

can be easily raised to the empty localized levels with the absorption of light. Whether or not, in a case of MgO, hole or electron conduction occurs cannot be deduced since, at the moment, the experiments do not clearly indicate the signs of the charge carriers. Although it was found that the various peaks in the afterglow are accompanied by the disappearance of the absorption bands which appear in magnesium-colored

crystals, the determination of the electronic model of the luminescent processes requires more experiments.

Acknowledgment should be given to Mr. T. Ichimiya and Mr. T. Shindo for their encouragement during these investigations. We wish to thank Mr. O. Mikami and Mr. K. Sawamoto and Mr. I. Mitsufuji for the measurements of optical absorption and spectroscopic analysis.

## Elastic Moduli of Tin at the Superconducting Transition

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A composite oscillator technique was used to measure the elastic moduli of tin in the normal and superconducting states. The experiments were performed on single crystals at about 50 kc/sec. A difference in moduli was observed, indicating that the velocity of sound is less in the superconducting than in the normal state. At 3.7°K the relative change at the superconducting transition is about 4 parts in  $10^6$  for the longitudinal modulus  $S_{11}$  and about 6 parts in  $10^6$  for the torsional modulus,  $2(S_{44}+S_{66})$ . These relative changes increase with decreasing temperature. At room temperature, the adiabatic modulus  $S_{11}$  was found to be  $1.55 \times 10^{-12}$  cm<sup>2</sup>/dyne, and  $2(S_{44}+S_{66})$  was  $9.4 \times 10^{-12}$  cm<sup>2</sup>/dyne.

### I. INTRODUCTION

**M**ANY experiments have been carried out that indicate no change in elastic properties of tin at its superconducting transition.<sup>1-3</sup> Nevertheless, a change of approximately one part in  $10^5$  is predicted by thermodynamics.<sup>4</sup> An experimental determination was undertaken with sufficient accuracy to verify this change. Tin was used as the superconducting material, and the elastic moduli were determined by a resonant frequency method. A precision of about one part in  $10^6$  was obtained in measuring the difference in resonant frequency between the superconducting and normal states. The measurements show that the velocity of both longitudinal and transverse sound is less in the superconducting than in the normal state. The magnitude of the relative velocity change is dependent on crystallographic orientation and on the temperature and amounts to several parts per million near the transition temperature.

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† The work described in this paper, which has been presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy, was carried out in the Institute for the Study of Metals of the University of Chicago.

<sup>1</sup> W. J. de Haas and M. Kinoshita, *Leiden Comm. No. 187b* (1927).

<sup>2</sup> McLennan, Allen, and Wilhelm, *Trans. Roy. Soc. Can. III* **25**, 13 (1931).

<sup>3</sup> H. Bommel and J. L. Olsen, *Phys. Rev.* **91**, 1017 (1953).

<sup>4</sup> D. Shoenberg, *Superconductivity* (Cambridge University Press, Cambridge, 1952), p. 76.

### II. EXPERIMENTAL TECHNIQUES

The elastic moduli were determined by a composite oscillator technique using a single-crystal cylinder of tin glued coaxially to a piezoelectric quartz crystal.<sup>5</sup> The resonant frequency of the composite was compared with the frequency of a second quartz crystal which served as a standard. By using similar quartz crystals and by carefully adjusting the length of the tin crystal, a small difference in frequency was obtained between the standard and the composite. This difference in frequency was measured in both the normal and superconducting states. The change in the difference frequency was used to calculate the change in the elastic moduli of the tin. This method eliminated the need for an accurate determination of the absolute frequency.

A schematic diagram for the frequency measurement is shown in Fig. 1. Both the composite and standard quartz crystals were in a vacuum enclosure in the helium cryostat. Each was connected to a separate amplifier immediately at the top of the cryostat. The crystals served as filter elements<sup>6</sup> in the positive feedback loops of the amplifiers. The oscillators, thus formed, operated at approximately the resonant frequencies of the crystals. The two oscillator frequencies were mixed and filtered to give the difference frequency,

<sup>5</sup> S. Quimby, *Phys. Rev.* **25**, 558 (1925).

