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Elastic Constants of β Tin from 4.2°K to 300°K

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The adiabatic elastic constants of β tin have been measured in the temperature range 4.2 to 300°K using the ultrasonic pulse technique. An unusually large variation with temperature of the shear constant $\frac{1}{2}(c_{11}-c_{12})$ has been observed. From the elastic constants extrapolated to 0°K, the limiting value of the Debye temperature of tin has been calculated. Using this value, the low-temperature specific heat data on both normal and superconducting tin have been re-evaluated.

I. INTRODUCTION

THE single crystal elastic constants of β tin were first measured, at room temperature, by Bridgman[1] using a static method. More recently, Mason and Bömmel[2] obtained values for these constants using ultrasonic waves. As can be seen from Table I, there is considerable disagreement between these two sets of values. Furthermore, there existed no detailed study of the variation of the constants with temperature. The work described in this paper was undertaken to remedy this situation. A precise knowledge of the elastic constants and their variation with temperature is of interest in the theory of solids. From their values at 0°K, the limiting value θ_0 of the Debye temperature can be computed. This is particularly useful for metals with a low θ_0, where the usual calorimetric method of determining θ_0 is not very accurate. The shear elastic constants can be related to certain details of the Fermi surface in the metal.

This paper describes the measurement of the elastic constants of β tin between 4.2°K and 300°K. From the extrapolated values at 0°K, θ_0 is computed. The existing data on the specific heat of β tin in the normal and superconducting states are reconsidered in the light of this new value of θ_0. An unusually strong dependence of certain shear constants on temperature is pointed out, and it is suggested that this is connected with overlap electrons (and possibly holes) across certain faces of the Brillouin zone.

II. EXPERIMENTAL DETAILS

The starting material was tin, stated to be 99.999% pure, obtained from the Vulcan Detinning Company. Cylindrical single crystals, 2.5 cm in diameter and up to 20 cm long, were grown in an alumina crucible using a nitrogen atmosphere by a modified Bridgman technique. The crystals were oriented by the back-reflection Laue method, and suitably oriented specimens cut using a high-speed water-cooled carborundum wheel. The samples were then lapped to remove the damaged surface layer (about 0.025 cm) and to produce opposite faces which were flat and parallel to each other to within 0.0005 cm. One specimen was further electropolished to remove the residual surface damage produced by the lapping. There was no detectable difference in the elastic constants measured on this sample before and after the electropolishing. It is therefore felt that the data are free from errors due to surface imperfections.

To enable adequate cross-checks on the elastic constants to be made, five crystals in all were used. The propagation and polarization directions are shown in Fig. 1. In each case the propagation direction was within 1° of the indicated crystallographic direction; this results in an error in the velocity of less than 1 part in 2000, which is negligible.

The ultrasonic measurements were made in the temperature range from 4.2°K to 300°K using an Arenberg pulsed oscillator and wide band amplifier in conjunction with a Tektronix 545 oscilloscope. Ten Mc/sec pulses of 1 μsec duration were used, the reflected pulses being observed without rectification to minimize transit time error. The details of the apparatus have been described in a previous paper.[3]

Considerable difficulty was experienced in making a bond between the quartz transducer and the tin crystal which would hold below liquid nitrogen temperatures. Both glycerol and Nonaq tended to crack below 77°K. A satisfactory bond was finally obtained using Dow Corning silicone of 2.5×10^6 centistokes viscosity and rapidly cooling the specimen by plunging it into liquid nitrogen. This procedure presumably allows the tin to undergo most of its thermal contraction before the bond solidifies, and thereby minimizes the thermal

TABLE I. Previous data on the elastic constants of β tin at room temperature. The values attributed to Mason and Bömmel were recalculated from their paper, using the x-ray density of 7.279 g cm^{-3} at 300°K as determined during the present investigation.

Authors	Elastic constants in 10^{11} dyne cm^{-2} c_{11}	c_{33}	c_{44}	c_{66}	c_{12}	c_{13}
P. W. Bridgman	8.39	9.67	1.75	0.741	4.87	2.81
W. P. Mason and H. E. Bömmel	7.33	8.74	2.19	2.25	2.38	2.48

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[1] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **60**, 305 (1925).

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

[3] J. A. Rayne, Phys. Rev. **115**, 63 (1959).

stresses in the latter on subsequent cooling to liquid helium temperatures.

