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SOLID STATE PHYSICS PROGRAM

PRESSURE VARIATION OF THE ELASTIC CONSTANTS OF f.c.c. INDIUM-THALLIUM ALLOYS

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ABSTRACT

The pressure variation of the adiabatic elastic constants of four f.c.c. indium-thallium alloys has been measured at 300°K using the ultrasonic pulse echo technique. The principal result is that the pressure derivative of the elastic constant C' is negative and the derivative increases rapidly as thallium concentration is lowered toward the boundary that marks the transformation to the f.c.t. phase. It has been confirmed that this shear constant vanishes in the vicinity of the phase boundary as previously reported by Novotny and J. F. Smith. An immediate consequence of the pressure study is that the phase boundary should move to higher thallium concentration as pressure is increased as anticipated by Novotny and J. F. Smith. Another consequence is that the temperature coefficient at constant volume of the constant C' is negative and extremely large. It can also be predicted that the very low temperature thermal expansion coefficient of f.c.c. alloys near the phase boundary should be negative, but this feature is probably not experimentally observable.

INTRODUCTION

The indium-thallium phase diagram contains an intermediate phase which is f.c.c. The transformation from the terminal f.c.t. phase on the indium side to the cubic phase has been studied by a number of investigators(1,2). The transformation is martensitic and appears to occur as a consequence of a pair of {110} $<\bar{1}10>$ shears. Such a deformation is associated with the elastic shear constant $C' = (C_{11} - C_{12})/2$.

The single crystal elastic constants of the f.c.c. phase have been studied in detail as functions of temperature and composition by Novotny and Smith. For the four compositions studied, the shear stiffness C' is extraordinarily small. This constant also appears to vanish at the f.c.c.-f.c.t. phase boundary and the existence of the phase boundary has been attributed by Novotny and Smith to the consequent absolute thermodynamic instability of the f.c.c. phase.

Further study of this pathological shear constant is clearly of interest and at the suggestion of Professor J. F. Smith of Iowa State University, we have undertaken the measurement of the effect of pressure on the elastic constants of these alloys. Considerable phenomenological insight can be obtained from such a study under pressure and in addition it was hoped that some microscopic insight could be obtained from an analysis of existing microscopic models for the elastic constant.

EXPERIMENTAL PROCEDURE

Sample Preparation and Material Data

The alloy samples used in this program were kindly supplied by Professor J. F. Smith of Iowa State University. They had been previously used in the investigation of the temperature dependence of the elastic constants by Novotny and Smith(3); the same paper describes the methods of growth and preparation. Four alloy compositions were used, 27.1, 30.16, 35.15, and 39.06 at.% thallium, the last three determined chemically at Iowa State and the first one as described below. Two crystals were supplied in each composition, one with two faces cut and lapped perpendicular to a [100] direction and the other with two faces cut and lapped perpendicular to a [110] direction. Prior to use the flat faces were given a light polish on a cloth wet with a 1:20 HNO_3-water solution. Orientations were determined by the X-ray back reflection Laue technique.

Precision lattice constants for these materials have already been determined(4) and were used here to calculate densities. Lattice constant and density are both linear functions of composition. Densities were checked by hydrostatic weighing and found to be within 0.1% of the X-ray values except for the lowest composition alloy which was about 1% low when the composition of 28.13 at.% of Novotny and Smith was used. Subsequently the elastic data for this specimen also appeared to be out of line with the others. A composition change to 27.1 at.% thallium rectifies both the density and the elastic data and has been adopted. Professor J. F. Smith informs us that there is indeed the possibility of a mix-up of several specimens of the lowest composition, and that re-analysis of the particular specimen sent to us confirms that the composition is definitely lower than 28.13 at.% thallium. Limited specimen size now available for analysis unfortunately sets the chemical precision lower than the precision of the composition determined indirectly by hydrostatic weighing; we have therefore adopted the latter.

Acoustic transducers were 10 MHz X- and Y-cut quartz crystals which were bonded to the metal crystals with phenyl salicylate. Electrical contacts were provided by the metal crystal and a thin layer of conductive silver paint on the open transducer face.

Elastic Constant Measurements

Although the elastic constants of these specimens had previously been determined by Novotny and Smith they were redetermined in this laboratory in order to be entirely consistent with the subsequent pressure measurements, in the reduction of which they are explicitly required. There were minor variations from Novotny and Smith in data analysis that improved the smoothness of the composition plots.

