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Elastic Constants of Indium from 1.4° to 300°K

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The adiabatic elastic constants of indium have been measured in the temperature range 1.4° to 300°K, using the ultrasonic pulse technique. At 1.4°K no difference between the elastic constants in the superconducting and normal states is observed to within the available accuracy of about 1 part in 10^4. The bearing of this observation on the recent calorimetric data for indium below 1°K is discussed. From the elastic constant data extrapolated to 0°K, the limiting value of the Debye temperature for indium is calculated to be 111.3°K, with an estimated uncertainty of 1%. An extremely large variation with temperature of the shear constant $(c_{11}-c_{12})/2$ is observed.

I. INTRODUCTION

THE single-crystal elastic constants of indium at room temperature have been measured by Winder and Smith[1] using the ultrasonic pulse technique. Heretofore, however, there existed no study of the temperature dependence of the elastic constants. A precise knowledge of this dependence is of interest in the theory of solids. In particular, the values of the elastic constants (extrapolated to 0°K) can be used to compute the limiting value of the Debye temperature[2] and thence the lattice heat capacity at low temperatures. This is of particular interest in the case of indium, since recent calorimetric measurements by Bryant and Keesom[3] have shown that, at any temperature below 0.5°K, the apparent lattice heat capacity in the superconducting state is significantly lower than that in the normal state. Such a difference might imply a corresponding change in the elastic constants of indium in going from the normal to the superconducting state.

This paper describes the measurement of the elastic constants of indium between 1.4° and 300°K. From the values in the normal state extrapolated to 0°K, the limiting value of the Debye temperature has been computed and found to agree with that obtained from the normal-state calorimetric data. No change is observed in the elastic constants at 1.4°K, on going from the normal to the superconducting state, greater than 1 part in 6×10^3. It is concluded, therefore, that there is no significant difference between the lattice heat capacities, due to thermal excitation of phonons, of the normal and superconducting phases of indium. A possible resolution of the apparent conflict between this result and the calorimetric data is discussed.

An unusually strong dependence of certain shear constants on temperature is observed. This behavior is in contrast to that of aluminum, which differs from indium only in its axial ratio. It is suggested that overlap electrons (and possibly holes) across certain faces of the Brillouin zone for indium are responsible for this strong temperature dependence.

II. EXPERIMENTAL DETAILS

The starting material was indium obtained from the Indium Corporation of America. The only impurities as revealed by spectrophotometric analysis were 0.0004% iron and 0.002% nickel. Cylindrical single crystals 2.5 cm in diameter and 10 cm in length were grown by a modified Bridgman technique in a tapered graphite crucible. Although indium has a very small coefficient of thermal expansion, possibly even negative, along the c axis, no difficulty was experienced in producing distortion-free single crystals. The crystals were oriented by the back-reflection Laue method, and suitably oriented specimens cut using an electric spark technique.[4] The cut surfaces of the resulting samples were free from damage, and only light lapping was necessary to produce opposite faces which were flat and parallel to within 0.0005 cm.

To enable adequate cross checks on the elastic constants to be made, four crystals in all were used. The approximate propagation and polarization directions, together with the corresponding velocities in terms of the elastic constants, are shown in Table I. Each of the actual directions is within one degree of that indicated, so that the misorientation correction to the transit time is negligible. It should be noted that the expressions for the quasi-longitudinal and

TABLE I. The approximate propagation and polarization directions, together with the corresponding ρv^2 in terms of the elastic constants, where ρ = density, and v = velocity.

