the electron mean free path l is less than unity have been interpreted with the free-electron theory of Pippard.[1] The measurements of MacFarlane, Rayne, and Jones[2] on copper are for frequencies up to 390 Mc/sec or for a maximum ql value of approximately 22; in the measurements reported below, the range of ql values is from 0.07 to 4.0. From the various measurements with $ql > 1$, one concludes that the free-electron model is not applicable, and that the deformation of the equilibrium form of the Fermi surface must be included. Pippard[3] has considered the effects of nonspherical Fermi surfaces in terms of a deformation parameter which is a function of position on the Fermi surface and the direction and polarization of the incident wave. Since the deviations of the Fermi surface of copper from the free-electron sphere are now quite accurately known, it would seem reasonable that the disparity between theory and experiment could be determined as a function of the deformations of the Fermi surface.

EXPERIMENTAL PROCEDURE AND RESULTS

Three single-crystal copper specimens were obtained from Metals Research Ltd., of Cambridge, England. Crystals 1 and 2 were cubes about 1.27 cm on a side, with spark-cut faces such that one face of the cube was in a (100) orientation, and the other two faces were in (110) and (1$\bar{1}$0) orientations. One of these samples was subsequently spark-cut for attenuation measurements in a (111) orientation. Crystal 3 was a cylinder about 1.27 cm in length and 1.27 cm in diameter with the end faces in a (111) orientation.

The attenuation in these samples was measured by the usual pulsed-echo technique, in which an ultrasonic pulse generated by a quartz transducer travels through the sample until reflected from the back surface, and then travels back to the transducer; the X-cut quartz crystals are both transmitters and receivers of the longitudinal vibrations. In our system a pulsed rf signal of 0.5 to 50 μsec was produced by an Arenberg pulsed oscillator; the repetition rate was maintained at about 60 cps throughout the measurements to prevent any heating of the samples. Attenuation measurements were made with a calibrated attenuator with a precision of the order of 0.14 dB over the frequency range of 8 Mc/sec to 72 Mc/sec. In the temperature region in which the attenuation decreases markedly with increasing temperature, both the measurement of temperature and the attainment of equilibrium were critical. Two 0.1-W 100-Ω Allen-Bradley carbon resistors calibrated against the 1958 He^4 vapor-pressure[4] scale and against a platinum resistor were used for measurements from the λ point to 30°K; above 30°K only the platinum resistor was used. The errors in temperature are estimated to be ±0.001°K in the helium region, and ±0.01°K in the nitrogen region. During each experimental run the velocity of the acoustic wave was measured by time-of-flight measurements to assure that the measured attenuation was not a function of changes in the acoustic velocity. A sine wave was displayed on the oscilloscope simultaneously with an echo pattern, and the frequency

* Supported in part by Grant No. G7694 from the National Science Foundation.
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[1] A. B. Pippard, Phil. Mag. **46**, 1104 (1955).
[2] R. E. MacFarlane, J. A. Rayne, and C. K. Jones, Phys. Letters **19**, 87 (1965); **24A**, 197 (1967); R. E. MacFarlane and J. A. Rayne, Phys. Rev. **162**, 532 (1967).
[3] (a) A. B. Pippard, Proc. Roy. Soc. (London) **A257**, 165 (1960); (b) A. B. Pippard, *The Dynamics of Conduction Electrons* (Gordon and Breach, Science Publishers, Inc., New York, 1960), pp. 110–122.
[4] Natl. Bur. Std. (U. S.), Monograph **10**, (1958).