The technique for determination of elastic constants by the ultrasonic pulse-echo method is presented in detail in many articles(5,6). Generally the problem is to determine the velocity of an acoustic wave in the crystal. This is done by injecting a 10 cycle pulse of 10 MHz waves with the quartz transducer and observing the time between successive echoes. Three independent cubic elastic constants can be determined from a single crystal with faces perpendicular to a [110] direction and a [100] crystal provides two, as shown in Table I. The [110] crystals were quite short because of the very slow C' wave which also has high attenuation. For this reason, C_{11} and C from the [100] crystal and C' from the [110] have been reported in this work, with C'_{11} and C from the [110] crystal used only as checks on internal consistency.

Velocities were calculated from the lengths of the crystals and the time between echoes. Except for the C' wave, all crystal acoustic impedances were only slightly smaller than that for the quartz transducer. The reflection coefficient at the crystal-transducer interface was around 10%. The effect of this on the appearances of the echoes

Table 1.

Crystal Orientation	Mode	Polarization	Stiffness
[100]	Longitudinal	Parallel to [100] direction	C_{11}
[100]	Transverse	Perpendicular to [100] direction	$C_{44} = C$
[110]	Longitudinal	Parallel to [110] direction	$\frac{1}{2}(C_{11}+C_{12}+2C_{44}) = C'_{11}$
[110]	Transverse	Perpendicular to [001] direction	$\frac{1}{2}(C_{11}-C_{12}) = C'$
[110]	Transverse	Parallel to [001] direction	$C_{44} = C$

is clearly described in a paper by Eros and Reitz(7). It is mentioned here because the echo time observed was in fact the time for the pulse to traverse the crystal and transducer twice because of the very low reflection coefficient. A correction for the transit time for the quartz transducer was required in order to determine the velocity in the crystal. This circumstance must also be recalled in the measurement of velocity variation with pressure, where another correction is required. In the case of C' waves, the reflection coefficient at the transducer interface was around 80% and no correction was required.

Stiffnesses are calculated from the velocities by the relation $C = \rho V^2$. Internal consistency was checked by calculating C'_{11} from C_{11}, C' and C, then comparing with the directly measured value. The stiffnesses C obtained from each crystal were also compared. The maximum deviation encountered in these comparisons was 0.2%.

Pressure Measurements

The purpose of this part of the work was to determine the change in elastic constants with pressure and hence with crystal volume. The crystal and transducer were placed in a steel bomb into which oil was pumped to the required pressures. The system is conventional and is described in another paper(6). Pressure was measured by a standard 300 ohm manganin resistance element in the oil. Resistance of the element is linearly related to pressure over the range covered, as described by Bridgman(8). For this gage, resistance changed by 0.7795 ohms per kilobar, as determined from the freezing pressure of mercury at 0°C. Resistance was measured by a Wheatstone bridge system with a sensitivity of about 0.002 ohms. Thermal e.m.f.'s were compensated by zeroing the bridge null detector with bridge excitation removed. Self heating of the element produced an undetectable effect as determined by measuring the gage resistance with one half and double the normal power dissipated in the gage. Sample temperature was measured with a copper-constantan thermocouple in contact with the crystal. During any one pressure run, data was taken only when the crystal temperature was within 1/4C° of the initial value. To reduce acoustic interference from the sample holder and surrounding bomb, electrical contacts were made to the sample with large area wire wool pads.

Variation of acoustic velocity with pressure is found from variation in arrival time of the acoustic echo. The details of the system and measurement are set out in an article from this laboratory(6). The only complication was the fact that the transit time included that for the pulse to traverse the transducer for all waves except C' in these alloys. Thus, the change in transit time for the pulse with pressure is the sum of the changes in the crystal and the transducer. Since the pressure derivatives of the quartz stiffnesses are known, this is a straightforward correction. In this case it is also small.

The pressure range used was 3 kilobars. This was sufficient to produce effects which were large compared to measurement uncertainty and was kept low to avoid possible phase transitions. Over this range, transit time of the echo was linear with pressure.

Internal consistency was determined by comparing dC_{11}/dP + dC/dP - dC'/dP with the directly measured dC'_{11}/dP, as well as comparing dC/dP from the two crystals. The maximum deviation encountered was 2.8%.

RESULTS

Reduction of the experimental data requires the use of independently determined material parameters. Table 2 contains data on the alloys. Lattice constants are from Meyerhoff and Smith(4), and from these the X-ray density has been computed. Specific heat and thermal expansion have not been measured on these materials at the time of writing, so values were taken by interpolation between pure indium and thallium(9,10,11). In both properties, indium and thallium differ by less than 0.5% and so the error introduced by interpolation will probably be small. In any case the specific heat and thermal expansion enter only in corrections.