It is necessary to know the lattice parameters of tin as functions of temperature in order to obtain the elastic constants from the measured sound velocities. The parameters were obtained by making x-ray measurements at 300, 77, and 4.2°K on two single crystal slices mounted such that the [100] and [001] directions, respectively, were parallel to the scattering vector of the x-ray beam. Crystal-monochromated molybdenum K_α radiation was used to obtain the Bragg angles for the (16,0,0) and (0,0,8) reflections, respectively, the lattice parameter in each case being taken as the mean of the values given by the α_1 and α_2 components. The lattice parameters at intermediate temperatures were obtained by interpolation. The results are shown in Table II, together with the values obtained by Lee and Raynor[4] (corrected to 300°K). It is felt that the agreement is satisfactory. The expansivities between 77°K and 300°K obtained in the present work are $\Delta_a=3.17\times10^{-3}$ along the a axis and $\Delta_c=6.69\times10^{-3}$ along the c axis, compared to the values obtained by Erfling,[5], viz., 3.15×10^{-3} and 5.81×10^{-3}, respectively. While the values for Δ_a are in good agreement, the discrepancy in Δ_c is outside the estimated combined experimental errors. It should be noted that the thermal expansion coefficient at room temperature along the c axis measured by various observers also shows similar discrepancies, the values ranging from 28.99×10^{-6} deg^{-1} obtained by Erfling to 36.4×10^{-6} deg^{-1} obtained by Lee and Raynor.

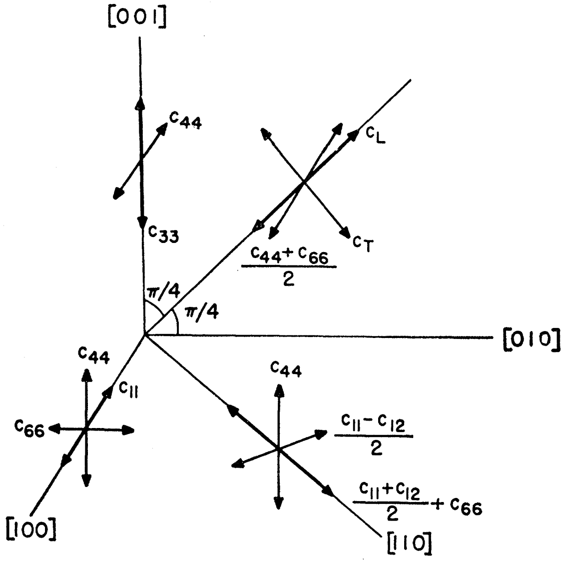

FIG. 1. Propagation and polarization directions for the various modes used in determining the elastic constants of tin. The constants associated with each mode are indicated.

TABLE II. The lattice parameters of β tin. All parameters are in angstrom units.

Parameter	Lee and Raynor's data at 300°K	Present measurements 300°K	77°K	4.2°K
a	5.83185	5.83152	5.81311	5.81187
c	3.18151	3.18280	3.16164	3.15743

III. RESULTS

Table III gives the experimental results at 300, 77, and 4.2°K in terms of ρv^2, ρ being the density of tin, and v the velocity calculated from the observed transit time. Both quantities have been calculated taking account of the thermal expansion. The total error in all cases except crystal d is estimated to be less than 0.7%. This arises mainly from the uncertainty in the transit time determination, and the possible effect of dislocations on the elastic constants. Owing to the somewhat impaired quality of the reflected pulses for the quasi-modes in crystal d, the error in transit time determination was higher. It is estimated that the total error in ρv^2 for these modes is 1.5%. Figure 1 shows the combinations of elastic constants corresponding to the various propagation modes as computed from Eqs. (A1) and (A3) of the Appendix. From the data of Table III, the elastic constants and their associated errors have been computed. These are shown in Table IV. The values at 300°K, obtained in the present work, are compared in Table V with those of Mason and Bömmel.* The latter have been recalculated using the

TABLE III. Summary of experimental data. The letters L and T in the second column refer to longitudinal and transverse modes, respectively. The appropriate combinations of constants are shown in Fig. 1. Equation (A6) of the appendix defines v_L and v_T.

