Amplitude-Dependent Ultrasonic Attenuation in Superconductors*

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(Received 8 April 1966)

An anomaly in the absorption of ultrasonic waves has been found in some very pure superconductors and and has been investigated in detail in superconducting lead. It consists in a strong dependence of the absorption on the amplitude of the ultrasonic waves. The amplitude dependence is only weakly present in the normal state. The effect is found to be strongly temperature-dependent, decreases as impurities are added to the crystal, and exhibits little or no change with frequency. Deformation and annealing have a pronounced effect on the anomaly. It appears that these characteristics can be understood in terms of a model, which is proposed here, based on the assumption of a strong interaction between the conduction electrons and the dislocations in the metal crystal. The presence of weakly pinned dislocations and their motion in the field of the sound wave is assumed. In the normal state, this motion is highly damped by the conduction electrons, and therefore, the dislocations cannot contribute much to the ultrasonic absorption. In the superconducting region, this damping decreases with the same temperature dependence as the ultrasonic absorption by the electrons. The dislocations become more free to move and therefore can cause an (amplitude-dependent) absorption by themselves. The mechanism for this absorption is thought to be dislocation unpinning similar to that discussed, for example, by Granato and Lücke.

INTRODUCTION

RECENT measurements[1–4] of the absorption of ultrasonic waves in superconductors show a dependence of the absorption on the amplitude of the sound wave. This amplitude dependence is strong near 1°K and diminishes rapidly as the temperature is raised to the superconducting transition temperature. Only a weak amplitude dependence is present in the normal state. The purpose of this paper is to present the results of a study to explain this effect. A model is proposed and discussed on the basis of experiments and calculations described herein. The main parts of the paper are (A) a brief review of the ultrasonic attenuation in metals, (B) a description of the effect in question, (C) the formulation of the physical model, and (D) the presentation of the experimental results.

A. BRIEF REVIEW OF ULTRASONIC ATTENUATION IN METALS

This section is to serve as a reminder of the general features of the absorption of ultrasonic waves in metals and will be useful as reference in later sections. For a comprehensive review on the subject see, for example, Morse.[5]

A large ultrasonic attenuation due to electron-phonon interactions is well known to occur in pure metals when the temperature is lowered into the liquid-helium range. Two important parameters of this interaction are the wave vector k of the ultrasonic wave and the mean free path l of the conduction electrons. In the case $kl \ll 1$ the ultrasonic attenuation is proportional to the square of the ultrasound frequency and has the temperature dependence of l; for $kl \gg 1$, the attenuation depends linearly on frequency and being independent of l has essentially no temperature dependence; also the attenuation for $kl<1$ is less than that for $kl>1$ by approximately the factor kl. The last fact is the reason that significant electronic attenuation is found only in reasonably pure materials and at liquid-helium temperature. A phenomenon called the magneto-acoustic effect is observed when a static magnetic field is applied. Under appropriate conditions, including the requirement $kl>1$, an oscillatory variation of attenuation with change of the magnetic field is observed. Useful information about the Fermi surface of several metals has been obtained with this technique.

In superconductors, the mechanism described above is suddenly quenched at the transition temperature. The general features of this drop in attenuation can be explained in terms of the Bardeen-Cooper-Schrieffer theory[6] of superconductivity. The change of the attenuation with temperature reflects the temperature dependence of the number of "superconducting" electrons or Cooper pairs relative to the number of "normal conducting" electrons. Specifically, the attenuation is given by twice the Fermi function of the temperature-dependent superconducting energy-gap parameter $2\epsilon_0(T)$. At zero °K this energy gap parameter is predicted to be a constant depending only on the transition temperature of the specimen, i.e., $2\epsilon_0(0)=3.5k_BT_c$

* This research is supported by Grant No. NSF GP2391 from the National Science Foundation.

† This work is based in part on a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of California at Los Angeles.

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[1] R. E. Love and R. W. Shaw, Rev. Mod. Phys. 34, 260 (1964).
[2] B. R. Tittmann and H. E. Bömmel, Bull. Am. Phys. Soc. 9, 713 (1964).
[3] B. R. Tittmann and H. E. Bömmel, Phys. Rev. Letters 14, 296 (1965).
[4] R. E. Love, R. W. Shaw, and W. A. Fate, Phys. Rev. 138, A1453 (1965).
[5] R. W. Morse, *Progress in Cryogenics* (Heywood and Company, Ltd., London, 1959), Vol. 1.
[6] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 106, 162 (1957); 108, 1175 (1957).

where k_B is Boltzmann's constant and T_c is the superconducting transition temperature. Initially, the theoretical result was derived only for $kl \gg 1$ but was later shown to hold over the entire range of kl. Experiments generally agree with theory for $kl<1$. For $kl>1$ however, deviations are encountered which would suggest values for the energy-gap parameter higher than predicted by the BCS theory.

With the application of the critical magnetic field, the normal conducting state is restored and the temperature dependence of the attenuation is that of a normal metal in the presence of the applied magnetic field. In the range $kl<1$ the attenuation is independent of the applied magnetic field, once the critical magnetic field has been exceeded. For $kl>1$ the magneto-acoustic effect mentioned earlier becomes strong and complicates the temperature dependence of the attenuation in the normal conducting state. If a correction for this effect is desired, it can be achieved by an extrapolation of the attenuation to zero applied field. For a superconductor with high critical magnetic fields an accurate extrapolation is difficult to achieve experimentally.

The typical behavior of the normal and superconducting attenuation as a function of temperature is demonstrated for tin[7] in Fig. 1.

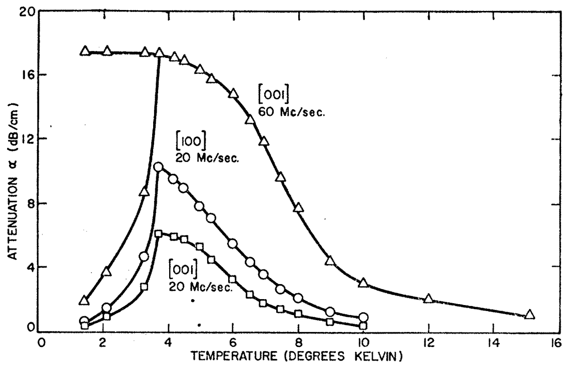

FIG. 1. Longitudinal wave attenuation measurements for single tin crystal along the [001] axis and along the [100] axis.

B. DESCRIPTION OF AMPLITUDE-DEPENDENT EFFECT

Most superconductors follow in general this same pattern of behavior for the ultrasonic attenuation differing only in the value of the superconducting transition temperature. In contrast, experiments in several very pure superconductors at higher amplitudes of the ultrasonic waves show a significant amplitude-dependent deviation in the superconducting state. This is illustrated for lead in Fig. 2. The normal-state attenuation curve has been corrected for the presence of the magneto-acoustic effect. This curve and the dashed curve for the superconducting state represent the typical behavior of most superconductors. The experimental curve in the superconducting state shows the attenuation at an intermediate amplitude of the ultrasonic wave. If the power in the ultrasonic wave is varied, a corresponding amplitude dependence in the attenuation results. This amplitude dependence is very weak above the superconducting transition temperature, but increases suddenly with the onset of superconductivity and becomes very strong near 1°K as is seen in Fig. 3. Figure 4 shows the amplitude dependence in the superconducting state relative to that in the normal state at constant temperature. Initially, as the amplitude is raised from the lowest value the effect is very small. With a further increase in the amplitude, however, the amplitude dependence starts to rise first slowly and then more quickly, somewhat similar to an exponential curve. This anomalous behavior, in particular the strong influence of temperature on the amplitude dependence of the ultrasonic attenuation, is not explicable in terms of a simple modification of the Bardeen-Cooper-Schrieffer theory.