The measured atmospheric pressure elastic stiffnesses were determined from the relation,

$$C_i = \rho v_i^2 = \rho \frac{4L^2}{t_i{}^2} \qquad (1)$$

where ρ is the crystal density, L the length of crystal, and t_i the crystal transit time. In the cases of low reflection coefficient at the crystal-transducer interface, the observed time was corrected for the transit time in the quartz.

Table 3 contains the results of these measurements, where C_{11}, C, and C' are from experiment, and B_s is calculated from the relation $B_s = C_{11} - 4C'/3$. These data are also displayed graphically with the stiffnesses shown as functions of composition in Fig. 1. As can be seen, C_{11} is essentially independent of composition, while the shear

Table 2. Basic data at 300°K used in reduction of acoustic measurements.

	Composition (at.% thallium)			
	27.1	30.16	35.15	39.06
Lattice constant (Å)	4.753	4.757	4.763	4.768
X-ray density (gm cm^{-3})	8.602	8.745	8.983	9.168
Specific heat C_p (cal deg^{-1} $mole^{-1}$)	6.48	6.48	6.47	6.46
Volume coefficient of thermal expansion β (10^{-6} deg^{-1})	92.0	92.0	92.0	92.0

Table 3. Adiabatic elastic stiffnesses.

	Composition (at.% thallium)			
	27.1	30.16	35.15	39.06
C_{11}	410.5	411.2	409.6	411.2
C	84.0	85.2	86.3	87.4
C'	2.37	3.84	6.11	7.69
B_s	407.3	406.1	401.5	400.9

Units are kilobars. Notation used is $C = C_{44}$, $C' = (C_{11} - C_{12})/2$, $B_s = C_{11} - 4C'/3$.