Crystal and propagation direction	Particle motion	ρv^2, in 10^{11} dyne cm^{-2} 300°K	77°K	4.2°K
a, [100]	[100]L	7.250	8.114	8.260
	[001]T	2.217	2.616	2.694
	[010]T	2.407	2.782	2.823
b, [001]	[001]L	8.840	10.040	10.310
	[100]T	2.199	2.620	2.689
c, [110]	[110]L	9.006	9.755	9.878
	[1$\bar{1}$0]T	0.666	1.184	1.271
	[001]T	2.193	2.624	2.702
d, at $\pi/4$ to	[100]T	2.311	2.626	2.691
[010] and	corresponding to v_L	8.005	9.005	8.996
[001] axes	corresponding to v_T	2.291	2.811	2.922
e, [100]	[100]L	7.209	8.190	8.287
	[010]T	2.393	2.780	2.813

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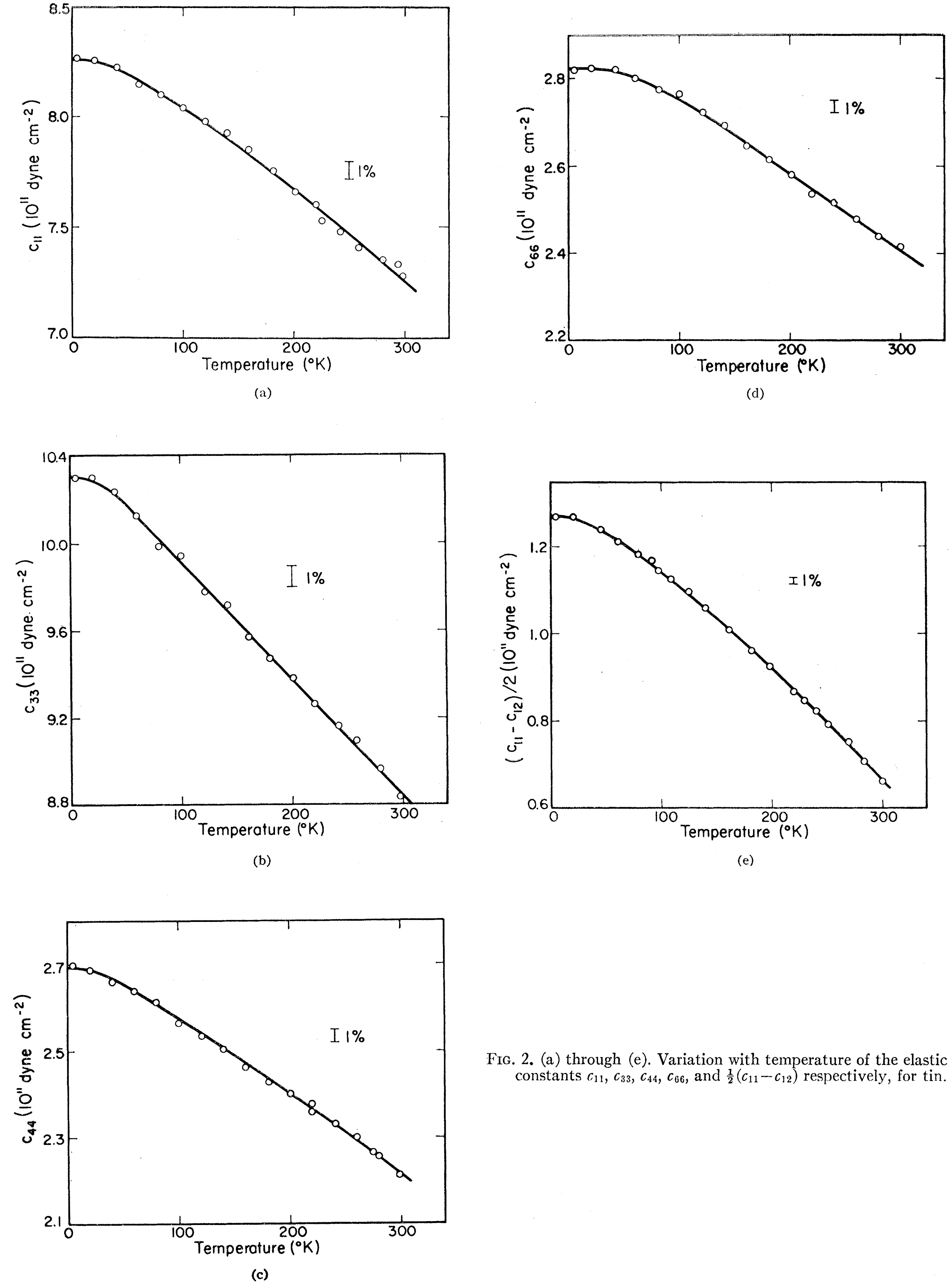
[4] J. A. Lee and G. V. Raynor, Proc. Phys. Soc. (London) **B67**, 737 (1954).