One of the first explanations attempted was based on the peculiar behavior of the thermal conductivity in lead. The thermal conductivity below about 5°K is considerably lower in the absence than in the presence of the critical magnetic field. As a result, in the interior of the specimen, local heating could occur due to the passage of the sound wave. A sizeable portion of the sample could become sufficiently "hot" to be normal conducting, and therefore to produce a higher ultrasonic attenuation than expected. The effect would increase with the amplitude of the sound wave, but would be absent in the normal state. Furthermore, the effect should diminish as the purity of the lead is decreased. Measurements of the ultrasonic attenuation in lead doped with 0.1% tin as impurity show indeed a significant lessening of the amplitude dependence as shown in Fig. 5. The ultrasonic measurements were made by using the standard pulse technique.[5] The product of pulse width and repetition rate is called duty cycle and when multiplied by the pulse peak power gives the average power of radiation. If the effect were caused by local heating in the interior of the specimen, then the attenuation in the superconducting region

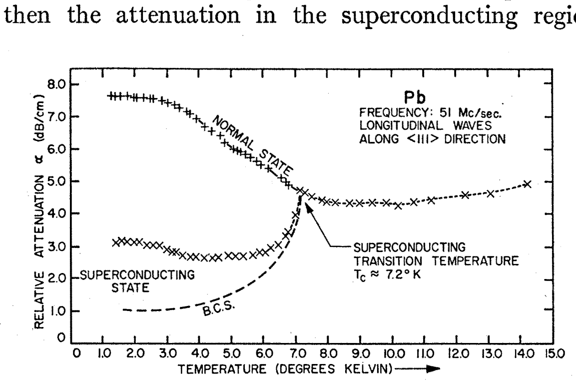

FIG. 2. Temperature dependence of ultrasonic attenuation at medium amplitude in 99.999% pure single-crystal lead.

[7] H. E. Bömmel, Phys. Rev. **100**, 758 (1955). W. P. Mason and H. E. Bömmel, J. Acoust. Soc. Am. **28**, 930 (1956).

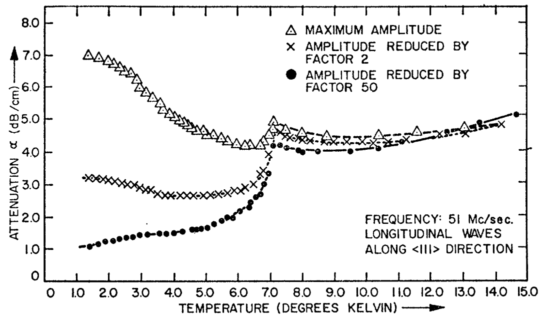

FIG. 3. Temperature dependence of attenuation in 99.999% pure single-crystal lead.

should not only be dependent on the peak power of the pulse, but also on the duty cycle. However, changing the duty cycle had a negligible effect.

C. PROPPSED MODEL

One mechanism which is known to give strong amplitude-dependent effects is dislocation damping. For example, Hiki[8] found an amplitude dependence of the ultrasonic attenuation in 99.99% pure single-crystal lead. Hiki's measurements were performed with longitudinal waves in the frequency range 64 to 192 kc/sec and in the temperature range 140°K and 340°K. He observed an attenuation which was amplitude-dependent but frequency-independent and interpreted this result in terms of dislocation damping. In particular, Hiki explained his findings on the basis of the well-known Granato-Lücke theory[9] which assumes an unpinning of dislocations from impurities and which will be described in some detail later. In our case, this mechanism seems to be ruled out at first glance because of the drastic influence of temperature on the effect. The assumption of an influence of the conduction electrons on dislocation motion, however, suggests a plausible model which explains the weakness of the effect in the normal state and its presence and temperature dependence in the superconducting state. The basic features of this model have already been presented by the authors.[2,3] According to this model, the conduction electrons behave as a "viscous gas" and the dislocation lines as vibrating strings whose motions are damped by the gas. With the onset of superconductivity and as the temperature is lowered further, the number of "normal" electrons decrease in favor of the number of Cooper pairs, which are assumed not to interact with the lattice. Consequently, the dislocations become increasingly free to move and can engage in a mechanism leading to a strong amplitude dependence of the ultrasonic attenuation.

Dislocation theory considers the dislocations as pinned down by impurity atoms and by the nodes of the dislocation network; in most cases, impurities will pin the dislocations at more frequent intervals than the network nodes. An incident ultrasonic wave causes a bowing out of the dislocation loops of length L_c. Let the displacement of the dislocation from its equilibrium position be given by ξ, and let y denote the coordinate of an element of the dislocation line.

The equation of motion of a pinned dislocation loop is taken to be that used by Koehler[10]:

$$A\frac{\partial^2\xi}{\partial t^2}+B\frac{\partial\xi}{\partial t}-C\frac{\partial^2\xi}{\partial y^2}=b\sigma,$$

where $\xi=\xi(x,y,t)$ and the boundary conditions are $\xi(x,0,t)=\xi(x,l,t)=0$. A is the effective mass per unit length, the term containing B is the damping force per unit length, the term containing C gives the force per unit length due to the effective tension in a bowed-out dislocation, and the term on the right is the force per unit length exerted on the dislocation by the external shearing stress σ. The constants are given by $A=\pi\rho b^2$, $C=2Gb^2/\pi(1-\nu)$, where ρ is the density of the material, b the Burger's vector, G the shear modulus, and ν is Poisson's ratio.

In addition, we may write the usual equation of motion obtained from Newton's law

$$\partial^2\sigma/\partial x^2-\rho\partial^2\epsilon/\partial t^2=0.$$

The strain ϵ comprises the elastic strain ϵ_{el} and the dislocation strain ϵ_{dis} due to the motion of the dislocations under the influence of the applied stress σ, i.e.

$$\epsilon=\epsilon_{el}+\epsilon_{dis},$$

the elastic strain is given by elasticity theory:

$$\epsilon_{el}=\sigma/G.$$

The dislocation strain produced by a loop of length l in a cube of unit dimensions is usually given by $\bar{\xi}lb$, where $\bar{\xi}$ is the average displacement of a dislocation of

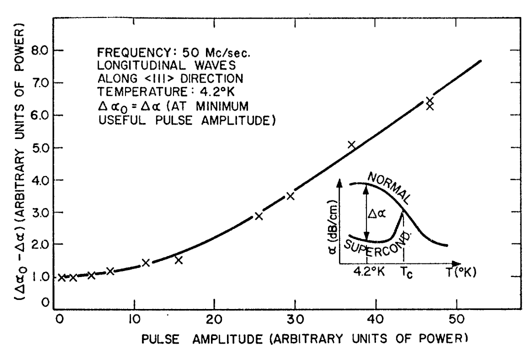

FIG. 4. Amplitude dependence of attenuation normalized to that at minimum amplitude in 99.999% pure single-crystal lead.

[8] Y. Hiki, J. Phys. Soc. (Japan) **13**, 1138 (1958).

[9] A. Granato and K. Lucke, J. Appl. Phys. **27**, 583 (1956); **27**, 789 (1956).

[10] J. S. Koehler, *Imperfections in Nearly Perfect Crystals* (John Wiley & Sons, Inc., New York, 1952), p. 197.