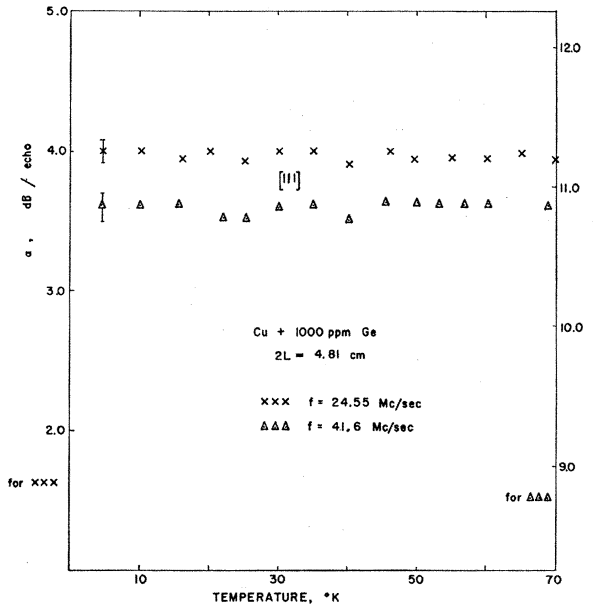

FIG. 1. Attenuation of longitudinal phonons in a single crystal of copper to which 1000 ppm of germanium have been added; the sample faces are in a (111) orientation. In this sample the electron-phonon interaction has been suppressed and the dislocation-phonon interaction appears to be negligible. From these results, the background attenuation can be assumed to be constant with temperature and to be a function of the frequency of the imposed wave.

of the wave was adjusted to give one wavelength between any two successive echoes; the period of the wave was measured with a Hewlett Packard frequency counter. The time between any two echoes combined with the length of the sample yields the velocity of sound to an accuracy of about 1%.

One of the experimental difficulties in determining the absolute electronic attenuation is that there is always a background attenuation which is usually assumed to be temperature-independent, and thus can simply be subtracted from the measured attenuation. This background attenuation is due to variations in the bonding of the transducer with the crystal, impedance matching throughout the measuring system, off-axis orientation of the sample face with respect to the crystal axis, and lack of parallelism in the geometry of the sample end faces. In order to test the temperature dependence of the background attenuation, measurements were made on a copper single crystal of the same purity as crystal 3 (to which 1000 ppm of germanium had been added) in which the electron-phonon interaction is suppressed and in which the dislocation-phonon interaction is negligible due to pinning. Figure 1 shows the results of such measurements; the attenuation is constant with temperature, and is a function of the frequency of the imposed wave.

In an earlier paper[5] the use of γ irradiation was indicated as a method for suppressing the attenuation due to the dislocation-phonon interaction. Figure 2 shows the attenuation of a copper crystal both before and after γ irradiation. One does not always observe such a complete suppression of the dislocation term; we have observed that in copper crystals with an im-

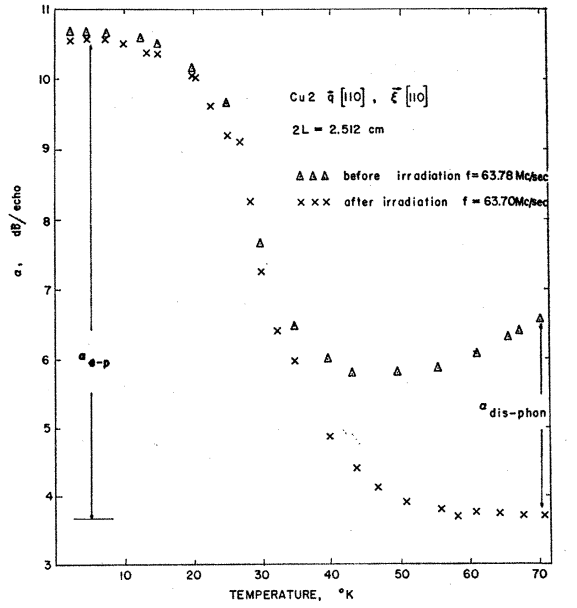

FIG. 2. Attenuation of longitudinal phonons in a copper single crystal both before and after γ irradiation; the sample faces are in a (110) orientation. In this case, after irradiation the attenuation due to the dislocation-phonon interaction was negligible.

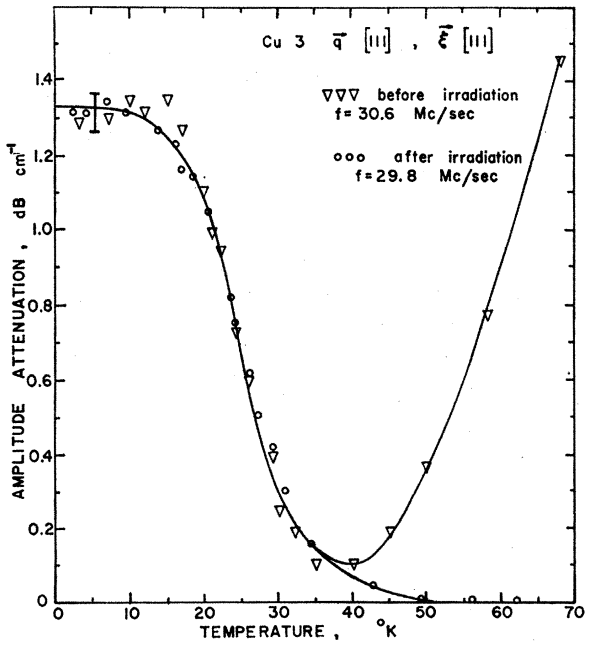

FIG. 3. Attenuation of longitudinal phonons in a copper single crystal both before and after γ irradiation; the sample faces are in a (111) orientation. In this case, also, after irradiation the attenuation due to the dislocation-phonon interaction was negligible.