[5] H.-D. Erfling, Ann. Physik **34**, 136 (1939).

* *Note added in proof.* D. G. House and E. V. Vernon, Brit. J. Appl. Phys. **11**, 254 (1960) have reported measurements of the coefficients of compliance of tin. Their values at 15°C and the values calculated from the present room temperature data are compared below (in units of 10^{-13} cm^2 dyne^{-1}):

	s_{11}	s_{33}	s_{44}	s_{66}	s_{12}	s_{13}
House and Church	41.6	14.9	45.6	42.8	−31.2	−4.8
Present work	43.6	14.5	45.4	41.7	−33.9	−3.94



(a)

(d)

(b)

(e)

(c)

FIG. 2. (a) through (e). Variation with temperature of the elastic constants c_{11}, c_{33}, c_{44}, c_{66}, and $\frac{1}{2}(c_{11}-c_{12})$ respectively, for tin.

value $\rho=7.279$ g/cm^3 obtained from the present x-ray measurements. For every elastic constant except c_{33}, there are at least two independent values, which agree to within the estimated error. The constant c_{33} was measured on a crystal 3.8 cm long having exceptionally good acoustic qualities; no cross-check was therefore felt to be necessary in this case. Boldface numbers have been used in Table IV to indicate the mean value of each constant, weighted in relation to the estimated errors where necessary. Figures 2(a) through 2(e) show the temperature dependence of each elastic constant. As may be seen, the internal consistency of each set of measurements is considerably better than the error estimates quoted above.

The agreement between the present results and those of Mason and Bömmel for the values at 300°K of c_{11}, c_{33}, and c_{44} is within the experimental error. There are, however, discrepancies in the values for c_{66}, c_{12}, and c_{13}, which are particularly severe for the latter two constants. No reason can be advanced for this discrepancy, but it may be pointed out that the values obtained in the present experiments have been verified by cross-checks, and are therefore considered to be more reliable. The agreement of the present results with Bridgman's values is very poor. Since his measurements were made by a static method, his results may have been influenced by the ease with which pure tin deforms plastically.

The compressibility K of tin calculated from the formula

$$K=(c_{11}+c_{12}+2c_{33}-4c_{13})/[c_{33}(c_{11}+c_{12})-2c_{13}^2]$$

is 1.821×10^{-12} cm^2 dyne^{-1} at 300°K. This agrees well with the mean value of $1.86\pm0.13\times10^{-12}$ cm^2 dyne^{-1} obtained by Bridgman[6] at 303°K.

Table IV. The elastic constants of β tin at 300, 77, and 4.2°K. Boldface numbers show the weighted mean values. The errors are shown only for the values at 4.2°K; these are used subsequently in the calculation of the uncertainty in θ_0. The units are 10^{11} dyne cm^{-2}.

Constant	Sample	Temperature 300°K	77°K	4.2°K
c_{11}	*a*	7.250	8.114	8.260
	c	7.209	8.190	8.287
	Mean	**7.230**	**8.152**	**8.274±0.062**
c_{33}	*b*	**8.840**	**10.040**	**10.310±0.077**
c_{44}	*a*	2.217	2.616	2.694
	b	2.199	2.620	2.689
	c	2.193	2.624	2.702
	Mean	**2.203**	**2.620**	**2.695±0.021**
c_{66}	*a*	2.407	2.782	2.823
	e	2.393	2.780	2.813
	Mean	**2.400**	**2.781**	**2.818±0.021**
c_{12}	*c* (transverse)	5.898	5.784	5.732
	c (longitudinal)	5.982	5.796	5.846
	Mean	**5.940**	**5.790**	**5.785±0.115**
c_{13}	*d* (transverse)	3.512	3.544	3.533
	d (longitudinal)	3.626	3.744	3.395
	Mean (see appendix)	**3.578**	**3.642**	**3.421±0.11**

Table V. A comparison of the values of the elastic constants at 300°K obtained in the present work, with those of Mason and Bömmel. The latter values have been recalculated using $\rho=7.279$ g cm^{-3} as determined in the present x-ray measurements. The unit is 10^{11} dyne cm^{-2}.