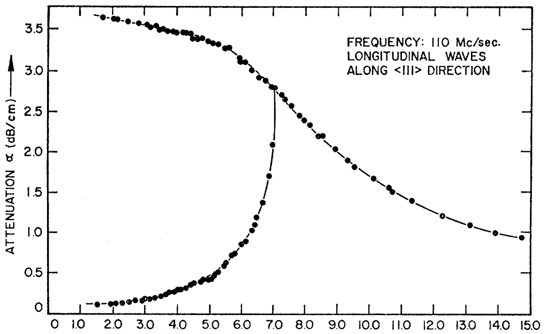

FIG. 5. Temperature dependence of attenuation in 99.9% pure single-crystal lead.

length l and is given by

$$\bar{\xi}=\frac{1}{l}\int_0^l \xi(y)dy,$$

where y is the coordinate on the dislocation line. Thus if Λ is the total length of movable dislocation line,

$$\epsilon_{\text{dis}}=\frac{\Lambda b}{l}\int_0^l \xi(y)dy.$$

These equations may be combined to give two simultaneous partial differential integral equations,

$$\frac{\partial^2\sigma}{\partial x^2}-\frac{\rho}{G}\frac{\partial^2\sigma}{\partial t^2}=\frac{\Lambda\rho b}{l}\frac{\partial^2}{\partial t^2}\int_0^l \xi dy,$$
$$A\frac{\partial^2\xi}{\partial t^2}+B\frac{\partial\xi}{\partial t}-C\frac{\partial^2\xi}{\partial y^2}=b\sigma, \qquad (1)$$

plus the boundary conditions for ξ. These have been solved by, for example, Granato and Lücke with the following results:

$$\xi=4b\sigma\sum_{n=0}^{\infty}\frac{1}{(2n+1)}\sin\frac{(2n+1)\pi y}{l}\frac{e^{i(\omega t-\delta_n)}}{[(\omega_n^2-\omega^2)^2+(\omega d)^2]^{1/2}},$$

with the substitutions

$$d=\frac{B}{A},\quad \omega_n=(2n+1)\frac{\pi}{l}\left(\frac{C}{A}\right)^{1/2},\quad \delta_n=\tan^{-1}\frac{\omega d}{\omega_n^2-\omega^2}.$$

The above form for $\xi=\xi(x,y,t)$ was derived by Granato and Lücke in preference to the closed form because the first term of the series already gives a very good representation of the function. That is, it can be shown that for low frequencies, the contributions of the higher order terms in n to the attenuation decrease like $1/(2n+1)^6$. Even when the driving frequency is equal to one of the odd harmonics of the fundamental frequency, the terms can be neglected if the damping is not small. Hence, the first term of the series only will be used in what follows. The above listed ξ and σ satisfy the system, Eq. (1), if the attenuation of the dislocation motion is

$$\alpha(\omega)=\frac{\omega}{2v}\frac{\Lambda\Delta_0\eta^2}{\pi}\frac{\omega d}{[(\omega_0^2-\omega^2)^2+(\omega d)^2]},$$

where v is the velocity

$$v(\omega)=v_0\left[1-\frac{\Lambda\Delta_0\eta^2}{2\pi}\frac{(\omega_0^2-\omega^2)}{[(\omega_0^2-\omega^2)^2+(\omega d)^2]}\right]$$

and

$$v_0=(G/\rho)^{1/2},\quad \Delta_0=8Gb^2/\pi^3C,\quad \eta^2=\pi C/A.$$

The displacement, the attenuation, and velocity of the dislocation motion depend on the damping force B through the term $d=B/A$. B is assumed to have two main contributions

$$B=B_p+B_e.$$

B_p is the result of the interaction of the dislocation with thermal phonons and is assumed to become negligible at temperatures much below the Debye temperature. This assumption appears reasonable since the temperatures considered are near 1°K. B_e is the result of the interaction between the conduction electrons and the moving dislocation. This problem was considered by Professor T. Holstein who calculated the relaxation time τ and damping term B using the deformation potential method. His results, derived in the Appendix, are

$$\frac{1}{\tau}=\frac{3}{4}\frac{(1-\nu)}{G[\ln(A/a)-1]}\frac{2\pi}{\hbar}\left(\frac{C}{E_F}\right)^2\frac{q_m}{k_F}\hbar^2k_F^2c_s^2N_eK,$$

$$B_e=\frac{3}{32}\frac{2\pi}{\hbar}\left(\frac{C}{E_F}\right)^2\frac{q_m}{k_F}\hbar^2N_eb^2K,$$

where ν is Poisson's ratio, G is the shear modulus, A and a are upper and lower limits for the shell of elastically distorted crystal surrounding the dislocation. C is the interaction constant, E_F is the Fermi energy, q_m is the maximum allowable phonon wave vector, k_F is the wave vector of an electron at the Fermi level, N_e is the concentration of conduction electrons, c_s is the sound velocity, b is the Burger's vector, and K is a number approximately equal to $\frac{1}{4}$.

If these expressions are evaluated for lead one obtains

$$1/\tau\approx 10^{11}\ \text{sec}^{-1},$$
$$B_e\approx 6\times 10^{-5}\ \text{dyn sec cm}^{-2}.$$

With the onset of superconductivity this damping disappears and it can be shown that as the temperature is lowered the damping diminishes in a manner similar to the superconducting ultrasonic attenuation. In other

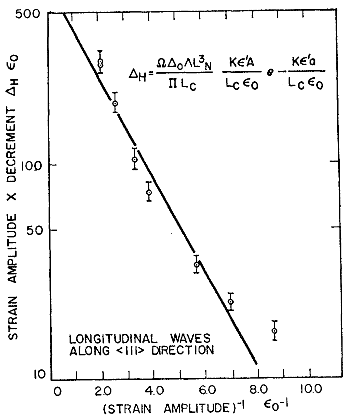

FIG. 6. Granato-Lücke plot of the ultrasonic attenuation at 99.999% pure single crystal of lead at 4.2°K.

words, near 0°K the damping of the dislocation motion is essentially zero.

The effect of removing the damping from a dislocation can be studied by considering the motion of dislocations under the action of an internal applied stress, i.e., the ultrasonic wave. As indicated above, the displacement of the dislocation is given by

$$\xi = 4b\sigma\left(\sin\frac{\pi y}{l}\right)\frac{1}{[(\omega_0{}^2-\omega^2)^2+(\omega d)^2]^{1/2}}e^{i(\omega t-\delta_n)}.$$

The maximum displacement is given by

$$\xi_{\max} = \frac{4b\sigma}{[(\omega_0{}^2-\omega^2)^2+(\omega d)^2]^{1/2}}.$$

The ratio of the maximum displacement in the superconducting state to that in the normal state is

$$\frac{\xi_{\max}{}^s}{\xi_{\max}{}^n} = \left\{\frac{(\omega_0{}^2-\omega^2)^2+(\omega d)^2}{(\omega_0{}^2-\omega^2)^2}\right\}^{1/2},$$

where it has been assumed that the damping term in the superconducting state is zero. When evaluated for lead at 100 Mc/sec the ratio becomes

$$\xi_{\max}{}^s/\xi_{\max}{}^n \approx 25.$$

If the amplitudes of the dislocations are increased sufficiently, the dislocations are torn away from the impurity atoms. According to Granato and Lücke, for example, this unpinning process is assumed also to be assisted by the thermal phonons. The dislocations are now pinned only at the nodes of the dislocation network and vibrate with length L_n. The unpinning process absorbs ultrasonic energy which is estimated at 0.1 eV per impurity atom. The higher the dislocation amplitudes, the more unpinning occurs and the higher is the absorption of energy from the ultrasonic wave. In this manner, an amplitude dependence can arise.

An impurity atom is bound to a (long, straight) dislocation by an attractive force f_c which in the first-order elastic approximation of Cottrell[11] and neglecting orientation dependence is

$$f_c \approx 4G\epsilon' b^4/Z^2,$$

where ϵ' is the difference in atomic radii divided by the atomic radius of the solvent atom, and Z is the distance of the impurity from the dislocation axis.