Crystal	Propagation direction	Polarization direction	ρv^2
a	[100]	[100]	c_{11}
		[010]	c_{66}
		[001]	c_{44}
b	[001]	[001]	c_{33}
		Transverse	c_{44}
c	[110]	Longitudinal	$C_L'=(c_{11}+c_{12}+2c_{66})/2$
		Transverse [1$\bar{1}$0]	$C'=(c_{11}-c_{12})/2$
d	In (100) plane, at an angle of $\theta=51.5°$ to [001] axis.	Longitudinal	$C_L''=(c_{11}+c_{33}+2c_{13}+4c_{44})/4$
		Transverse [100]	$c_{44}\cos^2\theta+c_{66}\sin^2\theta$
		Transverse [011]	$C''=(c_{11}+c_{33}-2c_{13})/4$

[1] D. R. Winder and Charles S. Smith, J. Phys. Chem. Solids 4, 128 (1958).
[2] For a review, see G. A. Alers and J. R. Neighbours, Revs. Modern Phys. 31, 675 (1959).
[3] C. A. Bryant and P. H. Keesom, Phys. Rev. Letters 4, 460 (1960).
[4] B. S. Chandrasekhar, Rev. Sci. Instr. 32, 368 (1961).

TABLE II. Experimental results at 300°, 77°, and 4.2°K in terms of ρv^2, in units of 10^{11} dyne cm^{-2}.

Crystal	ρv^2	Temperature 300°K	77°K	4.2°K
a	c_{11}	4.535	5.260	5.392
	c_{66}	1.210	1.607	1.684
	c_{44}	0.646	0.757	0.794
b	c_{33}	4.515	5.080	5.162
	c_{44}	0.655	0.770	0.800
c	$(c_{11}+c_{12}+2c_{66})/2$	5.458	6.120	6.278
	$(c_{11}-c_{12})/2$	0.258	0.556	0.748
d	$(c_{11}+c_{33}+2c_{13}+4c_{44})/4$	4.982	5.462	5.545
	$(c_{11}+c_{33}-2c_{13})/4$	0.185	0.313	0.333
	$c_{44}\cos^2\theta+c_{66}\sin^2\theta$	0.989	1.272	1.340

quasi-transverse modes in crystal *d* are only approximate; the error, however, is readily shown to be less than the experimental uncertainty in each case.

The ultrasonic measurements were made in the temperature range from 1.4° to 300°K using an Arenberg pulsed oscillator and wide-band amplifier in conjunction with a Tektronix 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.[5] Glycerol was found to give satisfactory bonds for all propagation modes below room temperature. Salol was used to obtain the room temperature values of the constants.

To detect any possible change in the elastic constants in going from the superconducting to the normal state, the sample was maintained at 1.4°K in zero magnetic field and a distant echo was observed on an expanded delayed sweep. A quenching field of about 800 gauss, which is more than twice the critical field at this temperature, was then applied. This field was produced by a solenoid immersed in the liquid nitrogen surrounding the helium Dewar. Any resulting change in the transit time could then be measured to an accuracy of 1 in 2×10^4, corresponding to a change in the associated elastic constant of 1 part in 10^4.

It is necessary to know the lattice constants of indium as a function of temperature in order to obtain the elastic constants from the measured sound velocities. The data of Graham *et al.*[6] were used in the temperature range 90–300°K, the values at lower temperatures being obtained by extrapolation. At 300°K, the density of indium calculated from their data is 7.2788 g cm^{-3}. The extrapolated density at 0°K is 7.4713 g cm^{-3}.

TABLE III. Elastic constants of indium at 300°, 77°, and 4.2°K, showing cross checks in the present work. The units are 10^{11} dyne cm^{-2}.