<sup>6</sup> W. G. Cady, *Piezoelectricity* (McGraw-Hill Book Company, Inc., New York, 1946), p. 491.

TABLE I. Orientation of the tin crystals. The angles are given between the casting axis and the X, Y, and Z directions of the unit cell.

| Crystal | Orientation (degrees)                     |         |        |
|---------|---|---------|--------|
|         | X   | Y       | Z      |
| 1       | (a axis about 1 degree from casting axis) |         |        |
| 2       | 8.0                                       | 4.5+90  | 6.0+90 |
| G1      | 3.8                                       | 0.8+90  | 3.4+90 |
| G5a     | 28.2                                      | 28.0+90 | 3.5+90 |

which was measured by counting the number of cycles in a given time with a scaler and clock.

Figure 2 is the circuit diagram for the oscillators. The amount of positive feedback was controlled by a potentiometer and during operation was adjusted to as low a value as possible, still allowing oscillation. The mixer was conventional, using a 6L7 pentagrid mixer tube. The output was fed to a scaling circuit. The frequency was measured by gating the scaler with an integer minute signal. This signal was obtained by an appropriate relay system from an accurate pendulum clock.

Single crystals of tin were used for all experiments. The tin was degassed in high vacuum and cast in 0.187-in. i.d. precision bore Pyrex tubing and had a measured purity of better than 99.99 percent. The crystals were grown by lowering through a gradient furnace. Orientation was determined by x-ray analysis, using the back reflection Laue technique. Data on the crystals used are compiled in Table I. Crystals G1 and G5a were from the same batch of tin but were grown individually. G1a', G1b, and G1c were cut from G1 and therefore have the same orientation.

Two sets of piezoelectric quartz crystals were used (see Table II). Each set was made up of two crystals of approximately equal frequency, one used as frequency standard and the other as driver of the composite oscillator. One set consisted of *x*-cut crystals vibrating longitudinally at about 58.7 kc/sec, and the other set consisted of *y*-cut crystals vibrating torsionally at about 41.1 kc/sec. (These were relapped later to 42.45 kc/sec.) The crystals were circular cylinders of 0.472-cm diameter.

The cryostat was of standard design, consisting of coaxial helium and nitrogen Dewars (see Fig. 3). A

TABLE II. The quartz crystals. The approximate frequency of the crystal set and the frequency difference between the two crystals in the set are indicated.

| Crystal set | Mode         | Length cm        | Approximate frequency kc/sec | Frequency difference cps |
|-------------|--------------|------------------|------------------------------|--------------------------|
| 1           | Longitudinal | {4.643<br>4.699} | 58.7                         | 10                       |
| 2           | Torsional    | {4.77<br>4.80}   | 41.22                        | 80                       |
| 2'          | Torsional    | {4.595<br>4.654} | 42.45                        | 25                       |

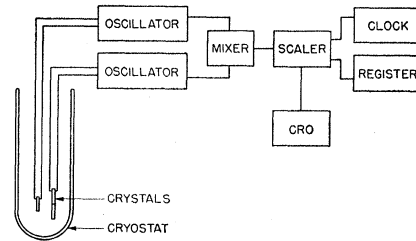


FIG. 1. Block diagram for the frequency measurement.

crystal holder isolated the crystals from the helium bath. Thermal contact between the crystals and the bath was obtained by use of about 0.1 mm Hg helium exchange gas. A pair of Helmholtz coils in the nitrogen Dewar provided a magnetic field coaxial with the crystals.

The  $Q$ , defined as usual as the ratio of inductive reactance to resistance, is a measure of the reciprocal of the damping of a crystal. The  $Q$ 's of the composite and standard quartz crystals were determined by decay time experiments and measurements of the crystal currents at series and parallel resonance.<sup>7</sup> The high  $Q$  necessary for good frequency stability was produced by careful lapping, plating, cleaning of the crystals, and operation at low temperatures and pressures. The  $Q$ 's obtained were about  $2 \times 10^5$ .