[5] R. J. Kolouch and K. A. McCarthy, Phys. Rev. 139, A700 (1965).

purity content of more than a few ppm and with a dislocation density of approximately 10^6 dislocations/cm^2, irradiation will not reduce the attenuation due to the dislocation-phonon interaction to a negligible amount. An attenuation resulting from the dislocation-phonon interaction was found for longitudinal waves propagated in the [110] direction, as shown in Fig. 2, and in the [111] direction, as shown in Fig. 3. However, no evidence of attenuation due to a dislocation-phonon interaction was found with longitudinal waves propagated in the [100] direction, as shown in Fig. 4.

The extensive attenuation measurements made on the samples discussed above can be used to determine the temperature and frequency dependence of the absolute attenuation due to the electron-phonon interaction. In crystals measured before irradiation, the measured attenuation is the sum of the attenuation associated with the electron-phonon interaction, $\alpha_{e\text{-}p}(T)$, the attenuation due to the dislocation-phonon interaction, $\alpha_{d\text{-}p}T$, and the background attenuation, α_b, which has been shown above to be temperature-insensitive.

In crystals measured after irradiation and in which the attenuation due to the dislocation-phonon interaction is negligible, the measured attenuation is the sum of the attenuation associated with the electron-phonon interaction and the background attenuation. It should be noted here, that at temperatures less than 10°K, the attenuation is also temperature-insensitive due to scattering by impurities.

In this paper we will analyze the propagation of longitudinal waves in normal metals in terms of the free-electron model of Pippard[7] in which the attenuation α may be written:

$$\alpha=\frac{Nm}{\rho v_s\tau}\left\{\frac{q^2l^2\tan^{-1}ql}{3(ql-\tan^{-1}ql)}-1\right\}, \tag{1}$$

where N is the electron density, m the electron mass, ρ the density of the metal, v_s the acoustic wave velocity, and τ the relaxation time for the electrons. For copper, the attenuation may be written

$$\frac{\alpha}{q}=\frac{5958}{v_sql}\left\{\frac{q^2l^2\tan^{-1}ql}{3(ql-\tan^{-1}ql)}-1\right\}. \tag{2}$$

l/v_0 is substituted for τ, where v_0 is the electron velocity at the Fermi surface. As shown in Figs. 2–4, the attenuation in the 15 to 30°K temperature region is markedly temperature-sensitive.

The above data will be analyzed in various parts. First, we will consider the attenuation at 30°K for frequencies from 9 to 64 Mc/sec and for the three orientations, indicated in Figs. 2–4. The crystals referred to in Figs. 2 and 4 as Cu 2 were grown from the same melt; l at 30°K for these crystals as calculated from Eq. (2) is constant within experimental error with a value of 6.1×10^{-4} cm for the above frequencies and for the (100) and (110) orientations. For these frequencies and this mean free path, the product ql is less than unity. These results suggest that for $ql<1$, the quantity l is not a function of orientation, as is consistent with the free-electron model. The crystal referred to as Cu 3 in Fig. 3 was grown from a different melt; the frequency range of measurements for this crystal was from 23 to 48 Mc/sec. As was the case for crystal Cu 2, l at 30°K as calculated from Eq. (2) was constant with a value of 9.4×10^{-4} cm; for these frequencies ql was also less than unity.

