Change in Velocity of Sound between Normal and Superconducting States in Tin

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(Received January 8, 1959)

The difference in the velocity of sound between the normal and superconducting state in tin was measured at 80 kilocycles sec^{-1}. A maximum change of $\sim$2 parts in 10^6 is found for a longitudinal wave in the [001] direction. Any change in velocity is $<$2 parts in 10^7 for a longitudinal wave along the [100] direction or a torsional wave along the [001] direction. This disagrees with some previous determinations, but is in accord with other thermodynamic measurements. The effect of strain amplitude and magnetic field on the velocity and attenuation of the sound wave in the normal state has also been investigated in some detail.

INTRODUCTION

A NUMBER of determinations of the change of the velocity of sound between the normal and superconducting states have been attempted. Most of this work has been with tin due to its convenient transition temperature, 3.73°K, in the middle of the readily accessible helium range, and its ease of handling. From thermodynamic considerations and the measured change of the transition temperature with pressure[1] it is found that the expected change in velocity is of the order of one to two parts in 10^6 at the transition temperature. In the early work[2–4] the sensitivity of measurement was not enough to detect this small change, and in fact, it was not this thermodynamic change which was being sought, but rather an attempt to see whether any grosser changes also occurred. More recent accurate determinations have been made. Measurements at 60 megacycles made by Bömmel and McSkimin[5] are in agreement with thermodynamic considerations. However, there have been notable discrepancies with the measurements at lower frequencies $\sim$50 kilocycles. Landauer[6] has measured longitudinal and shear velocities in single crystals of different orientations. For longitudinal modes changes of $\sim$5 in 10^6 at T_c were found whilst the shear mode gave even larger changes. More recently studies of Welber and Quimby[7] have disclosed a possible fault in the work of Landauer in that the velocity is strain amplitude dependent and the strain amplitude is different in the normal and superconducting states. This work has determined the changes in velocity for polycrystalline tin and while it gives the correct magnitude at T_c, the change with temperature is still in marked disagreement with the work at high frequencies. Furthermore Grenier[8] has recently measured the change of the critical field H_c under uniaxial deformation, from which can be deduced the changes in the velocity of sound in different directions. To clear the confusion existing in this low-frequency field it was felt necessary to use an oscillator of much greater stability than those previously used. With the availability of such an oscillator redeterminations have been carried out on a series of single crystals.

MATERIALS AND TECHNIQUES

The pure tin used in this investigation was obtained from the Vulcan DeTinning Company and is nominally 99.998% pure. The tin crystals were grown in a spectroscopically pure graphite boat in vacuo. Each specimen was cut from the crystal with an acid saw[9] which ensured that the specimen was not plastically deformed in any way. In each case the specimen was oriented along the reported axis to within $\pm 1°$. The specimen was then annealed for 2 hrs. at 210°C in vacuo before sealing to the quartz transducer. The seal was made with a thin film ($\sim$6 microns) of thiokol (Minnesota Mining Mineral E.C. 801 cement) which is cured at 160°F for 12 hrs.

The elastic moduli s_{ij} were measured by the composite piezoelectric resonance technique[10,11] at 80 kilocycles. In all cases the composite was driven in the fundamental mode where $E=4f^2l^2\rho$ and $l=\lambda/2$. The apparatus for making the measurements at helium temperatures has been described elsewhere.[12] The maximum strain amplitude, ϵ_{max}, developed in the composite resonator was obtained from the electrical impedance of the transducer as a function of frequency about the resonant frequency.[13] Because of the small change in frequency encountered in this investigation it was found necessary to use an oscillator whose stability was better than 2 parts in 10^7. A prototype oscillator capable of this stability, was kindly lent to us by Mr. J. Israel of Bell Laboratories, Murray Hill.

A magnetic field could be applied to the specimen

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[5] W. P. Mason and H. E. Bömmel, J. Acoust. Soc. Am. **28**, 930 (1956).
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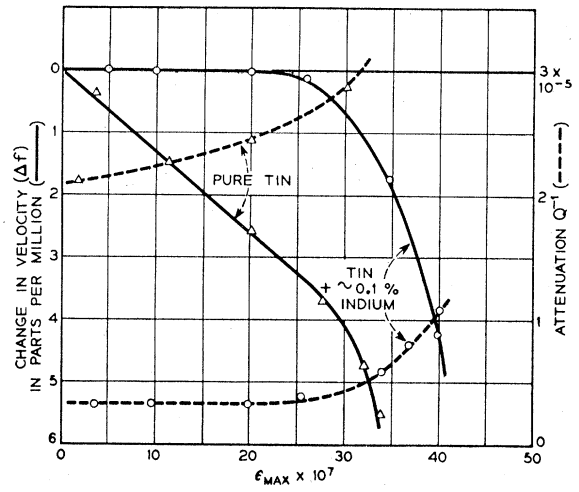