The error in measurement of the change in elastic modulus was composed of errors in the frequency and temperature measurements and fluctuations in the operating frequencies of the oscillators due to finite  $Q$ . The error in the frequency measurement was due to errors in timing and counting and with typical values amounted to about 4 parts in  $10^7$ . The temperature was determined by the vapor pressure of the helium bath using the Shoenberg and van Dijk conversion scale.<sup>8</sup> The error due to temperature measurement is less than 2 parts in  $10^7$ . Thus the total calculable error is less than 5 parts in  $10^7$ . The observed errors of about 1 part in  $10^6$  are of the magnitude to be expected for a  $Q$  of about  $2 \times 10^5$ . The limiting factor in the accuracy, therefore,

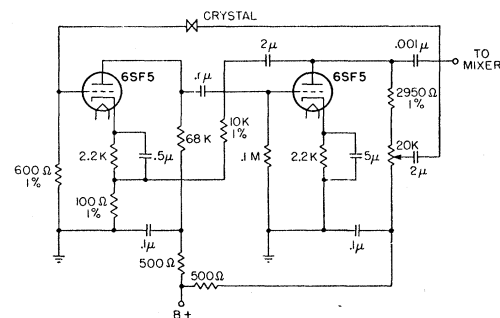


FIG. 2. Oscillator circuit.

<sup>7</sup> A. W. Lawson, Phys. Rev. **60**, 330 (1941).

<sup>8</sup> D. Shoenberg and H. van Dijk, Nature **164**, 151 (1949).

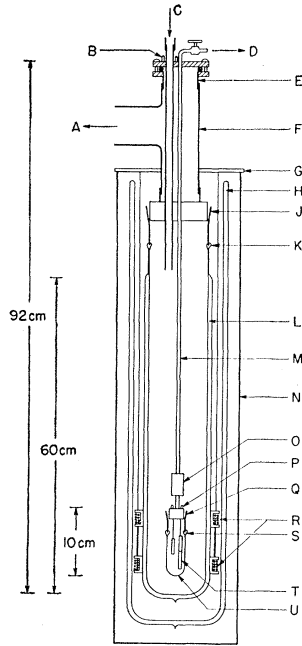


FIG. 3. The cryostat. (A) To Kinney pump and helium return line. (B) Kovar-glass terminals. (C) Helium transfer tube inlet. (D) High vacuum. (E) 2-in. i.d. Cu-Ni. (F) 2-in. i.d. Cu. (G)  $\frac{3}{8}$ -in. brass plate. (H) Nitrogen dewar. (J) Rose's Metal joint. (K) Cu-glass seal. (L) Helium Dewar. (M)  $\frac{1}{2}$ -in. Cu-Ni pumping tube. (N) Brass can. (O) Radiation trap. (P) Kovar-glass terminals. (Q) Rose's Metal seal. (R) Helmholtz coils. (S) Cu-glass seal. (T) Crystals. (U) Crystal holder.

is assumed to be due to the finite  $Q$ , and the indicated errors were calculated from the observed deviations.

The error in the absolute elastic moduli was introduced by uncertainty in the orientation of the tin crystals and amounted to about one percent.

### III. THEORETICAL CALCULATIONS

#### (a) The Elastic Moduli of Tin

Tin has a tetragonal structure, and its elastic properties can be specified by six elastic moduli  $S_{ij}$ .<sup>9,10</sup> If Wooster's notation<sup>11</sup> which differs from Voigt's<sup>12</sup> by a factor of four for moduli having indices 4, 5, and 6 is used,  $S_{11}$  is the appropriate modulus for longitudinal sound along the  $a$  axis, and  $2(S_{44}+S_{66})$  is appropriate for transverse sound. For arbitrary directions in the crystal various other moduli are involved. The effective longitudinal and transverse moduli for tin crystal  $G1$  and the effective longitudinal modulus for  $G5a$  are shown in Table III. Bridgman's<sup>13</sup> values for the moduli can be found in Table IV.

<sup>9</sup> R. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1948), Vol. 1, p. 13.

<sup>10</sup> W. A. Wooster, *A Textbook on Crystal Physics* (Cambridge University Press, Cambridge, 1938), p. 243.

<sup>11</sup> See reference 10, Chapter III.

<sup>12</sup> W. Voigt, *Lehrbuch Der Kristallphysik* (B. G. Teubner, Leipzig, 1928).