In Fig. 5, α/q is shown as a function of ql for a temperature of 30°K; the experimental data for the three orientations are plotted using the respective values of l given above. These data can also be considered in the limit $ql\ll1$, for which the more general theory of Pippard[7] gives the attenuation for longitudinal waves as

$$\alpha=\frac{\hbar q^2}{4\pi^3\rho v_s}\int\mathfrak{D}^2l\,dS, \tag{3}$$

where $\mathfrak{D}$ is the deformation parameter, and the integral is taken over the entire Fermi surface. Figure 6 shows the electron-phonon attenuation as a function of frequency in the limit $ql\ll1$; the proportionality to the square of the frequency is demonstrated. The differences in the three orientations in both Figs. 5 and 6 correspond to the differences in the sound velocities in the three respective directions. The attenuation is inversely

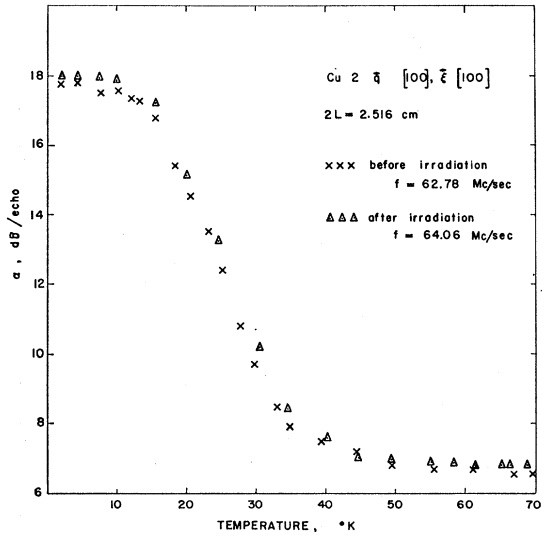

FIG. 4. Attenuation of longitudinal phonons in a copper single crystal both before and after γ irradiation; the sample faces are in a (100) orientation. It should be noted that for longitudinal waves propagated in the [100] direction, no evidence of attenuation due to a dislocation-phonon interaction was found.

[6] See comments by A. B. Bhatia and R. A. Moore, Phys. Rev. **121**, 1075 (1961).

[7] See Eq. (14) of Ref. 1, and pp. 173 and 174 of Ref. 3(a).

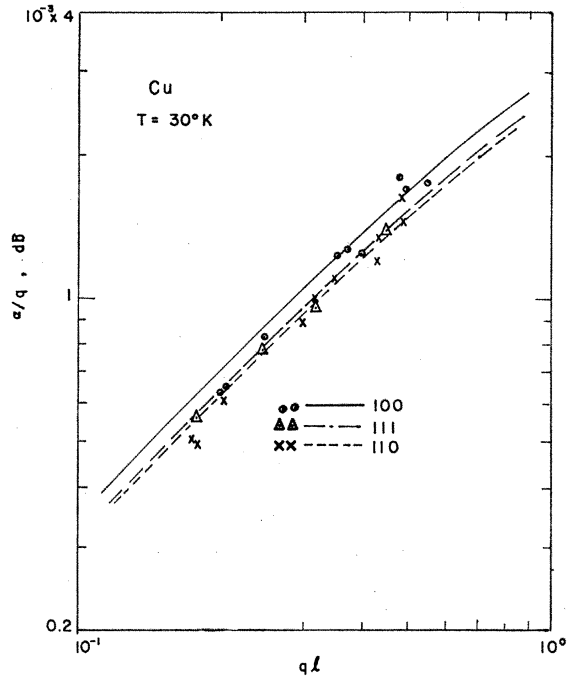

FIG. 5. α/q is plotted as a function of ql for copper, as given by Eq. (2). The data plotted are at a temperature of 30°K, and in a frequency range such that $ql \ll 1$.

proportional to the cube of the sound velocities; from time-of-flight measurements the ratio of the sound velocity in the [110] direction to that in the [100] direction is approximately 1.1, and within experimental error, that in the [111] direction is the same as that in the [110] direction. This result would suggest that for $ql \ll 1$, the integral in Eq. (3) is constant and not a function of orientation.

Secondly, we will consider the measurements made at 4.2°K and at sufficiently low frequencies that $ql \ll 1$. As above, l at 4.2°K and as calculated from Eq. (2) is constant, and is independent of orientation. A plot of α/q as a function of ql at a temperature of 4.2°K and at frequencies sufficiently low to satisfy the condition that $ql \ll 1$ is consistent with the predictions from the free-electron model.