The force exerted by the dislocation line on an impurity at any instant during a cycle is given by

$$f_\sigma = \pi C(\phi_1-\phi_2) = (4b\sigma/\pi)(l_1+l_2),$$

where πC is the loop tension, and ϕ_1 is the angle made by a loop of length l_1 at the impurity when the displacement is a maximum. Breakaway occurs when $f_\sigma > f_c$ or when

$$l_1+l_2 > \mathcal{L} = \pi f_m/4b\sigma,$$

where $\mathcal{L}$ is the so-called breakaway length and f_m is the maximum value of the binding force obtained. The breakaway gives rise to an irreversible strain and thus to a hysteresis. The process is complicated by the fact that it is catastrophic within the network length. That is, if $l_1+l_2 > \mathcal{L}$ the loop will not only break loose at this point, but afterwards successively at joining locking points, as certainly $(l_1+l_2)+l_3 > \mathcal{L}$, etc. This continues until the whole dislocation line between the two strongly pinned network points has broken away. A dependence of the ultrasonic attenuation on the strain (thus on the stress) amplitude follows immediately. The larger the shear stress σ or the less the damping of the dislocation movement B, the smaller the limiting length $\mathcal{L}$, and progressively shorter loop lengths can contribute to the irreversible strain. Granato and Lücke have derived an expression for the ultrasonic attenuation under three simplifying assumptions—the distance L_N between network nodes is constant for a given sample specimen, the distribution of the impurities along the dislocations follows an exponential law, and the ultrasonic frequency is less than the resonant frequency of the dislocation. They obtain

$$\Delta_H = \frac{\Omega\Delta_0\Lambda L_N{}^3}{\pi L_c}\,\frac{K\epsilon' A}{L_c}\,\frac{1}{\epsilon_0}\exp\left(-\frac{K\epsilon' a}{L_c}\,\frac{1}{\epsilon_0}\right),$$

where Ω, Δ_0, A, ϵ', and a are crystal-structure factors, Λ is the dislocation density, and ϵ_0 is the maximum values of the oscillating strain. A qualitative comparison of the experimentally observed amplitude dependence with this expression can be obtained in a plot which is sometimes referred to as "Granato-Lücke plot." It is a plot of the product of the amplitude and the attenuation versus the inverse of the amplitude, and is shown in Fig. 6. This graph is derived from Fig. 4 and is a plot of the experimental points calculated in the manner described with the best straight line through them.

[11] A. H. Cottrell, *Report Conference on Plastic Flow of Crystals* (Clarendon Press, Oxford, England, 1950).

D. EXPERIMENTAL RESULTS

As mentioned before the standard pulse technique was used for all measurements. The transmitter pulses available had peak powers of up to 5 W in the range 10 to 300 Mc/sec and up to 2000 W in the range 350–1500 Mc/sec. The accuracy in the pulse-comparitor calibration was 0.5 dB over about a 30-dB range. The repeatability observed particularly over small ranges of attenuation measurements was more like 0.1 to 0.2 dB.

1. Dependence on Temperature

Figures 2 and 3 show the ultrasonic attenuation as a function of temperature for various fixed values of sound-wave amplitude at fixed frequency and purity of the specimen. The graphs are plots of "processed" data rather than of the "raw" data recorded in the experiments. For example, Fig. 2 shows the temperature dependence of the ultrasonic attenuation at 50 Mc/sec and medium sound-wave amplitude. The temperature range of the data points is from 1.40 to 15.0°K. The attenuation given in dB per cm is relative to an arbitrary reference chosen on the basis of convenience during the experiment. The data were obtained for a specimen 0.3115 in. in length onto which a single transducer was mounted. The pulse on which the measurements were performed was the first echo pulse having traveled through the sample length twice. At the superconducting transition temperature $T_c=7.15$°K, the curve of data points splits into two curves; the lower one obtained in zero applied magnetic field, and the upper one in the presence of a magnetic field whose value is the temperature-dependent critical magnetic field for lead. Above the transition temperature, the application of the magnetic field had very little, if any effect on the ultrasonic attenuation. In the "raw" data, the upper curve exhibited a severe drop in attenuation at temperatures below 4.0°K which means that the sample was sufficiently pure at this frequency, i.e., $kl>1$, so that the magneto-acoustic effect became noticeable. The decrease in the attenuation represents an electron-phonon interaction which has been weakened by a shortening of the effective electron mean free paths which are now in the form of spirals. Consequently, an entire series of plots of the magnetic field dependence of the attenuation were obtained in the range of temperatures between 1.4 and 7.2°K. The curves were found to be all basically similar and were extrapolated to zero magnetic field. In this manner, the temperature dependence was reconstructed with the magneto-acoustic effect subtracted from the recorded values of attenuation. While this method is fairly accurate above 4.2°K, the error becomes large at low temperatures where a high critical magnetic field requires an extrapolation over a long stretch of the curve.

2. Dependence on Sound-Wave Amplitude

In order to see the effect of amplitude more clearly, curves of the temperature dependence of the attenuation for three different amplitudes were plotted on the same graph shown in Fig. 3. The curves were arbitrarily matched near the upper end of the temperature range. The curves for the normal conducting attenuation exhibited only a weak amplitude dependence and were left out to avoid confusion. The relative power levels are indicated on the graph. The term "sound wave amplitude" must be used with reservations since this quantity was not measured directly. Instead, the transmitter power output was measured, a quantity which is of course at best, proportional to the sound wave amplitude, but still useful since relative changes in amplitude are of main interest here. The amplitude dependence exhibited in Fig. 3 was more thoroughly explored at one particular temperature, namely 4.2°K. The result is shown in Fig. 4. The plot was obtained by observing the difference in the ultrasonic attenuation between the values obtained in the normal and superconducting state, i.e., $\Delta\alpha=\alpha_n-\alpha_s$. The value of $\Delta\alpha$ is largest for small amplitudes and diminishes as the amplitude is increased. The ordinates of the points were obtained by subtracting values of $\Delta\alpha$ obtained for high amplitudes from that obtained for the lowest amplitude. In effect, the ordinate reflects the amplitude-dependent part of the attenuation only, since the background attenuation has been subtracted out. The graph then exhibits the superconducting amplitude dependence relative to that in the normal state. Initially, as the amplitude (abscissa) is raised from the lowest value, the amplitude dependence is very small if not negligible. With a further increase in the amplitude, however, the amplitude dependence starts to rise first slowly and then more quickly. A direct comparison with the theoretical result derived by Granato and Lücke is shown in the graph of Fig. 6 which is sometimes referred to as "Granato-Lücke plot." It is a plot of the product of the amplitude and the attenuation versus the inverse of the amplitude. Comparison with Granato and Lücke's final expression written again in Fig. 6 shows that this plot should be a straight line on semilogarithmic graph paper. The figure displays the experimental points and the best straight line through them.

As seen in Fig. 3 the amplitude dependence changes strongly with temperature and appears to be most severe near 0°K. This can be understood on the basis of the model presented above. In contrast to, say, 4.2°K where there are still some "normal conducting electrons" hindering the free movement of the dislocation, very little limitation exists near 0°K and the Granato-Lücke unpinning mechanism can unfold to its full measure. The amplitude dependence was therefore explored at the lowest obtainable temperature and over as wide a range of amplitudes as possible. Exemplary results are shown in Figs. 7 and 8 for a constant

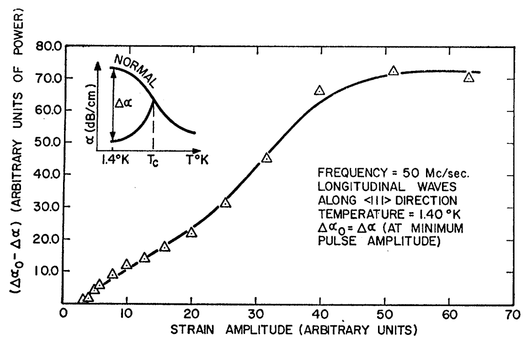

FIG. 7. Amplitude dependence of attenuation normalized to that at minimum amplitude in 99.999% pure single-crystal lead.