<sup>13</sup> P. W. Bridgman, Proc. Nat. Acad. Sci. U. S. 10, 411 (1924).

#### (b) The Change in the Elastic Moduli

The relationship between the resonant frequency of the composite and that of the tin can be specified and becomes quite simple under the experimental conditions used. The resonant frequency of the tin crystal is related to the resonant frequency of the composite oscillator and the quartz driver frequency by the equation:<sup>14</sup>

$$M_t f_t \tan(\pi f_c / f_t) + M_q f_q \tan(\pi f_c / f_q) = 0, \quad (1)$$

where  $M$  is the mass,  $f$  the resonant frequency, and  $t$ ,  $q$ , and  $c$  refer to the tin, quartz, and composite, respectively.

The resonant frequency of the tin crystal is related to its length  $L$ , its density  $\rho$ , and the appropriate elastic modulus  $S$  by

$$f_t = [2L(\rho S)]^{-1/2}. \quad (2)$$

A change in the frequency of the tin could be attributed to a change in either modulus or length. It can be seen from Eq. (8) (using the values in Table IV) that the change in volume at the transition is less than one part in  $10^7$ . Since the observed change in resonant frequency is greater than several parts in  $10^6$ , the size effect can be neglected, and the cause of the change can be attributed to a change in the modulus.

Under the conditions of the experiment, the composite, tin, and quartz frequencies are approximately equal, and all changes are small. Combining Eqs. (1) and (2) and neglecting small terms, we find the relative change in modulus to be related to the change in composite frequency by

$$\Delta S/S = -2(1 + M_q/M_t)\Delta f_c/f_c. \quad (3)$$

#### (c) The Thermodynamics of the Transition

An estimate of the change in compressibility at the superconducting transition can be made using thermodynamics and some previously measured quantities. Along the transition curve, the Gibbs free energy per mole  $G^s$  in the superconducting state is equal to the free energy  $G^n$  in the normal state. The difference in free energy for  $H=0$  is<sup>15</sup>

$$G^n - G^s = \Delta G = (1/8\pi)V_m H_c^2, \quad (4)$$

TABLE III. Effective moduli for the tin crystals.

| Crystal | Modulus              | Effective modulus  |
|---------|----------------------|--|
| G1      | $S_{11}$             | $0.991S_{11} + 0.001(S_{44} + S_{66}) + 0.007S_{13} + 0.013S_{44}$                 |
| G1      | $2(S_{44} + S_{66})$ | $0.996 \times 2(S_{44} + S_{66}) - 0.014S_{44} + 0.007(S_{11} + S_{33} - 2S_{31})$ |
| G5a     | $S_{11}$             | $0.652S_{11} + 0.016(S_{44} + S_{66}) + 0.668S_{66} + 0.342S_{12} + 0.008S_{13}$   |

<sup>14</sup> L. Balmuth, Phys. Rev. 45, 715 (1937), p. 716, Eq. (14).

<sup>15</sup> See reference 4, p. 73.

where  $H_c$  is the critical magnetic field and  $V_m$  is the molar volume. The critical field is related to the temperature, to good approximation, by  $H_c = H_0(1 - t^2)$ , where  $H_0$  is the critical field at absolute zero and  $t = T/T_c$  is the reduced temperature. Equation (4) becomes

$$\Delta G = (1/8\pi)V_m H_0^2 (1 - t^2)^2. \quad (5)$$

The difference in the specific heats per mole, calculated from Eq. (5), is equal to

$$\Delta C_p = (1/2\pi T_c^2)V_m H_0^2 (T - 3T^3/T_c^2), \quad (6)$$

where some very small terms have been neglected.