FIG. 1. Variation of attenuation and velocity of a longitudinal wave in [001] direction with maximum strain amplitude.

either parallel or transverse to the specimen axis. The direction of the transverse field could be rotated through 360° about the specimen axis.

RESULTS

When a specimen of the pure tin was excited in a longitudinal mode along the [001] direction at 4.2°K the attenuation (Q^{-1}) and resonant frequency of the sample were dependent upon the strain amplitude of the composite resonator. Figure 1 shows the attenuation and change in resonant frequency (Δf) of the specimen at 4.2°K as a function of the maximum strain amplitude, ϵ_{max}, and neither Q^{-1} nor Δf is independent of strain amplitude at any strain amplitude. However, the variation with ϵ_{max} appears to be linear when $\epsilon_{max} < 20\times10^{-7}$ so that it is possible to extrapolate to $\epsilon_{max}=0$. This is in accord with the observations of Welber and Quimby.[7] The situation is complicated further by the observation that at constant strain amplitude both Q^{-1} and Δf are dependent upon the magnitude of the magnetic field, either transverse or longitudinal. The transverse field is the more interesting and Fig. 2 shows the variation of attenuation with field strength (H) and Fig. 3 shows a polar plot of attenuation with the orientation of a constant transverse magnetic field about the [001] direction. In spite of these uncertainties it was possible to measure the change in velocity[14] between the normal and superconducting states of a longitudinal wave along the [100] direction as a function of temperature below T_c, this is plotted in Fig. 4 (the probable error is however large ~4.0 in 10^7). For specimens of the pure tin excited in a longitudinal mode along the [100] direction or a torsional mode along the [001] direction there was no observable change in frequency between the normal and superconducting states (i.e., any change must have been less than 2 in 10^7).

The values of the elastic moduli and attenuation at $\epsilon_{max}=0$ for the pure tin specimens at 4.2°K are given in Table I.

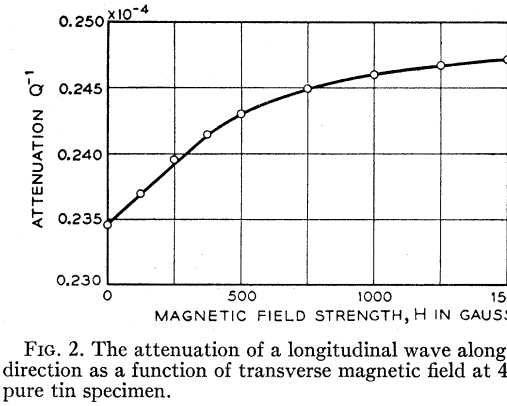

FIG. 2. The attenuation of a longitudinal wave along the [001] direction as a function of transverse magnetic field at 4.2°K for a pure tin specimen.

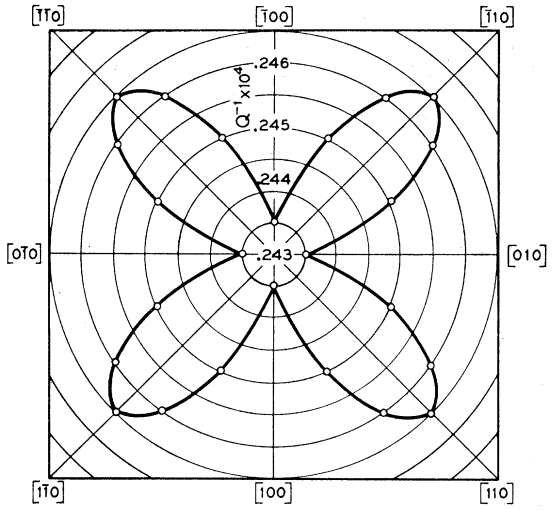

FIG. 3. The attenuation of a longitudinal wave along the [001] direction as a function of the orientation of a constant transverse magnetic field of 750 gauss.