Elastic constant	Sample	Value of the elastic constant 300°K	77°K	4.2°K
c_{11}	*a*	4.535	5.260	5.392±0.038
c_{33}	*b*	4.515	5.080	5.162±0.036
c_{44}	*a*	0.646	0.757	0.794
	b	0.655	0.770	0.800
	Mean	0.651	0.764	0.797±0.006
c_{66}	*a*	1.210	1.607	1.684
	d	1.203	1.593	1.683
	Mean	1.207	1.600	1.684±0.012
c_{12}	*c*(from $C_L'-C'$)	3.993	3.964	3.846
	c(from C')	4.019	4.148	3.896
	Mean	4.006	4.056	3.871±0.038
c_{13}	*d*(from $C_L''-C''$)	4.146	4.385	4.415
	d(from C'')	4.155	4.529	4.611
	Mean	4.151	4.457	4.513±0.045

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

III. RESULTS

Table II gives the experimental results at 300°, 77°, and 4.2°K in terms of ρv^2, ρ being the density of indium and v the velocity calculated from the observed transit time after correcting for the thermal expansion. The total error, arising mainly from the uncertainty in transit time determination and the possible effect of dislocations on the elastic constants, in each case is estimated to be less than 0.7%. From the data of Table II, the elastic constants and their associated errors have been computed and are shown in Table III. The values obtained from 300°K in the present work are compared with those of Winder and Smith[1] in Table IV. There is satisfactory agreement between the two sets of results. It should be noted that in the present work at least two sets of independent values for the constants c_{44}, c_{66}, c_{12}, and c_{13} have been obtained, and these agree to within the estimated error. Figures 1(a) through 1(e) show the temperature dependence of each constant. As can be seen, the internal consistency of the data is considerably better than the quoted error.

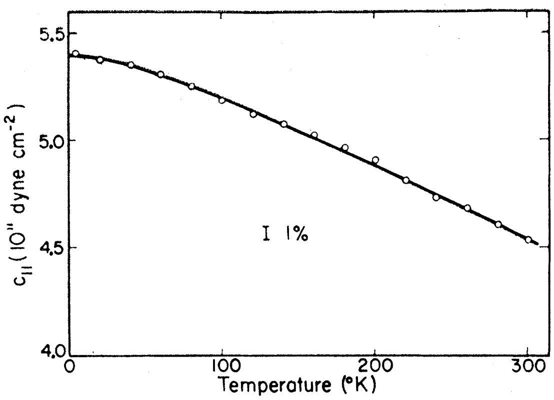
The measurements at 1.4°K showed no change greater than 1 part in 10^4 in any of the elastic constants on going from the superconducting to the normal state. While the sensitivity of the present measurements is insufficient to detect the much smaller changes in elastic constants predicted thermodynamically,[7] the

TABLE IV. A comparison of the values for the elastic constants of indium at 300°K obtained in the present work with the room temperature values of Winder and Smith recalculated using $\rho=7.28$ g cm^{-3}. The units are 10^{11} dyne cm^{-2}.

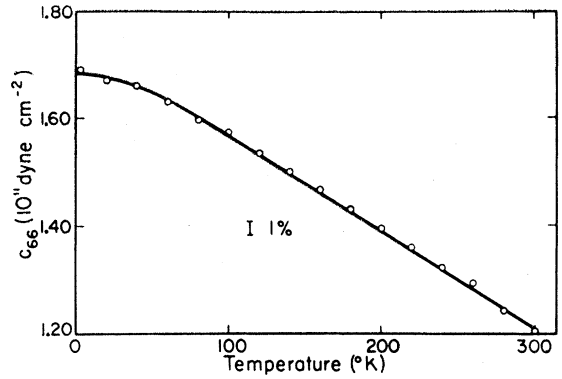
	c_{11}	c_{33}	c_{44}	c_{66}	c_{12}	c_{13}
Present work	4.535	4.515	0.651	1.207	4.006	4.151
Winder and Smith	4.44	4.43	0.653	1.22	3.94	4.04

[6] J. Graham, A. Moore, and G. V. Raynor, J. Inst. Metals **84**, 86 (1955).