Thirdly, we will consider measurements at 4.2°K and at sufficiently high frequencies that ql had values as high as 4. In the free-electron model in the limit $ql \gg 1$,

$$\alpha = \pi N m v_0 q / 6 \rho v_s^2 . \tag{4}$$

Here we see that the attenuation is independent of l. In the more general Pippard model in the limit $ql \gg 1$, and for an acoustic wave traveling in the x direction,

$$\alpha = \frac{\hbar q}{4\pi^2 \rho v_s} \int R K_x^2 d\psi , \tag{5}$$

where R is the reciprocal of the Gaussian curvature of the Fermi surface, K_x is the value of $\mathfrak{D}$ on the effective zone, ψ is the azimuthal angle, and the integral is taken around the effective zone. The effective zone refers to that part of the Fermi surface for which the electrons are moving normally to the wave vector $\mathbf{q}$. Here one is concerned only with those electrons whose velocity component in the direction of $\mathbf{q}$ equals v_s.

Analysis of the data at 4.2°K shows that for frequencies such that $ql > 1$ the measured values deviate markedly from the predictions of the free-electron model. The attenuation for the (110) orientation in the limit $ql > 1$ is less than predicted from the free-electron model; the attenuation for the (100) orientation is larger than predicted, and that for the (111) orientation deviates only slightly from the predictions of Eq. (2).

In both models the attenuation is a linear function of the frequency. The results reported here assume that the integrand is not a sensitive function of the frequency; these results can be compared with those of MacFarlane, Rayne, and Jones and the predictions of the free-electron model by determining the slope of the attenuation versus frequency for values of $ql \gg 1$. Table I gives such a comparison. Figure 7 shows the attenuation as a function of frequency for the three principal orientations for values of ql up to 4. As was demon-

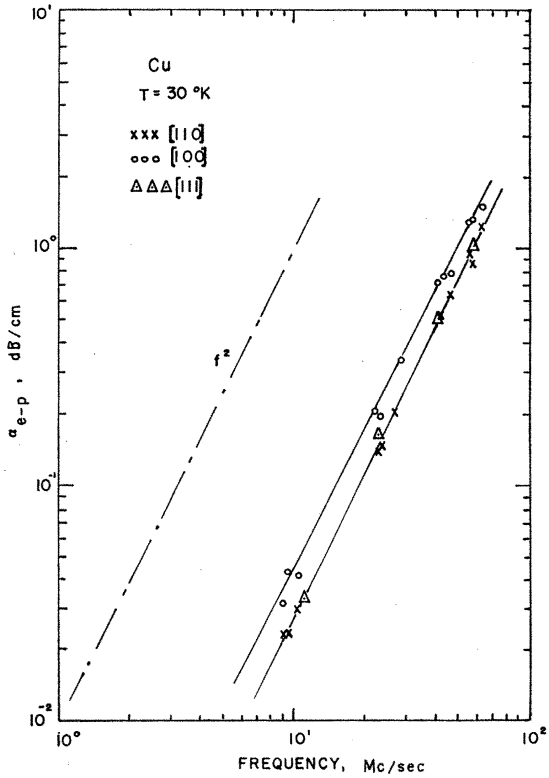

FIG. 6. Attenuation as a function of frequency (logarithmic plot) for longitudinal phonons in two copper crystals for the (100), (110), and (111) orientations at 30°K. The expected f^2 dependence in sketched to the left of the data points.

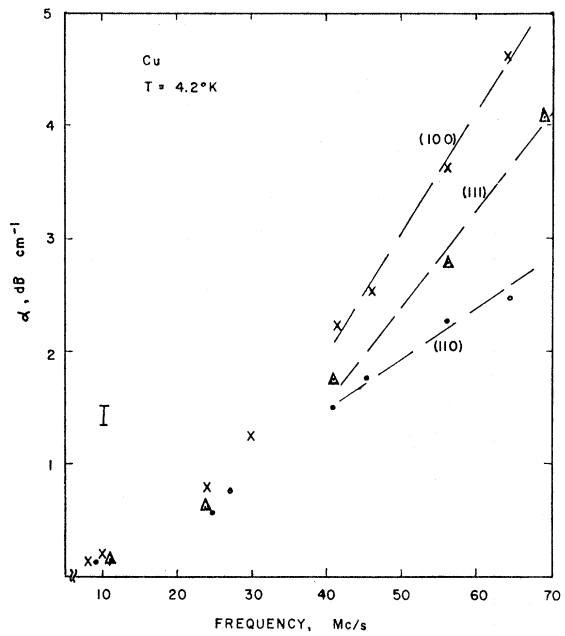

FIG. 7. Attenuation as a function of frequency at 4.2°K for longitudinal phonons propagated in the [100], [110], and [111] directions. The slope in the high frequency limit is sketched, and is tabulated in Table I. An estimate of accuracy is indicated.

strated by MacFarlane *et al.*, the slope to be considered is the value in the limit $ql \gg 1$; their data for values of ql up to 22 compare well with the data here for the (111) and (110) orientations. Our value for the (100) orientation is lower than that of MacFarlane, but is consistent with their lower-frequency data.