Constant	Mason and Bömmel	This work
c_{11}	7.33	7.230
c_{33}	8.74	8.840
c_{44}	2.19	2.203
c_{66}	2.25	2.400
c_{12}	2.38	5.94
c_{13}	2.48	3.58

IV. DISCUSSION

A. Temperature Dependence of the Elastic Constants

Figures 2(a) through 2(e) show that the temperature variation of all constants, except the shear constant $(c_{11}-c_{12})/2$, is normal. The increase on going to 4.2°K from 300°K is about 15 to 20%; this increase is somewhat larger than that quoted by Mason and Bömmel.[2] Since they do not present detailed data on the temperature variation observed by them, it is not possible to assess the significance of the discrepancy.

The shear constant $C'=(c_{11}-c_{12})/2$ has an exceptionally large temperature coefficient, increasing by about 100% on going from 300°K to 4.2°K. This behavior is in contrast to, for example, an increase of 15% in silver over the same temperature range. Other experiments like the de Haas-van Alphen effect and cyclotron resonance in tin have shown the presence of pockets of electrons and holes in the higher Brillouin zones.[7] It seems likely that these pockets contribute to the elastic constants in a manner similar to that discussed by Leigh[8] for aluminum. Since the configuration of these pockets should be sensitive to temperature, one would expect a resulting marked dependence of certain elastic constants on temperature. Such a mechanism may be responsible for the anomalous behavior of C'.

B. The Limiting Value of the Debye Temperature

At very low temperatures, only phonons of long wavelength are excited in a solid, so that the effects of dispersion may be neglected and the system treated as an elastic continuum. The thermal properties in this region, and in particular θ_0, the limiting value of the Debye temperature, may be calculated from a knowledge of the elastic constants. Thus θ_0 is readily

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[6] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **58**, 165 (1922).

[7] D. Shoenberg, *Progress in Low-Temperature Physics*, edited by J. C. Gorter (North Holland Publishing Company, Amsterdam, 1957), Vol. 2, p. 226.

[8] R. S. Leigh, Phil. Mag. **42**, 139 (1951).

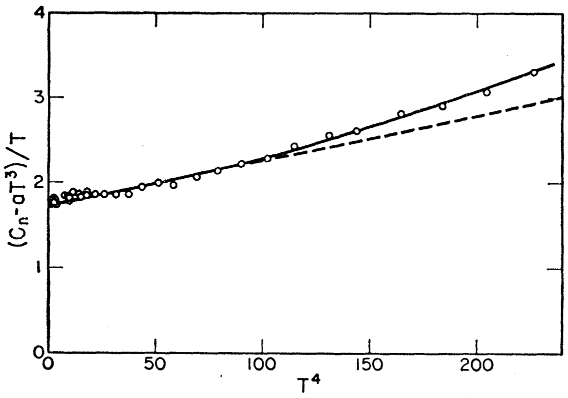

FIG. 3. A plot of $(C_n-aT^3)/T$ versus T^4 to determine the coefficient γ of the linear term in the low-temperature specific heat of tin in the normal state. The broken line represents a least squares fit to the linear part of the curve.

shown to be given by

$$\theta_0^3=\frac{9N}{V\rho^{\frac{3}{2}}}\left(\frac{h}{k}\right)^3\sum_{i=1}^{3}\int\frac{d\Omega}{\xi_i^{\frac{3}{2}}},\qquad(1)$$

where N = the Avogadro number, V = molar volume, ρ = density, and h and k have their usual meaning. The ξ_i are the eigenvalues of the propagation matrix, whose elements are defined in Eqs. (A2) and (A3) of the Appendix. The summation with respect to i is over the three normal modes corresponding to the propagation direction which lies within the element of solid angle $d\Omega$, and the integration is over the total solid angle of 4π. The tetragonal symmetry of tin permits one to rewrite Eq. (1) as

$$\theta_0^3=\frac{9N}{16V\rho^{\frac{3}{2}}}\left(\frac{h}{k}\right)^3\sum_{i=1}^{3}\int_{\theta=0}^{\pi/2}\int_{\phi=0}^{\pi/4}\frac{\sin\theta d\theta d\phi}{\xi_i^{\frac{3}{2}}}.\qquad(2)$$