Since it is believed that the dependence of the attenuation and velocity on magnetic field was a result of the appreciable mean free path of the conduction electrons in the pure tin, crystals were obtained[15] containing ~0.1% indium in solid solution which appreciably decreases the conductivity. Figure 1 shows Q^{-1} and Δf as a function of ϵ_{max} for such a specimen excited in a longitudinal mode along [001] direction at 4.2°K. It can be seen that below $\epsilon_{max}\sim20\times10^{-7}$, Δf is independent of strain amplitude. For these impure

[14] In the composite resonator technique it can be shown[10] that the actual change in frequency of the specimen is $[(m_1+m_2)/m_2]\Delta f_{obs}$, where m_1 is the mass of quartz transducer and m_2 the mass of specimen. The velocity of an acoustic wave is given by $v=2fl$ for the fundamental mode, therefore the change in velocity $\Delta v/v$ is equal to $\Delta f/f$.

[15] These crystals were kindly supplied by A. L. Schawlow and G. E. Devlin of the Bell Telephone Laboratories.

specimens there was no observable effect of the magnetic field on either Q^{-1} or Δf. This enabled a much more accurate extrapolation to zero strain amplitude. Figure 5 shows Δf as a function of $\epsilon_{\max}$ in the normal and superconducting states at 3.67°K. The change in velocity between the two states as a function of temperature is plotted in Fig. 4. These points have a much smaller probable error than for the pure specimens and the curve is drawn taking into account only the results from the impure sample. It is emphasized that there is good agreement between the values obtained from the pure and alloy specimens considering the higher probable error in the pure tin.

DISCUSSION

From the thermodynamics of the normal to superconducting phase change it can be shown that there is a difference in the compressibility of the two phases. In brief this is derived from the relation

$$G_n - G_s = (H_c^2/8\pi)V_s, \tag{1}$$

which says that the difference in the free energy of the two phases equals the magnetic energy required to destroy the superconductivity in the volume of the superconductor by the critical field H_c.

TABLE I. Elastic moduli and attenuation for pure tin.

	s_{ij} (cm² dyne⁻¹)	Q^{-1}
Longitudinal mode in [001] direction	$s_{33}=1.16\times10^{-12}$	2.2×10^{-5}
Longitudinal mode in [100] direction	$s_{11}=1.45\times10^{-12}$	3.0×10^{-5}
Torsional mode in [001] direction	$s_{66}=3.89\times10^{-12}$	2.0×10^{-5}

Now the entropy S and the strains u_{ij} are direct functions of G of Eq. (1) according to the equations

$$S=-(\partial G/\partial T)_{u_{ij}}; \quad u_{ij}=-(\partial G/\partial T_{ij})_T. \tag{2}$$

Differentiating the strain difference $u_{ij}^s-u_{ij}^n$ by T_{kl}, the stress

$$(\partial/\partial T_{kl})(u_{ij}^s-u_{ij}^n)=(s_{ijkl}^s-s_{ijkl}^n)$$
$$=\frac{1}{4\pi}\left[H_c\frac{\partial^2 H_c}{\partial T_{ij}\partial T_{kl}}+\frac{\partial H_c}{\partial T_{ij}}\frac{\partial H_c}{\partial T_{kl}}\right]. \tag{3}$$

Specifically at T_c and using the standard two number notation for moduli

$$\Delta s_{11}=s_{11}^s-s_{11}^n=(1/4\pi)(\partial H_c/\partial T_1)^2,$$
$$\Delta s_{33}=(1/4\pi)(\partial H_c/\partial T_3)^2,$$
$$\Delta s_{66}=(1/4\pi)(\partial H_c/\partial T_6)^2.$$

It is our object to show that the measured changes of sound velocity are in good agreement with the changes of H_c under uniaxial deformation as measured by Grenier.[8] Before completing this comparison it is necessary to consider any applicable corrections. First, if there is a change in length of the specimen between the two states there will be a change in the resonant frequency without there having to be a change in the elastic constants, such that

$$\Delta f/f=\Delta l/l.$$

The measurements of Lasarew and Sudovstov[16] show that at T_c, $\Delta V/V$ is zero and rises to approximately 10^{-7} at 2°K. Thus the maximum change in resonant frequency due to this cause is less than 1 part in 10^7 which is below the limit of accuracy of the measurements.