DISCUSSION OF ATTENUATION RESULTS

The results of the measurements of the attenuation of longitudinal waves in copper at low temperatures and at high frequencies suggest that further consideration should be given to a non-free-electron model for noble metals and that details of the Fermi surface of copper and their effect on the attenuation should be specifically included. Pippard has considered the effect of the propagation of a longitudinal wave on the electron distribution, and those forces which act on the electron at the Fermi surface. In his model, he examines both the change in the wave vector **k** of the electrons as seen by an observer fixed in the lattice and the deformation of the Fermi surface. He characterizes the deformation of the Fermi surface by a vector **K** as a function of **k** and as a function of position on the Fermi surface. For longitudinal waves propagated along the x axis, Pippard has shown that

$$\alpha = \frac{\hbar q}{4\pi^3 \rho v_s}\left\{\int \frac{\mathfrak{D}^2 q l dS}{1+q^2l^2\cos^2\varphi} + \left[\int \frac{\mathfrak{D} dS}{1+q^2l^2\cos^2\varphi}\right]^2 \Big/ \int \frac{ql\cos^2\varphi dS}{1+q^2l^2\cos^2\varphi}\right\}, \quad (6)$$

where $\mathfrak{D} = K_x + k_x \cos\varphi$, and φ is the angle between the x axis and the normal to the element of the Fermi surface, dS. A comparison of Eq. (6) with Eq. (5) indicates that the quantities which may be orientation-dependent lie inside the integral, with the exception of the group velocity whose orientation dependence has been measured.

From all the results on noble metals and recent measurements on potassium,[8] it appears that the details of the Fermi surface do contribute to the anisotropic behavior of the attenuation. Certain contributions can be approximated, as will be shown below. It appears, however, that the deformation parameter is the principal contributor to the anisotropy, and its behavior as a function of orientation has not been calculated.

The departure of the Fermi surface of copper from the free-electron sphere is now well understood. The anomalous-skin-effect measurements of Pippard,[9] the magnetoacoustic measurements of Bohm and Easterling[10] and Kamm,[11] and the de Haas–van Alphen measurements of Shoenberg and Roaf[12] are in good agreement with the theoretical work of Burdick[13] and Segall.[14] The surface is known in sufficient detail that one can approximate the first term in Eq. (7); except for values of $ql \sim 1$, the other terms in Eq. (7) are negligible. Hall[15] has shown from a geometrical calculation that the necks do not account for the magnitude of the measured anisotropy, although their contribution to the attenuation is found to be a function of orientation. Breecher[16] has examined the first integral of Eq. (7), assuming that $\mathfrak{D}$ is not a function of orientation for $ql \gg 1$, and has shown that for values of ql greater than 3, the integral is independent of q within the experimental error of the measured attenuation. This result is in agreement with the approximation by Pippard[17] in which he

TABLE I. The slope of the attenuation versus frequency for copper at 4.2°K. The results from the above data are compared with the predictions of the free-electron model, and the limiting slopes given by MacFarlane *et al.*

Orientation	Polarization	These results	Free-electron	MacFarlane *et al.*
(100)	(100)	0.12[a]	0.100[a]	0.19[a]
(111)	(111)	0.08	0.070	0.07
(110)	(110)	0.05	0.076	0.05

[a] Units are dB cm^{-1} $(Mc/sec)^{-1}$.