θ_0 was evaluated from Eq. (2) using an electronic computer. To obtain the eigenvalues ξ_i, the propagation matrix was diagonalized at 450 points in the solid angle defined by the limits of integration indicated in Eq. (2). The resulting value of θ_0 is

$$\theta_0=201.6\pm2.6^\circ\mathrm{K}.\qquad(3)$$

The uncertainty in this figure was obtained by direct calculation from Eq. (2), using the extremal values of the elements of the propagation matrix corresponding to the error estimates in Table IV.

The calorimetric value obtained by Corak and Satterthwaite[9] is

$$\theta_0=195.0\pm0.6^\circ\mathrm{K},\qquad(4)$$

the error being the standard deviation for the least squares fit of their specific heat data to the equation

$$C_n=\gamma T+aT^3,\qquad(5)$$

where C_n is the specific heat in the normal state. Barron and Morrison[10] have re-examined these data assuming a heat capacity of the form

$$C_n=\gamma T+aT^3+bT^5,\qquad(6)$$

and find a better fit with $\theta_0=205^\circ$K. The value of a calculated from the present $\theta_0=201.6^\circ$K has been used to obtain the best fit of the calorimetric data to Eq. (6) by plotting $(C_n-aT^3)/T$ versus T^4 (see Fig. 3). The deviation from linearity of this plot shows that at temperatures beyond 3°K the lattice heat capacity should also include higher order terms in T.[11] A least squares analysis of the linear region gives

$$\gamma=1.76\times10^{-3}\text{ joule deg}^{-2}\text{ mole}^{-1},$$

which agrees well with the value of $(1.75\pm0.01)\times10^{-3}$ joule deg^{-2} mole^{-1} given by Corak and Satterthwaite, but differs considerably from that obtained by Barron and Morrison, viz., $\gamma=1.9\times10^{-3}$ joule deg^{-2} mole^{-1}.

The new values of θ_0 and γ have been used to recalculate the constants in the equation for the electronic specific heat C_{es} given by the Bardeen, Cooper, and Schrieffer theory[12]:

$$C_{es}/\gamma T_c=a\exp(-bT_c/T).\qquad(7)$$

As shown by Bardeen and Schrieffer,[13] this equation is approximately valid in the region $2.5\leq T_c\leq6$ with $a=8.5$ and $b=1.44$. We obtain for these two constants the values $a=10.03$ and $b=1.528$.

V. CONCLUSIONS

The elastic constants of tin have been measured in the temperature range of 4.2 to 300°K. Although the room temperature results differ in part from those of Bridgman, and Mason and Bömmel, it is felt that the present data are more reliable, since adequate cross-checks were made. The shear constant $\frac{1}{2}(c_{11}-c_{12})$ shows an unusually large variation with temperature, which is presumably associated with the presence of small pockets of electrons and holes in the Fermi surface of tin. The elastic constants extrapolated to 0°K have been used to compute θ_0, the limiting value of the Debye temperature of tin. Using this value of θ_0, the low-temperature specific heat data of tin in the normal state have been reanalyzed to obtain a more reliable estimate of γ, the coefficient in the electronic term. The specific heat data in the superconducting state have also been re-evaluated to obtain new estimates of a and b in the equation $C_{es}=a\gamma T_c\exp(-bT_c/T)$.

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[9] W. S. Corak and C. B. Satterthwaite, Phys. Rev. **102**, 662 (1956).

[10] T. H. K. Barron and J. A. Morrison, Can. J. Phys. **35**, 799 (1957).

[11] *Note added in proof.* Recent measurements of the specific heat of tin below 0.5°K by N. V. Zavaritskii, *Progress in Cryogenics*, edited by K. Mendelssohn (Heywood & Co., Ltd., London, 1959), Vol. I, p. 217, give $\theta_0=202\pm3^\circ$K in good agreement with the value obtained in the present work.

[12] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

[13] J. Bardeen and J. R. Schrieffer (to be published).

ACKNOWLEDGMENT

The help of P. A. Flinn in programming the computation of θ_0 is gratefully acknowledged.