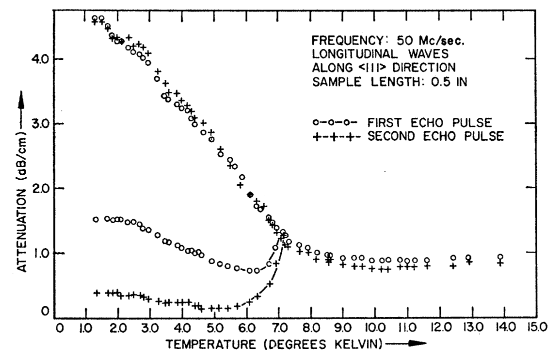

FIG. 9. Temperature dependence of attenuation of first and second echo pulse in 99.999% pure single-crystal lead.

temperature of 1.40°K. Figure 7 is similar to Fig. 5 and displays the amplitude dependence of the superconducting attenuation relative to that in the normal state.

Almost all observations of amplitude-dependent ultrasonic absorption arising from unpinning processes show that the damping initially increases with increasing strain amplitude. As the amplitude is increased further, the theory predicts that the attenuation will approach a limiting value corresponding to the unpinning of all the dislocations while the stress will continue to increase. In Fig. 7 the amplitude dependence appears to level out at high strain amplitudes. However, the experimental error in the region for these very high amplitudes is quite large, mainly because of electronic problems such as receiver saturation. Figure 8 shows the corresponding Granato-Lücke plot. The deviation from the expected straight line lies within the same degree of agreement as with experiments of several other authors and may have its reasons in the simplifying assumptions for the theory.[12] Therefore, within these limitations the Granato-Lücke theory explain our data as well as those encountered at higher temperatures.

Another way to observe the amplitude dependence is to measure and compare the attenuation of several echo pulses. The temperature dependencies of two consecutive echo pulses is shown in Fig. 9 in which the two curves have been matched in the normal state. The second echo pulse having traveled twice as long a path length as the first has suffered twice as much reduction in amplitude. Since the graph is plotted in dB per cm, only the effect on the amplitude dependence becomes apparent. An even clearer change of the amplitude dependence with temperature is shown in Fig. 10. Here, the attenuation of the second pulse is plotted relative to that of the first. In this manner, all nonamplitude-dependent features such as the electron-phonon interaction and its decrease in the superconducting state are eliminated. The superconducting part of the curve is then a measure of the lessening of the dislocation-electron interaction or a freeing of the dislocations to engage in the Granato-Lücke mechanism as the temperature is reduced below the transition temperature.

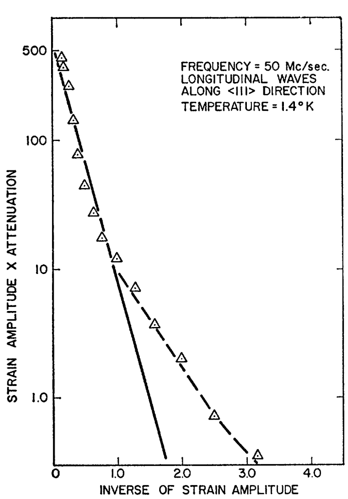

FIG. 8. Granato and Lücke plot of the attenuation in 99.999% pure single-crystal lead at constant temperature.

3. Dependence on Ultrasound Frequency

According to Granato and Lücke, the effect should be frequency-independent. Measurements on the effect were conducted at 30, 40, 70, 110, and 130 Mc/sec. The accuracy of a frequency-dependence study is limited, since the frequency response of the electronic equipment associated with both transmission and reception is not flat over a wide band and the acoustic properties of the transducer and the bond change with frequency. As was mentioned in Sec. A, the interaction between the electrons and ultrasonic waves is frequency-dependent. This frequency dependence is theoretically and experimentally well established and can therefore be used as a guide line. At a temperature of about 4.2°K, the curve of attenuation versus temperature has a minimum in the superconducting region at medium pulse amplitudes. At each frequency, the transmitter power level was so adjusted and the echo pulse to be measured was so selected that the pulse height at 4.2°K was approxi-

[12] For a discussion of these deviations see Granato and Lücke (Ref. 9) and D. H. Niblett and J. Wilks, Advan. Phys. 9, 1 (1960).

mately the same and the change in attenuation between $T=4.2°K$ and $T=T_c$ was also approximately the same. This condition meant that at each frequency the sound waves had about the same power level for the majority of their paths through the sample, i.e., medium amplitude. No detailed temperature measurements were obtained, but rather the attenuation increases were recorded between 4.2°K and 1.9°K, corresponding to dislocation damping and the increase between 4.2°K and $T=T_c$ corresponding to electron-phonon interaction. The result is presented in Fig. 11 which is a plot of $\Delta\alpha_{\mathrm{disl}}$ and $\Delta\alpha_{\mathrm{ep}}$, respectively, as a function of frequency. $\Delta\alpha_{\mathrm{ep}}$ has a dependence that one might expect for a specimen of lead for which $kl=1$ at about 100 Mc/sec which is not unreasonable considering its purity of 99.999%. In contrast, $\Delta\alpha_{\mathrm{disl}}$ shows a slight increase with frequency. This result suggests that if there is a frequency dependence it is certainly weaker than that of electron-phonon interaction. The frequency dependence of the attenuation was also investigated in the 99.9% pure lead. Since the purity of the specimens is so low, $kl=1$ must occur at high frequencies. This appears to be verified by the plot in Fig. 12 which shows as a function of the square of the frequency the change in attenuation at 1.4°K with the application of the critical magnetic field. Again, within the limitation of the experimental technique, the effect appears to be frequency-independent.

4. Effect of Crystal Deformation

If the amplitude dependence is caused by dislocations, then deforming and annealing the crystal should have a pronounced effect. According to Granato and Lücke, the amplitude dependence should increase with the number of dislocations in the specimen. There is a limit, however, which occurs when the number of dislocations is so large that they pin each other at intervals equal to or smaller than the average impurity pinning distance. No unpinning can then take place and the amplitude dependence becomes weak. This effect has been well substantiated experimentally by, for example, Weertman and Koehler in copper.[13] Figure 13 examines these predictions in a series of plots obtained in a similar way to those of Figs. 4 and 7. The graph shows the amplitude dependence before and after a peripheral deformation at liquid nitrogen. The amplitude dependence immediately after the deformation was considerably reduced, corresponding to the case of an excessive number of dislocations. After approximately a day of annealing at liquid-nitrogen temperature, the amplitude dependence had increased again and was indeed stronger than it had been before the deformation. This corresponds to the case where there are more dislocations than before the deformation and the unpinning process has not yet been impaired. Finally, after long-term annealing, the number of dislocations returned to approximately the number that were in the crystal before the deformation. Correspondingly, the amplitude dependence should have returned to its initial behavior. The fact that it was actually found to be weaker could possibly be explained if one assumes that other crystal defects are most likely to have been created during the deformation. These would be scattering centers for the ultrasonic waves and therefore cause an additional reduction in sound-wave amplitude with a resulting reduction of the amplitude dependence.

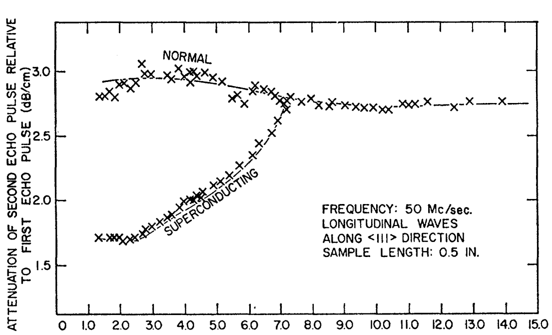

FIG. 10. Temperature dependence of attenuation of second echo pulse relative to that of first echo pulse in 99.999% pure single-crystal lead.