[8] G. G. Natale and I. Rudnick, Phys. Rev. **167**, 687 (1968).
[9] A. B. Pippard, Phil. Trans. Roy. Soc. London **250A**, 325 (1957).
[10] H. V. Bohm and V. J. Easterling, Bull. Am. Phys. Soc. **6**, 438 (1961).
[11] G. N. Kamm, Bull. Am. Phys. Soc. **11**, 446 (1966).
[12] D. Shoenberg and D. Roaf, Phil Trans. Roy. Soc. London **A255**, 85 (1962).
[13] G. A. Burdick, Phys. Rev. **129**, 138 (1963).
[14] B. Segall, Phys. Rev. **125**, 109 (1962).
[15] L. H. Hall, Phys. Rev. **153**, 779 (1967).
[16] J. D. Breecher, Tufts University (private communication).
[17] See p. 174 of Ref. 3(a).

considers that the dominant contribution to the integral taken for large values of ql comes from those parts of the Fermi surface where the electrons are moving normal to $\mathbf{q}$; in this case the integral carried out in terms of the variable $\pi/2-\varphi$ is independent of ql. Of more importance is Breecher's calculation of the effect of the real Fermi surface on the attenuation. Again he has assumed that $\mathfrak{D}$ is not a function of orientation, and has calculated the relative contributions of the first term in Eq. (7) for the (100) and (110) effective zones. He concludes that the ratio of the contribution of the (100) zone to that from the (110) zone is approximately 1.1. If one now includes the reciprocal of the square of the ratio of the group velocities in the respective directions, and writes these results in terms of α/f, then $(\alpha/f)_{100}/(\alpha/f)_{110}=1.4K_{x100}^2/K_{x110}^2$. The experimental data summarized in Table I shows that this ratio should be larger. One then concludes that the deformation parameter as a function of orientation must be the significant quantity.

ACKNOWLEDGMENTS

The authors are grateful to Professor J. R. Christman for many helpful discussions, and to Mr. J. D. Breecher for the use of his calculations. The computations for this work were done at the Tufts University Computation Center. The preliminary phases of this work were supported in part by Contract No. AF 19(628-4029) of the U. S. Air Force.

APPENDIX: TEMPERATURE DEPENDENCE OF THE ELECTRON MEAN FREE PATH

The temperature dependence of the electron mean free path has been deduced from the attenuation measurements using Eq. (2). At temperatures less then 10°K both impurity scattering and lattice scattering must be considered. From Matthiessen's rule, $1/l=1/l_0+1/l(T)$, one can obtain the temperature dependence of the electron mean free path, $l(T)$. Figure 8 shows $1/l(T)$ as a function of temperature for the three orientations and for $ql<1$. The temperature dependence of $1/l(T)\alpha T^5$ is in agreement with the predictions[18] of the Bloch model. The intercept of $1/l(T)$ is 9.2×10^{-28} esu as compared to 2.9×10^{-28} esu from the electrical conductivity measurements of Berman and MacDonald.[19]

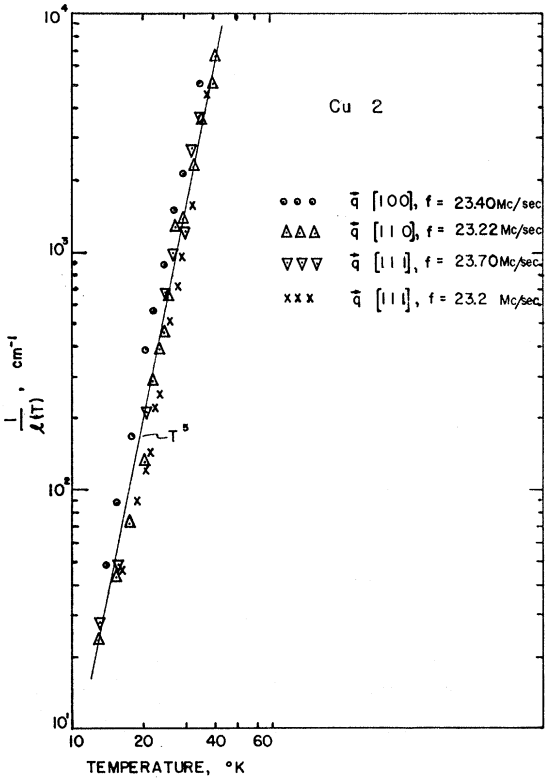

FIG. 8. Reciprocal of the temperature-dependent part of the electron mean free path for copper as a function of temperature. These values were determined from attenuation measurements using Eq. (2), and from calculations described in the Appendix.

[18] See, for example, C. Kittel, *Introduction to Solid-State Physics* (John Wiley & Sons, Inc., New York, 1966), 3rd ed., pp. 218–220.
[19] R. Berman and D. K. C. MacDonald, Proc. Roy. Soc (London) **A211**, 122 (1952).