It can be shown from the electron theory of metals that the specific heat in the normal state contains a term linear with the temperature.<sup>16</sup> Its coefficient  $\gamma$  is proportional to  $V_m^{2/3}$ .<sup>17</sup> Identification between  $\gamma$  and the linear term in Eq. (6) is made. In what follows this assumption amounts to neglect to the pressure dependence of the effective mass of the electrons. Equation (5) can be rewritten

$$\Delta G = (1/4)\gamma T_c^2 (1 - t^2)^2. \quad (7)$$

The difference in volume, expansion coefficient  $\alpha$ , and the isothermal compressibility  $\chi_T$ , can be calculated from Eq. (7). Near  $t=1$ , the following hold approximately:

$$\Delta V = (1/2)\gamma T_c \beta (1 - t^4); \quad (8)$$

$$\Delta \alpha = -2\gamma \beta^2 / V_m; \quad (9)$$

and

$$\Delta \chi_T = - (1/2V_m)\gamma [\beta^2 (1 + 3t^4) + T_c (1 - t^4) (d^2 T_c / dP^2)_T]; \quad (10)$$

TABLE IV. Thermodynamic values for tin.

| Quantity        | Value  | Remarks   | Reference |
|-----------------|--|---|-----------|
| $C_p$           | 0.0053 cal/mole/deg  | Normal state at $T_c$   | a         |
| $C_p$           | 0.0078 cal/mole/deg  | Superconducting state at $T_c$  | a         |
| $\chi_S$        | $10^{-12}$ cm <sup>2</sup> /dyne                           | Estimated at $T_c$  | b         |
| $S_{11}$        | $1.85 \times 10^{-12}$ cm <sup>2</sup> /dyne               | Bridgman's isothermal   | b         |
| $S_{33}$        | $1.18 \times 10^{-12}$ cm <sup>2</sup> /dyne               | Values for room   | b         |
| $S_{44}$        | $1.42 \times 10^{-12}$ cm <sup>2</sup> /dyne               | Temperature using reference 13  | b         |
| $S_{12}$        | $-0.99 \times 10^{-12}$ cm <sup>2</sup> /dyne              | Wooster's notation  | b         |
| $S_{13}$        | $-0.25 \times 10^{-12}$ cm <sup>2</sup> /dyne              |   | b         |
| $S_{33}$        | $3.38 \times 10^{-12}$ cm <sup>2</sup> /dyne               |   | b         |
| $V_m$           | 16.3 cc/mole   |   | c         |
| $T_c$           | 3.72 deg K   | From this experiment  |           |
| $\alpha$        | $5.6 \times 10^{-8}$ deg <sup>-1</sup>                     | Calculated from Gruneisen's law. $\alpha$ and $C_p$ from reference 21 | e         |
| $\Delta \alpha$ | $5.7 \times 10^{-8}$ deg <sup>-1</sup>                     | Calculated from Eq. (9')  |           |
| $dH_c/dT$       | -147 gauss/deg   | At $T_c$  | d         |
| $dT_c/dP$       | $-3.3 \times 10^{-11}$ deg/(dyne/cm <sup>2</sup> )         | Revaluated to 95 kg/cm <sup>2</sup>                                   | e         |
| $\gamma$        | $1.4 \times 10^4$ erg deg <sup>-2</sup> mole <sup>-1</sup> |   | f         |

a See reference 20.

b See reference 13.

c See reference 21.

d See reference 22.

e See reference 23.

f See reference 17.

<sup>16</sup> F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 152.

<sup>17</sup> F. London, *Superfluids* (John Wiley and Sons Inc., New York, 1950), Vol. 1, p. 24.

TABLE V. The adiabatic elastic moduli. The units are  $10^{-12}$  cm<sup>2</sup>/dyne. The Bridgman values are for room temperature.

| Modulus              | Absolute temperature |      |      | 295  | Bridgman |
|----------------------|----------------------|------|------|------|----------|
|                      | 3.7                  | 78   | 194  |      |          |
| $S_{11}$             | 1.34                 | 1.37 | 1.45 | 1.55 | 1.73     |
| $2(S_{44} + S_{66})$ | 5.79                 | 6.0  |      | 9.4  | 9.6      |

where

$$\beta = (dT_c/dP)_T.$$

At  $t=1$ , these reduce to

$$\Delta V = 0, \quad (8')$$

$$\Delta \alpha = -2\gamma \beta / V_m \quad (9')$$

and

$$\Delta \chi_T = -2\gamma \beta^2 / V_m. \quad (10')$$

Similar results could have been obtained directly from Eq. (5) by neglecting certain of the derivatives. Using the values from Table IV we find the change in isothermal compressibility at  $t=1$  to be  $\Delta \chi_T = -1.9 \times 10^{-18}$  cm<sup>2</sup>/dyne.