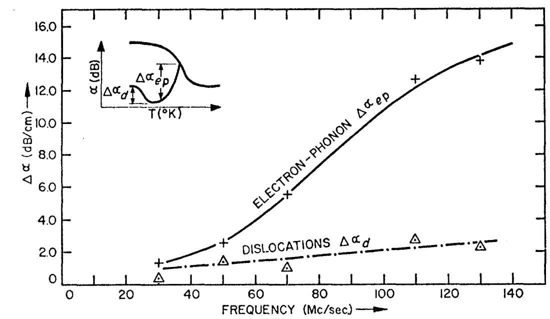

FIG. 11. Frequency dependence of dislocation hump and electron-phonon peak in 99.999% pure single-crystal lead.

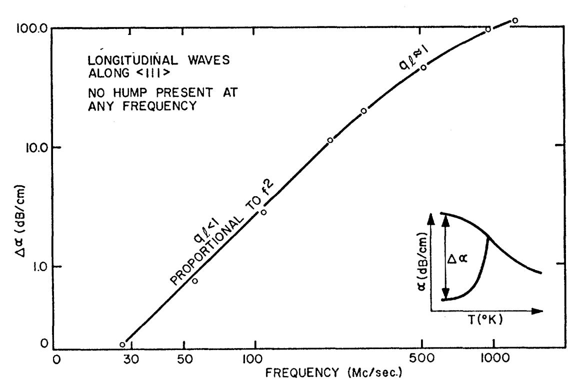

FIG. 12. Frequency dependence of attenuation in 99.9% pure single-crystal lead.

[13] J. Weertman and J. S. Koehler, J. Appl. Phys. 24, 624 (1953).

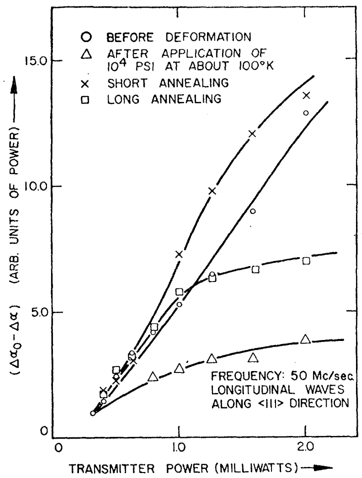

FIG. 13. Effect of severe deformation and subsequent annealing in 99.999% pure single-crystal lead.

5. Dependence on Specimen Purity

Most of the experiments discussed in the previous sections were performed on 99.999% pure lead. According to the Granato-Lücke model, an increase in impurity concentration should decrease the ultrasonic amplitude dependence. Such an effect has indeed been observed by Weertman and Salkovitz in lead-bismuth alloys at room temperature.[14] They varied the concentration of bismuth in single-crystal lead from 0.035 to 0.053 to 0.65% and found a corresponding reduction in amplitude dependence. On the basis of the physical model, the impurities present in the alloy drift to the dislocation lines and pin them at more frequent intervals than those in the pure crystal. As a result, the loop lengths are shortened and a more severe applied stress is needed to unpin the dislocation lines. Hence, for the same applied stress the number of breakaway processes and therefore the amplitude dependence is reduced in the alloy as compared to the pure specimen.

We have performed experiments on several 99.9% pure samples of lead with tin as impurity. Temperature dependences of the attenuation in the presence and absence of the critical magnetic field were obtained at 1030 Mc/sec (Fig. 14), 950, 210, 110, and 50 Mc/sec (Fig. 15). In none of the graphs is there to be found a rise in the attenuation near 2°K. A test for amplitude dependence was made at 510 Mc/sec (Fig. 16), at 270, and 50 Mc/sec with the result that power changes by as much as a factor of 3000 were required to produce any significant amplitude dependence.

6. Time-Dependent Effects

A test for the presence of breakaway processes is the observance of irreversibility effects in the attenuation. Amplitude dependence of this type has been observed in single crystals of zinc by Wert[15] and in single crystals of aluminum and magnesium by Chambers.[16] These effects are difficult to measure quantitatively, but were observed in a particularly good specimen of lead grown from 99.9999% lead stock. Measurements performed at 50 Mc/sec showed the presence of magneto-acoustic oscillations which indicates that $kl \approx 3$. In this specimen an observance of the amplitude dependence at high amplitude showed a marked decrease in the amplitude dependence as a function of time; that is, if at a given amplitude the same measurement was repeated within short time intervals the apparent amplitude dependence decreased. If, however, the measurement was interrupted for approximately one-half hour, the amplitude dependence was again as strong as in the initial measurement. This irreversibility is seen to arise as a result of a complete breakaway of the dislocation line from its few pinning points during the stress wave applied initially. Later stress waves find the dislocation still unpinned, and the amplitude dependence is therefore inhibited. However, given enough time the dislocation will be pinned again and can engage anew in the breakaway process.

7. Observations in Other Metals

One might expect an electron-dislocation interaction to be present in all metals to a smaller or larger extent depending on their properties such as the Debye temperature, lattice structure, electron density, the density of the dislocations and the nature of the pinning point imperfections. Thus, the anomalous amplitude dependence might be difficult to observe at low temperature (below 4.2°K) in most nonsuperconducting metals. In these metals two effects combine to limit the unpinning mechanism: If the specimen is impure so that the mean free path of the conduction electrons is short and the dislocation-electron interaction is weak, the impurities pin the dislocation lines at such frequent intervals that the applied stress of the ultrasonic wave is unable to activate the breakaway process. If the specimen is a pure single crystal such that the dis-

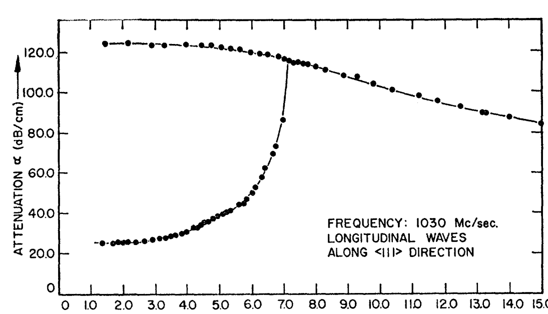

FIG. 14. Temperature dependence of attenuation in 99.9% pure single-crystal lead.

[14] J. Weertman and E. I. Salkovits, Acta Met. 5, 692 (1955).
[15] C. A. Wert, J. Appl. Phys. 20, 29 (1949).
[16] R. H. Chambers, Technical Report of Carnegie Institute of Technology AT (30-1)-1193 (unpublished); R. H. Chambers and R. Smoluchowski, Phys. Rev. 117, 725 (1960).

location lines are pinned for only few crystal imperfections, then the electrons have a long mean free path which allows (according to the calculation in the Appendix) a strong electron-dislocation interaction. On the other hand, the anomaly should be observable in other superconductors again to an extent dictated by properties of the lattice, the electrons, and the dislocations.

We have observed the same effect in single crystals of indium and very pure tin. In the latter, the effect was very weak; in indium the amplitude dependence was similar but somewhat weaker than in lead.

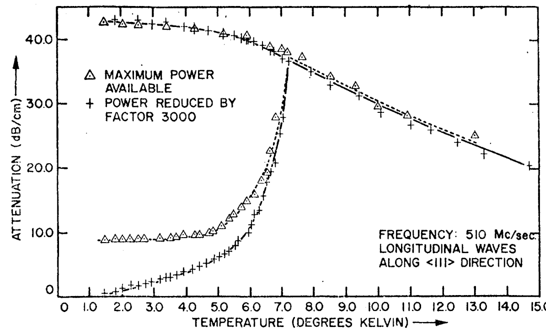

FIG. 16. Attenuation versus temperature for two amplitudes in 99.9% pure single-crystal lead.