In the measurement of the velocity of sound at a particular frequency it is necessary to decide whether the conditions of measurement are adiabatic or isothermal. In a longitudinal wave there are temperature

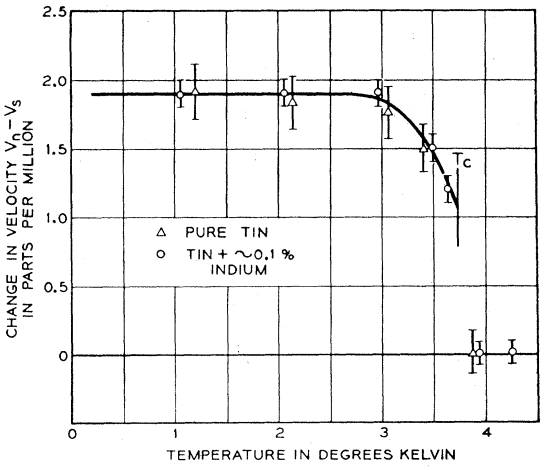

FIG. 4. The change in velocity between the normal and superconducting states of a longitudinal wave along the [001] direction as a function of temperature.

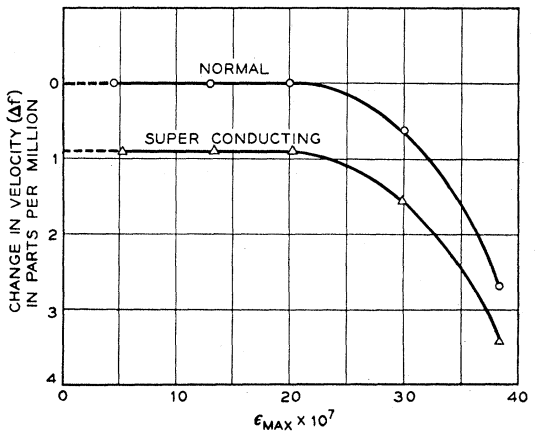

FIG. 5. The change in velocity between the normal and superconducting states for a longitudinal wave along the [001] direction as a function of maximum strain amplitude at 3.67°K. (Velocity not corrected for mass ratio between specimen and transducer.)

[16] B. G. Lasarew and A. I. Sudovstov, Doklady Akad. Nauk. S.S.S.R. **69**, 345 (1949).

TABLE II. Thermodynamic values for tin.

Quantity	Value	Reference
C_{pn}	0.0218 joules mole^{-1} °K^{-1} at T_c	a
C_{ps}	0.0345 joules mole^{-1} °K^{-1} at T_c	a
V_m	16.3 cm^3 mole^{-1}	
$\partial H_c/\partial T$	-151 oersted °K^{-1} at T_c	b
$\partial H_c/\partial p$	6.8×10^{-9} oersted dyne^{-1} cm^2 at T_c	c
B	4.5×10^{11} dyne cm^{-2}	d
γ	1	e

[a] W. H. Keesom and P. H. van Laer, Physica 5, 193 (1938).
[b] See reference 1.
[c] N. L. Muench, Phys. Rev. 99, 1814 (1955).
[d] See reference 5.
[e] It has been shown by one of us, D. F. Gibbons, Phys. Rev., 112, 136 (1958), that at temperatures low compared to the Debye temperature, Grüneisen's factor, γ, is reduced from its high-temperature value and so choosing $\gamma=1$ is even an overestimate.

changes at the nodes relative to the antinodes. Conditions are isothermal if the path length necessary for thermal equilibrium ($\lambda/2$) is short enough to establish this equilibrium in the time of a half cycle of the sound wave.

It can be easily shown that the time constant for thermal equilibrium is given approximately by

$$cl^2/8K,$$

where c is specific heat in joules cm^{-3}, l is path length to come into equilibrium, K is thermal conductivity in watts °K^{-1} cm^{-1}. The path length, l, to come into equilibrium is a half wavelength of the sound wave,

$$l=\lambda/2=v/2f,$$

where v is the velocity of sound and f the frequency of measurement. The cross-over region from adiabatic to isothermal conditions is then given by

$$1/2f=cv^2/32Kf^2 \quad \text{or} \quad f=cv^2/16K. \tag{4}$$

We can make an estimate of this for tin at T_c. Since the thermal conductivity varies from specimen to specimen only a very approximate estimate can be made. Using $K=\frac{1}{2}$ watt °K^{-1} cm^{-1}, $v=2.5\times10^5$ cm sec^{-1}, and c from Table II, it is found that

$$f\simeq10^6 \text{ cycles sec}^{-1}.$$

Thus the measurements described at 80 kilocycles are essentially adiabatic, whilst those above 1 megacycle are isothermal.