A calculation based on a formula of Zener's<sup>18</sup> shows that the moduli of tin are essentially adiabatic at the frequency and temperature used. The change in adiabatic compressibility should therefore be calculated and compared with the experimental results. The relation between the two compressibilities is<sup>19</sup>

$$\chi_S = \chi_T - \alpha^2 T V_m / C_p. \quad (11)$$

By making use of the above equations and values in Table IV,<sup>13,17,20-23</sup> it is found that the adiabatic compressibility at  $t=1$  is less in the normal than in the superconducting state by  $\Delta \chi_S = -4.1 \times 10^{-18}$  cm<sup>2</sup>/dyne.

#### (d) The Effect of Damping on the Resonant Frequency of the Tin

The resonant frequency of a circuit is dependent on the degree of damping. It is necessary to show that the observed change in frequency of several parts in  $10^6$  is larger than that to be expected from any possible change in damping, which could amount to, at the most, several percent.

Two effects due to change in damping are considered. The smaller effect is the change in resonant frequency of the tin. For a  $Q$  of  $2 \times 10^5$ , a five percent change in damping causes a change in resonant frequency of

<sup>18</sup> C. Zener, *Elasticity and Anelasticity of Metals* (University of Chicago Press, Chicago, 1948), p. 90.

<sup>19</sup> E. A. Guggenheim, *Thermodynamics* (North Holland Publishing Company, Amsterdam, 1949), p. 100, Eq. (4.24.6) and p. 102, Eq. (4.26.6).

<sup>20</sup> W. H. Keesom and J. A. Kok, Leiden Comm. No. 221e (1932).

<sup>21</sup> *International Critical Tables* (McGraw-Hill Book Company, Inc., New York, 1933), Vol. 1, p. 104.

<sup>22</sup> E. Maxwell, Phys. Rev. **86**, 235 (1952).

<sup>23</sup> G. J. Sizoo and H. Kamerlingh Onnes, Leiden Comm. No. 180b (1925).

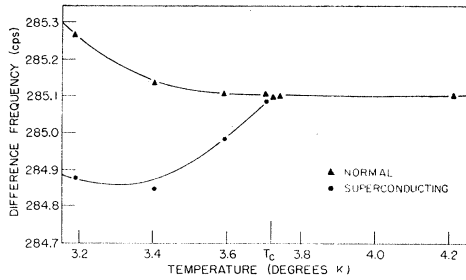


FIG. 4. Isothermal experiments, I. The difference in frequency between the composite oscillator and the standard longitudinal quartz crystal is shown for tin G5a. Below  $T_c$  values for the normal state were obtained by use of a sufficiently strong magnetic field.

about one part in  $10^{10}$ . The second effect is in connection with change in operating point of the oscillator. Because the amplifier and crystal leads introduce a phase shift, the crystal oscillates sufficiently off resonance to make a total phase shift of zero. The further the crystal is off resonance, the more the frequency changes for a given change in damping. A calculation of this effect shows that a five percent change in  $Q$  leads to a relative frequency change of  $2 \times 10^{-8}$ . One would not, therefore, expect damping effects to contribute appreciably to the observed change in frequency.

IV. EXPERIMENTAL RESULTS

(a) The Absolute Moduli

The absolute values of the elastic moduli were calculated from the resonant frequency of the composite oscillator, using Eqs. (1) and (2). In Table V, the experimental values of  $S_{11}$  and  $2(S_{44} + S_{66})$  are given and compared with the results of Bridgman. The moduli measured in these experiments are adiabatic while those of Bridgman are isothermal. A correction of 6.6 percent was subtracted from Bridgman's  $S_{11}$  to make the results comparable at room temperature [see Eq. (11)]. For the torsional modulus the correction is zero.