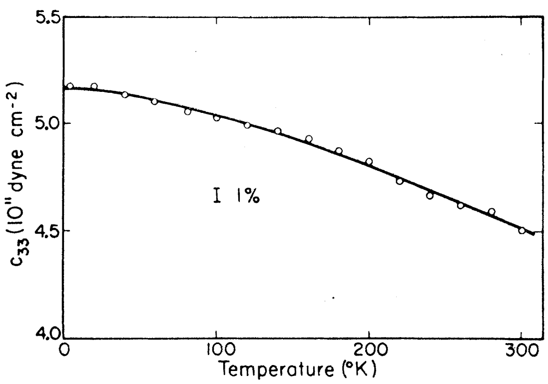
[7] D. Shoenberg, *Superconductivity* (Cambridge University Press, New York, 1952), p. 74.



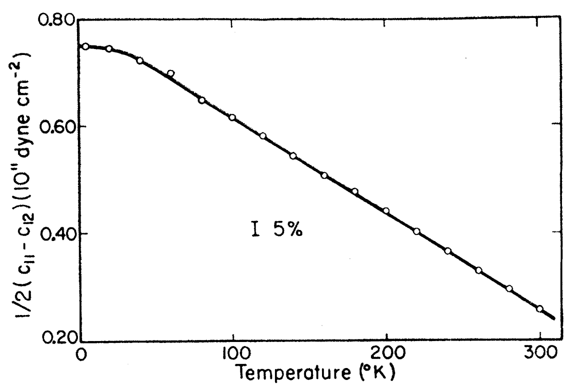
(a)



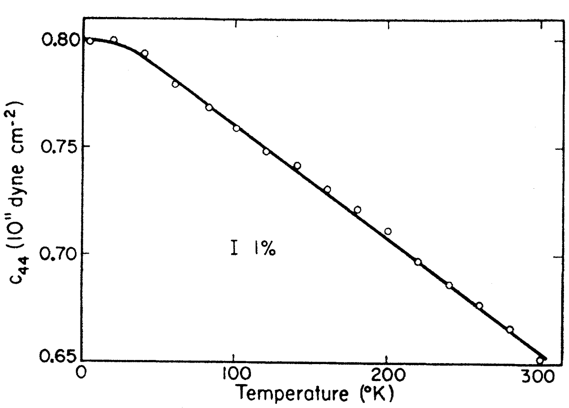
(d)



(b)



(e)



(c)

FIG. 1. (a)–(e) Temperature variation of elastic constants c_{11}, c_{33}, c_{44}, c_{66}, and $(c_{11}-c_{12})/2$, respectively, for indium.

absence of any change within the present limit of detectability is adequate for the discussion of the calorimetric data[3] given in Sec. IV.

IV. DISCUSSION

A. Temperature Dependence of the Elastic Constants

Figures 1(a) through 1(e) show that the temperature variation of all constants except $C'=(c_{11}-c_{12})/2$ is normal. The value C' increases by a factor of three between 300°K and 4.2°K, in contrast to an increase of 10% in the case of aluminum, which is also trivalent and has almost the same crystal structure. A similar singularly large temperature dependence was observed for the shear constant $C''=(c_{11}+c_{33}-2c_{13})/4$. It seems likely that this unusual behavior of indium is connected with the pockets of electrons in the third and possibly fourth Brillouin zones. A quantitative understanding

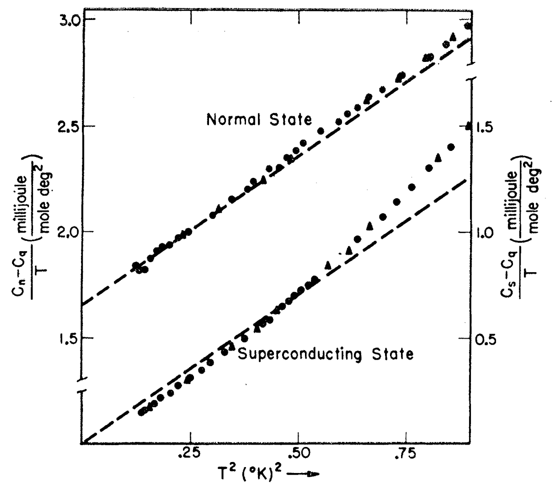


FIG. 2. Plot of $(C-C_q)/T$ versus T^2 for normal and superconducting indium. The dashed lines are calculated from the elastic data extrapolated to 0°K.

of these effects, however, must await a precise determination of the Fermi surface for indium.