In order to compare these adiabatic velocity changes with Grenier's isothermal data, consideration must be taken of the difference between the adiabatic and isothermal moduli. Zener gives[17]

$$(s_{ij}{}^a-s_{ij}{}^i)/s_{ij}=\alpha_i\alpha_j T/s_{ij}c_v, \tag{5}$$

where α is the linear coefficient of expansion, c_v is the specific heat in erg cm^{-3} °K^{-1}. (The superscript, a, represents an adiabatic change and, i, an isothermal change.)

[17] C. Zener, *Elasticity and Anelasticity of Metals* (University of Chicago Press, Chicago, 1948), p. 89.

Now along with the change in compressibility there is also expected to be a change of expansivity[1] given by

$$\Delta\alpha=\alpha_n-\alpha_s=\frac{1}{4\pi}\frac{\partial H_c}{\partial T}\frac{\partial H_c}{\partial p} \quad \text{at} \quad T_c.$$

Using the values given in Table II

$$\Delta\alpha=8.2\times10^{-8}.$$

Since no experimental values exist, α_n can only be deduced in order of magnitude from Grüneisen's factor

$$\alpha B/c_v=\gamma.$$

Whence, using the values given in Table II, at T_c

$$\alpha_n=3\times10^{-8}.$$

Therefore,

$$\alpha_s=-5.2\times10^{-8}.$$

These esimated values of α_n and α_s are the coefficients of volume expansion. In lieu of any knowledge of the anisotropy, the coefficient of linear expansion can be estimated as $\frac{1}{3}$ of the coefficient of volume expansion.

$$\left(\frac{\Delta s_{33}}{s_{33}}\right)^a-\left(\frac{\Delta s_{33}}{s_{33}}\right)^i=\frac{T_c}{s_{33}}\left(\frac{\alpha_s{}^2}{c_{vs}}-\frac{\alpha_n{}^2}{c_{vn}}\right).$$

The right-hand side of this equation gives 3×10^{-9} and this is well below the limits of experimental error. Thus the experimental values of the change of resonant frequency of the specimen can be directly compared to Grenier's results.

$$2\frac{\Delta f}{f}=\frac{\Delta s_{ij}}{s_{ij}}=\frac{1}{4\pi s_{ij}}\left(\frac{\partial H_c}{\partial T_i}\right)^2. \tag{6}$$

Grenier[8] has found that $\partial H_c/\partial T_1=0.6\times10^{-9}\varphi$ cm^2 dyne^{-1}, $\partial H_c/\partial T_3=6.4\times10^{-9}\varphi$ cm^2 dyne^{-1}, $\partial H_c/\partial T_6<1.0\times10^{-9}\varphi$ cm^2 dyne^{-1}. Using the value for s_{33} of 1.16×10^{-12} cm^2 dyne^{-1}, given in Table I, we get from Eq. (6)

$$\Delta s_{11}/s_{11} \text{ and } \Delta s_{66}/s_{66}<10^{-7} \text{ and } \Delta s_{33}/s_{33}=28.2\times10^{-7},$$

from Grenier. Whilst from present results

$$\Delta s_{11}/s_{11} \text{ and } \Delta s_{66}/s_{66}<\pm4\times10^{-7} \text{ and } \Delta s_{33}/s_{33}=(32\pm4)\times10^{-7}.$$

Thus at the transition temperature there is good agreement between the two different types of experiment. Actually the measurement of Δf was made at 3.67°K which is below T_c. Since Δf is increasing rapidly near T_c (Fig. 4) the value of Δf at T_c will be less and the agreement closer still.

It remains to be seen what conclusions can be drawn from the temperature variation of $\Delta s_{33}/s_{33}$ determined. According to Grenier's data, $(\partial H_c/\partial T_3)^2$ at 1°K is one

third of its value at T_c. Equation (3) can then be used to determine the magnitude and temperature variation of $\partial^2 H_c/\partial T_3^2$, which is found to be $\sim 2\times 10^{-19}\varphi$ cm^4 dyne^{-2} at 1°K and $\sim 4\times 10^{-19}$ at T_c. This is subject to error such that the results are compatible with a constant value of $\partial^2 H_c/\partial T_3^2 \simeq 3\times 10^{-19}$. To this we can contrast the data of Chester and Jones[18] on the change of critical temperature with pressure. Their data has been fitted to a straight line assuming $\partial^2 H_c/\partial p^2 = 0$. The possible error in their data would allow for a value of $\partial^2 H_c/\partial p^2$ up to 1.5×10^{-19}. Without further information it is not possible to compare in more detail the relationship of these second derivatives, one being a volume effect and the other a uniaxial effect. It must, however, be considered satisfactory that they are only a factor 2 apart.