(b) The Change in Moduli at the Transition

Most of the experimental results were derived from isothermal measurements where the difference in frequency between the composite oscillator and the standard quartz crystal was measured as a function of

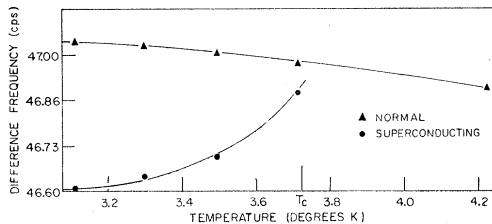


FIG. 5. Isothermal experiments, II. The difference in frequency between the composite oscillator and the standard torsional quartz crystal is shown for tin G1a'.

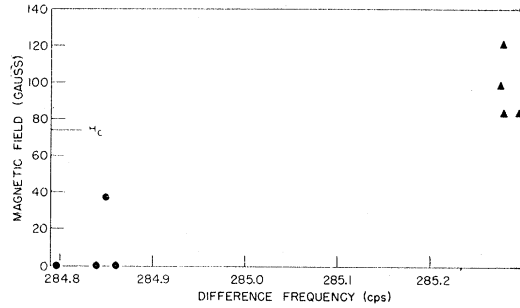


FIG. 6. Isothermal experiment. The difference in frequency between the composite oscillator and the standard longitudinal quartz crystal is given as a function of magnetic field at 3.190 deg K for tin G5a.

magnetic field at constant temperature. At temperatures below the superconducting transition, the difference frequency had two values, depending on the state of the tin. Therefore in an isothermal experiment below the transition temperature a change in difference frequency was produced by magnetic fields of sufficient strength to change the state of the tin. Above the transition temperature, of course, no change was observed. Figures 4 and 5 show the experimental values of the difference frequency for two of the tin crystals. Each point is the average of the number of measurements indicated in Table VI.

At a given temperature, changes in the magnetic field did not alter the difference frequency except in the neighborhood of the critical field. A typical example of the difference frequency as a function of field strength is shown in Fig. 6. Above the transition temperature, the frequency was not affected by fields as high as 150 gauss.

The frequency difference between the longitudinal quartz crystals was compared from 4.2 degrees to 3.0 degrees. No change was observed to within the experimental error of 3 parts in  $10^6$  per degree.

Isothermal experiments were performed for five tin crystals. At each temperature, a number of measurements were made in both states. The difference in fre-

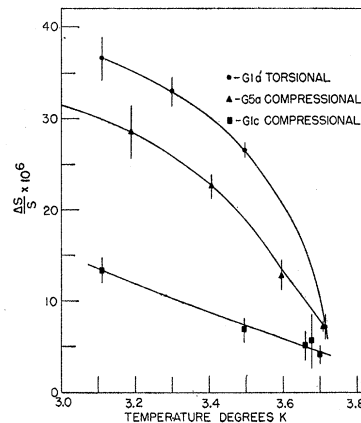


FIG. 7. The change in elastic moduli at the superconducting transition.

quency was converted into change in elastic modulus by use of Eq. (3) and the results are given in Table VI and Fig. 7. The indicated error is the square root of the sum of the squares of the average deviations in the two states.

Several measurements were made on the change in moduli in a zero-field transition, and the results agree roughly with those obtained isothermally. Because of the time delay necessary to establish temperature equilibrium, these results are probably not as reliable as those obtained isothermally.

In all cases the moduli were greater in the superconducting than in the normal state.

For longitudinal vibrations the oscillator voltage increased by about thirty percent as the composite was brought into the superconducting state. This effect was characteristic of the tin only and indicates a decrease in damping in the superconducting state. Absolute determinations indicated no change in  $Q$  within the experimental error of about five percent. Calibration showed that the oscillator voltage increased about ten times as fast as the  $Q$  under typical feedback conditions. The voltage change of thirty percent could be accounted for by a change in  $Q$  of about three percent in the longitudinal mode.

## V. CONCLUSIONS

### (a) Comparison with Thermodynamics

The observed changes in moduli at the superconducting transition cannot be compared directly with the thermodynamic predictions since an insufficient number of moduli were investigated to obtain an experimental value for the compressibility.