CONCLUSION

The experiments discussed in the previous sections appear to bear out the predictions of the proposed model. The assumption of a strong electron-dislocation interaction is substantiated by the observed dependence of the attenuation on temperature above the superconducting transition temperature and in the presence of the critical magnetic field below the transition temperature. The rapid increase in the amplitude dependence as the temperature is lowered in the superconducting state is qualitatively predicted by the model and is seen to occur as a result of the condensation of the conduction electrons into the superconducting ground state. Once in the ground state, the electrons are incapable of interacting with the dislocations and the temperature dependence of the population in the ground state reflects the temperature dependence of the anomaly.

Once the dislocations become sufficiently free to move, i.e., the electron-dislocation interaction disappears near 2°K, the model predicts the occurrence of a dislocation mechanism similar to that discussed by Granato and Lücke. Again, the experiments bear out this prediction. The behavior of the amplitude dependence with signal amplitude, impurity concentration, ultrasonic frequency, and apparent dislocation density, strongly supports a type of mechanism based on a process in which the dislocations break away from their pinning points under the applied stress of the ultrasonic wave. The Granato-Lücke model is not the only model for dislocation mechanisms. It was used here mainly because of its simplicity. More refined theories might even give better agreement.

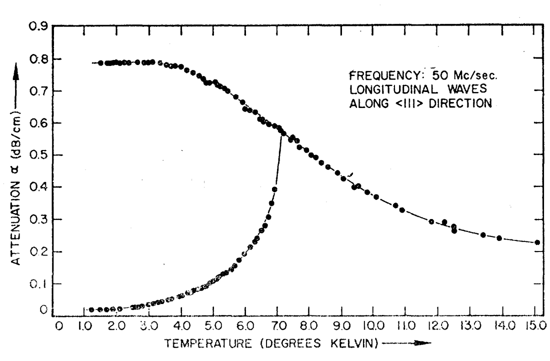

FIG. 15. Temperature dependence of attenuation in 99.9% pure single-crystal lead.

Although the proposed model thus offers an explanation of the effect, several questions have been left unanswered. For example, what is the nature of the pinning imperfections at such low temperatures where the assistance by thermal phonons is almost negligible? The pinning forces obviously have to be weak.

The authors wish to thank Floyd Lacy for his help, especially in the sample preparation. One of us (B.R.T.) would like to thank Professor W. F. Libby for support out of National Aeronautics and Space Administration Grant No. NASA NSG-237 during part of this work.

APPENDIX

The authors are indebted to T. Holstein for the following discussion:

This is intended as a short calculation to estimate roughly the damping of the motion of a dislocation in a metallic crystal. The damping mechanism is assumed to result primarily from an interaction of the dislocation with the conduction electrons in the metal. The method assumes a free-electron gas in the absence of any static magnetic field.

Consider the moving dislocation representable as a displacement field $\mathbf{u}(\mathbf{r})$ which moves with velocity $\mathbf{w}$ so that we have $\mathbf{u}(\mathbf{r}-\mathbf{w}t)$ as the space-time dependence. We may Fourier-analyze this by writing

$$\mathbf{u}(\mathbf{r})=\sum_{\mathbf{q}}\mathbf{u}_{\mathbf{q}}e^{i\mathbf{q}\cdot\mathbf{r}},\quad \mathbf{u}_{-\mathbf{q}}=\mathbf{u}_{\mathbf{q}}^{*}.$$

Hence,

$$\mathbf{u}(\mathbf{r}-\mathbf{w}t)=\sum_{\mathbf{q}}{}'\,\mathbf{u}_{\mathbf{q}}\exp[i\mathbf{q}\cdot(\mathbf{r}-\mathbf{w}t)]+(\text{complex conjugate})$$

is the *real* displacement field.

The deformation potential is

$$V_p(\mathbf{r})=\sum_{\mathbf{q}}{}'\,i\mathbf{q}\cdot\mathbf{u}_{\mathbf{q}}\exp i[\mathbf{q}\cdot\mathbf{r}-\mathbf{q}\cdot\mathbf{w}t]+(\text{complex conjugate}).$$

The probability per unit time that an electron will be scattered from $\mathbf{k}_0$ to $\mathbf{k}'=\mathbf{k}_0+\mathbf{q}$ is

$$P(\mathbf{k}_0\to\mathbf{k}')=(2\pi/\hbar)C^2|\mathbf{q}^*\cdot\mathbf{u}_\mathbf{q}|^2\delta(E_\mathbf{k}-E_{\mathbf{k}'}+\hbar\mathbf{q}\cdot\mathbf{w}).$$

Similarly the probability that an electron will be scattered from $\mathbf{k}'$ to $\mathbf{k}_0$ is

$$P(\mathbf{k}'\to\mathbf{k}_0)=(2\pi/\hbar)C^2|\mathbf{q}\cdot\mathbf{u}_\mathbf{q}^*|^2\delta(E_{\mathbf{k}'}-E_\mathbf{k}-\hbar\mathbf{q}\cdot\mathbf{w}).$$

We average over an electron ensemble in thermal equilibrium and formulate the total collision rate,

$$\begin{aligned}\frac{dW}{dt}&=\sum_{\mathbf{kq}}\hbar(\mathbf{q}\cdot\mathbf{w})\{f(\mathbf{k}_0)[1-f(\mathbf{k}')]-f(\mathbf{k}')[1-f(\mathbf{k}_0)]\}\\&\qquad\times(2\pi/\hbar)|\mathbf{q}\cdot\mathbf{u}_\mathbf{q}|^2C^2\delta(E_{\mathbf{k}'}-E_\mathbf{k}-\hbar\mathbf{q}\cdot\mathbf{w})\\&=\sum_{\mathbf{kq}}\hbar(\mathbf{q}\cdot\mathbf{w})[f(\mathbf{k}_0)-f(\mathbf{k}')](2\pi/\hbar)C^2|\mathbf{q}\cdot\mathbf{u}_\mathbf{q}|^2\\&\qquad\times\delta[(\hbar^2/m)(q^2/2+\mathbf{q}\cdot\mathbf{k})-(\hbar\mathbf{q}\cdot\mathbf{w})],\end{aligned}$$

where $E=\hbar^2k^2/2m$ as for a free-electron gas. For $v\ll k\hbar^2/m$ we may neglect $\hbar\mathbf{q}\cdot\mathbf{w}$. Also we may make the following approximation:

$$f(E_{\mathbf{k}+\mathbf{q}})-f(E_\mathbf{k})\cong\mathbf{q}\cdot\partial f/\partial\mathbf{k}=(\hbar\mathbf{q}\cdot\mathbf{w})\partial f/\partial E,$$

since for a free-electron gas, $\mathbf{p}=\hbar\mathbf{k}$, $\mathbf{v}=\mathrm{grad}_\mathbf{p}E=\mathbf{p}/m$, and $E=\hbar^2k^2/2m$. Thus we have that

$$\begin{aligned}dW/dt=&\sum_\mathbf{q}(\hbar\mathbf{q}\cdot\mathbf{w})^2(2\pi/\hbar)|\mathbf{q}\cdot\mathbf{u}_\mathbf{q}|^2C^2\delta(E_\mathbf{k}-\mu)\\&\times\delta[(\hbar^2/m)(q^2/2+\mathbf{q}\cdot\mathbf{k})],\end{aligned}$$

where μ is a constant. We now wish to determine the quantity $|\mathbf{q}\cdot\mathbf{u}_\mathbf{q}|^2\equiv|\Delta(\mathbf{q})|^2$. At this point it is assumed that the electrons interact with the stress field of a dislocation and not with its core directly so that the dislocation can be viewed as a long thin cylinder at $\mathbf{r}=0$ and its disturbance, in, for example, the y direction is described by (see for example Seeger),[17]