These results can now be compared with the other similar determinations which have been made in this frequency range. In Landauer's work no account was taken of the effect of strain amplitude on the resonant frequency of the specimen. Since he worked with pure material there would undoubtedly be a different loss in the normal and superconducting states. Thus for the same driving voltage the measurements would correspond to different strain amplitudes and cannot be directly compared in the absence of further data. In the work of Welber and Quimby this effect was detected and corrected for, indeed, at T_c their measured change in velocity is of the correct order of magnitude. But the change is the same as their experimental accuracy and so no actual value can be assigned. The most marked disagreement with the present experiments comes at temperatures below T_c. By 3.0°K they find that $\Delta f/f = 6\times 10^{-6}$. From the foregoing reasoning, ascribing changes to the term in $\partial^2 H_c/\partial p^2$, their results are no longer compatible with the data of Chester and Jones. Since they had used a polycrystalline sample, a check experiment was then performed to see if this could be the cause. A different oscillator with a stability of $\pm 1.5\times 10^{-6}$ was used and at 1°K any change was less than the oscillator stability; this is in close agreement with the single crystal results. There is no obvious reason why the two results on polycrystalline material should differ.

The least understood aspect of this work is the reason for the variation in Δf with strain amplitude (Fig. 1) in the pure tin specimen at 4.2°K. When $\epsilon_{\max}$ is large, $>20\times 10^{-7}$, both alloyed and pure specimens behave in a similar manner, and this is presumably an anelastic effect caused by the motion of dislocations in the stress fields of the acoustic wave. However, when $\epsilon_{\max}$ $<20\times 10^{-7}$ the pure tin is still dependent upon $\epsilon_{\max}$ whereas the alloyed specimen is invariant. It seems unlikely that dislocations would contribute an anelastic effect at such small strains. A more probable reason, it is felt, for the variation of Δf and Q^{-1} in the pure tin, is that it is a dispersion effect associated with the conduction electrons. That is, there is a strain amplitude dependence of attenuation due to the large mean free path of the conduction electrons in the pure specimen.

The observed orientation dependence of the loss in a transverse field is of considerable interest. Since the effect is not observed in alloyed crystals it is reasonable to assume that it is a result of the difference in mean free path of the conduction electrons between the pure and alloyed specimens. The theories of Mason,[5] Kittel,[19] and Pippard[20] predict a loss which is proportional to the conductivity when the mean free path for electrons (l) is of the same order as the acoustic wavelength (λ). This has been confirmed by Bömmel.[5] A more interesting effect akin to a "geometrical cyclotron effect"[20] occurs in a magnetic field when $l>\lambda$. The tin used in this investigation is of comparable purity to that reported by Kunzler and Renton[21] in which $l\sim 0.05$ cm; however, $\lambda\sim 4$ cm, therefore the effect reported here is most probably the result of a normal magneto-resistance. In fact, the variation of loss with field direction about the [001] direction agrees with the magneto-resistance data for Kunzler[22] as measured by a dc technique for specimens of similar purity. It is hoped to make a more detailed comparison after the magneto-resistance of this specimen has been measured.

CONCLUSION

Good agreement has been found to exist between the most recent determinations of the change of elastic constants between the normal and superconducting states. Specifically it is shown that, in contrast to some previous results, the change in the velocity of sound at 80 kc. in the two states at T_c is that expected from thermodynamic arguments. Some new data is presented showing that even at these low frequencies the conduction electrons have a measurable effect upon the attenuation of a sound wave. An acoustic magneto-resistance exactly analogous to the electrical magneto-resistance has been found. This, in conjunction with the acoustic magneto-resistance determined at higher frequencies should prove useful in the understanding of the "geometrical cyclotron effect."

[18] P. F. Chester and G. O. Jones, Phil. Mag. **44**, 1281 (1953).

[19] C. Kittel, Acta Met. **3**, 295 (1955).

[20] A. B. Pippard, Phil. Mag. **46**, 1104 (1955).

[21] J. E. Kunzler and C. A. Renton, Phys. Rev. **108**, 1397 (1957).

[22] J. E. Kunzler (private communication).