For the longitudinal modulus in tin crystal  $G1c$ , the observed relative change at  $t=1$  is  $\Delta S_{11}/S_{11} \approx 4 \times 10^{-6}$ . This is close to the predicted change in compressibility of  $\Delta \chi_s/\chi_s \approx 4.1 \times 10^{-6}$ . For the torsional case, the adiabatic and isothermal moduli are equal. However, since the compressibility does not involve the torsional modulus, the derived results do not apply to the observed results for tin  $G1a'$ .

It should be noted that tin  $G5a$ , although excited longitudinally, has a relatively large change in modulus (see Fig. 7). This can be accounted for by the high percentage of  $S_{66}$  present in its effective modulus, thus making its behavior more nearly like  $G1a'$ .

### (b) General

A number of arguments and experiments have been introduced to show that the observed change in differ-

TABLE VI. The change in moduli at the transition.  $n$  refers to the normal state and  $s$  to the superconducting state.

| Date     | Tin crystal | Quartz crystals | Temp. | $(\Delta S/S) \times 10^6$ | Measurements $n$ | $s$ |
|----------|-------------|-----------------|-------|----------------------------|------------------|-----|
| 10-25-52 | 1           | Long.           | (H=O) | $7.4 \pm 6$                | 10               | 10  |
| 11- 1-52 | 1           | Long.           | (H=O) | $6.4 \pm 4$                | 5                | 5   |
| 12-16-52 | 2           | Long.           | 3.685 | $6.8 \pm 2.2$              | 6                | 10  |
|          |             |                 | 3.556 | $10 \pm 4$                 | 2                | 7   |
| 4- 4-53  | $G1b$       | Tor.            | 3.668 | $16 \pm 6$                 | 8                | 6   |
| 4-11-53  | $G1c$       | Long.           | 3.676 | $5.6 \pm 3.0$              | 7                | 17  |
| 4-26-53  | $G1c$       | Long.           | 3.660 | $5.2 \pm 1.6$              | 23               | 26  |
| 5- 9-53  | $G5a$       | Long.           | 3.708 | $7.2 \pm 0.3$              | 3                | 3   |
|          |             |                 | 3.596 | $12.9 \pm 1.6$             | 4                | 6   |
|          |             |                 | 3.407 | $22.6 \pm 1.2$             | 3                | 4   |
|          |             |                 | 3.190 | $28.6 \pm 3.0$             | 4                | 4   |
| 5-19-53  | $G1c$       | Long.           | 3.669 | $4.2 \pm 1.0$              | 3                | 3   |
|          |             |                 | 3.495 | $6.9 \pm 1.4$              | 3                | 5   |
|          |             |                 | 3.110 | $13.4 \pm 1.4$             | 3                | 4   |
| 6-29-53  | $G1a'$      | Tor.            | 3.714 | $7.2 \pm 1.4$              | 6                | 6   |
|          |             |                 | 3.497 | $26.6 \pm 0.8$             | 6                | 6   |
|          |             |                 | 3.300 | $33.0 \pm 1.6$             | 6                | 6   |
|          |             |                 | 3.112 | $36.6 \pm 2.4$             | 6                | 6   |

ence frequency is indeed due to a change in the elastic modulus of tin at the superconducting transition. To recapitulate, it was found that, without the tin crystal, no change in difference frequency was observed, and with the tin a change at a given temperature was produced only by a critical magnetic field. It was shown that changes in damping and physical size did not cause the effect. Added credibility is given by the agreement of the change in modulus in zero field and that obtained isothermally near the transition temperature. The magnitude of the change is in good agreement with the thermodynamic prediction. The results were consistent for several crystals with similar orientation and were reproducible over long periods.

That there is a change in the velocity of sound at the superconducting transition is in accord with the electron-lattice theories.<sup>24,25</sup> The lowering of the velocity in the superconducting state is in agreement with Wentzel's prediction.<sup>26</sup> However, due to the relatively large observed change in the torsional modulus, it appears that a complete theory of superconductivity must include the interaction of the electrons with transverse as well as longitudinal lattice vibrations.

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<sup>24</sup> H. Frohlich, Phys. Rev. **79**, 845 (1950).

<sup>25</sup> J. Bardeen, Phys. Rev. **80**, 567 (1950).

<sup>26</sup> G. Wentzel, Phys. Rev. **83**, 168 (1951).