B. The Limiting Value of the Debye Temperature for Normal and Superconducting Indium

Using the values of the elastic constants extrapolated to 0°K, the Debye temperature θ_0 for indium was computed numerically by the method described in a previous paper.[8] The value so obtained is

$$\theta_0 = 111.3°\text{K}, \quad (1)$$

with an estimated uncertainty of 1%.

At sufficiently low temperatures, the heat capacity of superconducting indium can be expressed as

$$C_s = \alpha T^3 + C_q, \quad (2)$$

where the first term on the right is the lattice heat capacity and C_q is the nuclear quadrupole heat capacity. Thus a plot of $(C_s - C_q)/T$ versus T^2 should be a straight line through the origin. Such a plot obtained from the calorimetric data[3] is shown in Fig. 2, together with a straight line through the origin drawn to give a slope corresponding to the value of Debye temperature obtained above. A parallel straight line has been drawn through the normal-state points. It can be seen that this latter line gives a good fit to the data below about 0.7°K; the corresponding value of the coefficient of the electronic heat capacity is $\gamma = 1.65$ millijoule mole^{-1} deg^{-2}. This figure is slightly different from the value of 1.61 mjoule mole^{-1} deg^{-2} obtained by Bryant and Keesom[3]; the difference is presumably due to the difficulty of determining *a priori* the temperature range over which the lattice heat capacity can be represented by a term cubic in the temperature.

As can be seen from Fig. 2, the calorimetric data in the superconducting state for temperatures less than 0.5°K lie considerably below the computed line. The discrepancy is well outside the combined experimental uncertainty for the calorimetric and elastic data, and must therefore be significant. In the present experiments it has been established that the superconducting-to-normal transition does not affect the dispersion relation for phonons having an effective temperature up to 0.001°K (i.e., frequency of 10 Mc/sec). The measured specific heat, however, involves phonons of effective temperature of about 1°K. The dispersion relation for these phonons may be modified by their interaction with the electrons involving excitation of the latter across the energy gap.[9] However, since the energy is of the order of $3.5kT_c$, it is difficult to understand why the dispersion relation should be modified significantly for phonons of energy as low as $0.2kT_c$. An alternative suggestion[10] is that the normal-to-superconducting transition produces a slight change in the entire phonon spectrum leading to a temperature-dependent zero-point energy in the superconducting state. Such an effect would significantly influence the measured heat capacity in the superconducting state, but not the elastic constants.

V. CONCLUSION

The adiabatic elastic constants of indium have been measured in the temperature range 1.4° to 300°K, From the elastic-constant data extrapolated to 0°K the limiting value of the Debye temperature for indium has been calculated to be 111.3°K with an estimated uncertainty of 1%. At 1.4°K no detectable difference between the elastic constants in the superconducting and normal states was observed. The bearing of this result on the recent calorimetric data on indium, which showed that the lattice heat capacity in the superconducting state is less than that in the normal state, is discussed.

ACKNOWLEDGMENTS

Helpful discussions with C. A. Bryant, T. D. Holstein, A. A. Maradudin, and J. L. Olsen are gratefully acknowledged.

[8] J. A. Rayne and B. S. Chandrasekhar, Phys. Rev. **120**, 1658 (1960). The summed terms in Eqs. (1) and (2) of this paper should be transferred to the denominators of the right-hand side.

[9] *Note added in proof*. Such an effect has been recently predicted; see Richard A. Ferrell, Phys. Rev. Letters **6**, 541 (1961).

[10] J. G. Daunt and J. L. Olsen, Phys. Rev. Letters **6**, 267 (1961).