APPENDIX

The equation giving the velocity of propagation of plane waves in an aeolotropic solid medium is

$$|\lambda_{ij}-\rho v^2\delta_{ij}|=0, \tag{A1}$$

where

$$\lambda_{ij}=c_{ik,jl}\alpha_k\alpha_l. \tag{A2}$$

In Eq. (A2) $c_{ik,jl}$ is the elasticity tensor, and the α_i are the direction cosines of the propagation vector. Consider now a tetragonal crystal, and choose the 1 and 2 axes along the a axes, and the 3 axis along the c axis. Then the λ_{ij} are given in terms of the usual elastic constants by

$$\begin{aligned}
\lambda_{11}&=c_{11}\alpha_1^2+c_{66}\alpha_2^2+c_{44}\alpha_3^2,\\
\lambda_{22}&=c_{66}\alpha_1^2+c_{11}\alpha_2^2+c_{44}\alpha_3^2,\\
\lambda_{33}&=c_{44}(\alpha_1^2+\alpha_2^2)+c_{33}\alpha_3^2,\\
\lambda_{12}&=(c_{12}+c_{66})\alpha_1\alpha_2,\\
\lambda_{23}&=(c_{13}+c_{44})\alpha_2\alpha_3,\\
\lambda_{31}&=(c_{13}+c_{44})\alpha_3\alpha_1,
\end{aligned} \tag{A3}$$

and all the other λ_{ij} vanish.

As shown by Waterman,[14] the only propagation directions giving pure longitudinal as well as pure transverse modes are [100], [110], and [001]. For a propagation direction making an angle of $\pi/4$ with the [010] and [001] directions, Eqs. (A1) and (A3) lead to the determinantal equation

$$\begin{vmatrix}
\frac{1}{2}(c_{44}+c_{66})-\rho v^2 & 0 & 0\\
0 & \frac{1}{2}(c_{11}+c_{44})-\rho v^2 & \frac{1}{2}(c_{13}+c_{44})\\
0 & \frac{1}{2}(c_{13}+c_{44}) & \frac{1}{2}(c_{33}+c_{44})-\rho v^2
\end{vmatrix}=0. \tag{A4}$$

From this equation, it is clear that there is a pure shear mode polarized in the [100] direction, with a velocity corresponding to $\rho v^2=\frac{1}{2}(c_{44}+c_{66})$. The other two waves are quasi-longitudinal and quasi-shear modes with velocities given by the equation

$$\begin{vmatrix}
\frac{1}{2}(c_{11}+c_{44})-\rho v^2 & \frac{1}{2}(c_{13}+c_{44})\\
\frac{1}{2}(c_{13}+c_{44}) & \frac{1}{2}(c_{33}+c_{44})-\rho v^2
\end{vmatrix}=0. \tag{A5}$$

This equation can be solved approximately to give

$$\begin{aligned}
c_L&=\rho v_L^2=\frac{c_{11}+c_{33}}{4}+\frac{c_{13}}{2}+c_{44}-\epsilon,\\
c_T&=\rho v_T^2=\frac{c_{11}+c_{33}}{4}-\frac{c_{13}}{2}+\epsilon,
\end{aligned} \tag{A6}$$

where v_L and v_T are the velocities of the quasi-longitudinal and quasi-transverse modes, and ϵ is a small correction term

$$\epsilon=(c_{11}-c_{33})^2/16(c_{13}+c_{44}).$$

It can readily be shown that the particle motion for the quasi-longitudinal and quasi-transverse modes makes angles β and $\pi/2+\beta$, respectively, with the propagation direction, where

$$\beta=\pi/4-\tfrac{1}{2}\tan^{-1}[(c_{13}+c_{44})/(c_{11}-c_{33})].$$

In the present case $\beta\simeq 4°$, so that these two modes are in fact almost pure.

The elastic constants corresponding to the various propagation modes used in the present work are shown in Fig. 1. Except for c_{13}, the calculation of the elastic constants from the measured values of ρv^2 is straightforward. The constant c_{13} was computed from each of the two Eq. (A6), and also from their difference. The last value has the least uncertainty, and is taken as the best estimate of c_{13}. The constant ϵ is obtained iteratively.

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[14] P. C. Waterman, Phys. Rev. **113**, 1240 (1959).