$$\Delta(\mathbf{r})=(y/r^2)\mathbf{b},$$

where $\mathbf{b}$ is the Burgers vector and $\mathbf{r}$ is the radial distance. Then in $\mathbf{q}$ space with cylindrical coordinates it can be shown that

$$\Delta(\mathbf{q})=\int_0^\infty e^{-i\mathbf{q}\cdot\mathbf{r}}\frac{\mathbf{b}y}{r^2}d^3r=\frac{\mathbf{b}q_y}{iq^2L^2},$$

where L is the length of the dislocation. Thus

$$\frac{dW}{dt}=\sum_\mathbf{q}\hbar^2(\mathbf{q}\cdot\mathbf{w})^2\frac{2\pi}{\hbar}C^2b^2\left(\frac{q_y^2}{L^4q^4}\right)F(q),$$

where

$$\begin{aligned}F(q)&=\sum_\mathbf{k}\delta(E_\mathbf{k}-\mu)\delta[(\hbar^2/2m)(q^2+2\mathbf{q}\cdot\mathbf{k})]\\&=\frac{L^3}{8\pi^2}\int k^2dk\delta(E_\mathbf{k}-\mu)\int_0^1 2\pi d\xi\delta\left[\frac{q^2}{2}+qk\xi\right]\\&=\left(\frac{m}{\hbar}\right)^2\frac{L^3}{4\pi^2}\frac{1}{q}=\frac{k_F}{q}L^3\frac{N_e}{E_F^2}\left(\frac{3}{16}\right)\end{aligned}$$

where $E_F=\hbar^2k_F^2/2m$ is the Fermi energy and

$$N_e=(8\pi/3)k_F^3/8\pi^2$$

is the electron density. Now

$$\begin{aligned}\frac{dW}{dt}&=\frac{1}{L}\sum_q\hbar^2(\mathbf{q}\cdot\mathbf{w})^2\frac{2\pi}{\hbar}\frac{q_y^2}{q^4}b^2\frac{C^2}{E_F^2}\frac{k_F}{q}\frac{3}{16}N_e\\&=L\int_0^{q_m}d\mathbf{q}\left\{\int_0^{2\pi}d\Omega\cos^2\phi\cos^2\theta\right\}\\&\qquad\times\frac{2\pi}{\hbar}N_ek_F\frac{3}{64\pi^2}\frac{C^2}{E_F^2}b^2\hbar^2w,\end{aligned}$$

where ϕ is the angle between $\mathbf{q}$ and $\mathbf{w}$, θ is the angle between $\mathbf{q}$ and $\mathbf{j}$, the unit vector in the y direction, and $d\Omega$ is the solid angle of q. Upon integration we obtain

$$\frac{dW}{dt}=\frac{3L}{32\pi}\frac{2\pi}{\hbar}\frac{C^2}{E_F^2}\frac{q_m}{k_F}k_F^2\hbar w^2N_eb^2K,$$

where K is the quantity in the brackets and equals about $\frac{1}{4}$. The kinetic energy of a dislocation in the presence of the sound wave with velocity c_s is (see for example Seeger)[17]

$$E_{\mathrm{kinetic}}=\frac{1}{2}\frac{w^2}{c_s^2}L\frac{Gb^2}{4\pi(1-\nu)}\left(\ln\frac{A}{a}-1\right),$$

where G is the shear modulus, ν is the Poisson ratio ($\nu\approx0.3$ for most metals) and A and a are appropriate upper and lower limits for the shell of elastically distorted crystal surrounding the dislocation. This expression can be written in terms of

$$dW/dt=E_{\mathrm{kinetic}}/\tau,\quad \tau=\text{relaxation time},$$

$$\frac{1}{\tau}=\frac{3}{4}\frac{(1-\nu)}{G[\ln(A/a)-1]}\frac{2\pi}{\hbar}\left(\frac{C}{E_F}\right)^2\left(\frac{q_m}{k_F}\right)\hbar^2k_F^2c_s^2N_eK.$$

The damping B is given by

$$dW/dt=BLw^2,$$

$$B=\frac{3}{32}\frac{2\pi}{\hbar}\left(\frac{C}{E_F}\right)^2\left(\frac{q_m}{k_F}\right)k_F^2\hbar^2N_eb^2K.$$

[17] A. Seeger, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1955), Vol. 7, p. 383.

Note added in manuscript: Recently, during the preparation of this article, another theory was proposed by W. P. Mason.[18] This theory is based on the concept of electron-viscosity which, in turn, applies only to $ql \ll 1$. (l is the mean free path of the conduction electrons and the wave vector **q** is the typical Fourier component of the strain field associated with the dislocation). However, it is now to be noted that in fact the typical value of q is always of the order of the reciprocal of an atomic dimension so that the above condition is grossly violated. The present authors are therefore of the opinion that the theory of Ref. 18 is invalid. (The same objections apply to the later paper by W. P. Mason.)[19]

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PHYSICAL REVIEW VOLUME 151, NUMBER 1 4 NOVEMBER 1966

Apparent Superconducting Energy Gap in Lead from Ultrasonic Measurements*

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(Received 8 April 1966)

The apparent superconducting energy gap in lead was obtained from ultrasonic measurements in the range of $kl \leq 1$. The gap parameter is about $5.0k_bT_c$ and is approximately frequency-independent over the range from 50 to 1050 Mc/sec.

SOME interest has recently been placed on the value of the apparent superconducting energy gap in lead.[1–3] One means of investigating the energy gap is by ultrasonic measurements.[4,5] The evaluation of the ultrasonic data has been complicated by the presence of an amplitude dependence of the attenuation which is a strong function of the temperature in the superconducting state.[1,2,6,7] This effect has been studied in detail by the authors and can be understood in terms of a model based on the assumption of a strong interaction between the conduction electrons and the dislocations in the metal crystal.[8] One of the conclusions of this study was that the amplitude dependence becomes very weak as the impurity concentration is increased. Ultrasonic measurements on crystals with controlled amounts of impurity would be expected to yield more meaningful values for the energy gap.

The following describes briefly the results of measurements on single crystals of 99.9% pure lead. The lead was obtained from 99.999% pure stock and then doped with 0.1% tin. Ultrasonic data obtained in the normal state in the frequency range from 50 to 1050 Mc/sec gives evidence that $kl < 1$ in this range, where k is ultrasonic wave vector and l is the mean free path of the conduction electrons.[8] All the measurements were performed with longitudinal sound waves propagating in the $\langle 111 \rangle$ direction of the crystal. The pulse technique was employed and the apparatus was essentially the standard design.[5,8,9] Calculations of the energy gap were performed in the usual way with the help of the equation

$$\alpha_s/\alpha_n = 2\{\exp[\epsilon_0(T)/k_BT]+1\}^{-1}$$

derived by Bardeen, Cooper, and Schrieffer[4] and the

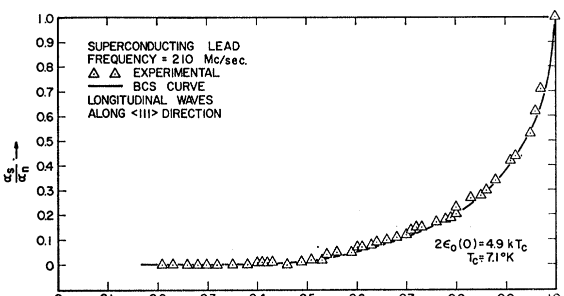

FIG. 1. Normalized attenuation versus reduced temperature for 99.9% pure lead along $\langle 111 \rangle$ direction.

* This research is supported by Grant No. NSF GP 2391 from the National Science Foundation.

† Also at North American Aviation Science Center, Thousand Oaks, California.

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[9] B. R. Tittmann, University of California at Los Angeles, Ph.D. dissertation, 1965 (unpublished); may be obtained from University Microfilm, Ann Arbor, Michigan.