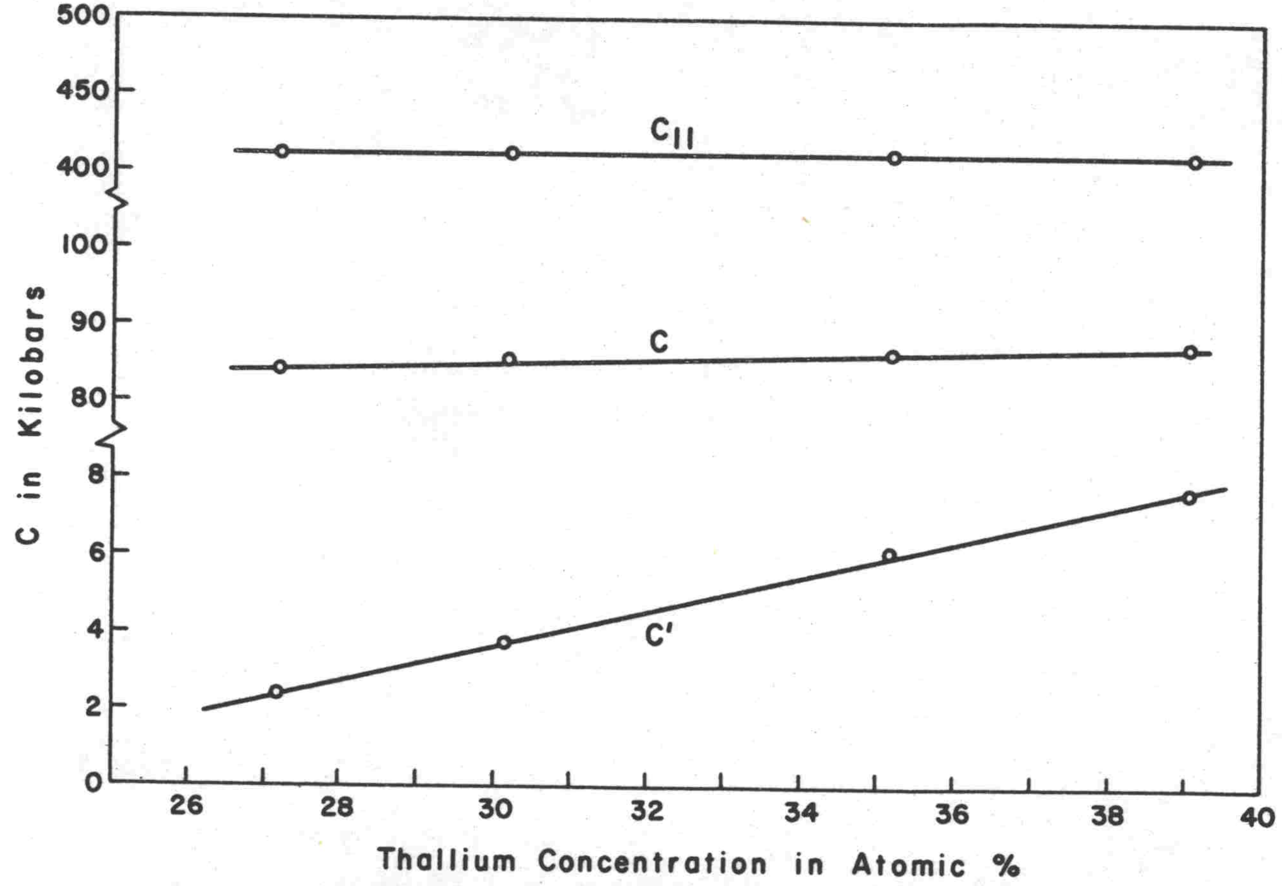

Fig. 1. The dependence of elastic stiffnesses for the indium-thallium alloys vs. alloy composition at room temperature and zero pressure. The ordinate has been broken twice to allow detail of the variation to be shown.

constants C and C' increase linearly with increasing thallium content, the former mildly and the latter drastically. The bulk modulus, B_s, also varies linearly and mildly with thallium concentration. The very low value of C' is particularly to be remarked. These data are all essentially in agreement with those of Smith and Novotny(3), especially in regard to C'. As pointed out in that paper(3), C' vanishes at the composition which marks the boundary between f.c.c. and f.c.t. indium-thallium alloys. In our measurements, C' extrapolates to zero in the range of 21.5 to 22 atomic % thallium, which compares favorably with the 21.3% found by Smith and Novotny.

The main purpose of this work was to determine the effect of pressure on the elastic constants. The standard experiment is to measure the change in arrival time, t, of an echo as a function of pressure. This is expressed as $d\ln t/dP \equiv t_o^{-1} dt/dP$ where t_o is the zero pressure arrival time, and dt/dP is to be evaluated at zero pressure. As already mentioned, observed dt/dP were corrected where necessary for the dt/dP of the transducer. Differentiation of Eq. (1) and evaluation at zero pressure yields the relation,

$$\frac{d\ln C}{dP} = \frac{1}{3B_T} - \frac{2 d\ln t}{dP}, \qquad (2)$$

where the first term on the right accounts for the pressure variation of dimensions and density. The isothermal bulk modulus B_T was computed from the adiabatic bulk modulus, B_s, using the relation $B_s/B_T = 1 + TV\beta^2 B_s/Cp$ and the data of Table 2. The pressure results can also be expressed in the useful form $d\ln C/d\ln r = -3B_T d\ln C/dP$, where r is a crystal distance, and in the dimensionless form $dC/dP = C\ d\ln C/dP$. All of these forms are exhibited in Table 4. The simplest statement to make regarding the precision of the numbers shown in that table is that the reproducibility of independent pressure runs was $\pm 0.05 \times 10^{-3}$ kbar^{-1} in $d\ln t/dP$, with corresponding uncertainty in the derived forms.

Inspection of Table 4 shows that the effect of pressure on the stiffnesses C_{11}, B_s and C is remarkably independent of composition. The magnitudes are also quite normal. A range of dB_s/dP of 4-6 has been found for almost all materials, metals and non-metals. Values

Table 4. Pressure data expressed in several forms.

Composition at.% thallium		dlnt/dP	dlnC/dP	dlnC/dlnr	dC/dP
27.1	C_{11}	-6.05	12.96	-15.24	5.32
27.1	C	-7.53	15.92	-18.62	1.34
27.1	C'	36.27	-71.69	+83.88	-0.170
27.1	B_s		13.62	-15.93	5.55
30.16	C_{11}	-5.99	12.84	-15.00	5.28
30.16	C	-7.58	16.03	-18.71	1.37
30.16	C'	15.86	-30.86	+36.03	-0.119
30.16	B_s		13.40	-15.64	5.44
35.15	C_{11}	-6.05	12.98	-15.00	5.31
35.15	C	-7.60	16.06	-18.56	1.39
35.15	C'	6.11	-11.36	+13.13	-0.069
35.15	B_s		13.47	-15.57	5.41
39.06	C_{11}	-6.16	13.19	-15.24	5.42
39.06	C	-7.60	15.98	-18.47	1.40
39.06	C'	1.94	-3.01	+ 3.48	-0.023
39.06	B_s		13.60	-15.72	5.45

The time, t, is the acoustic wave transit time in the crystal and r is a crystal distance. Units of dlnt/dP and dlnC/dP are 10^{-3} kbar^{-1}.

of dC/dP $\simeq$ 2 have been reported(12) for the shear constants of aluminum and magnesium, the (polyvalent) metals that one would expect to be similar to these indium-thallium alloys.

In marked contrast is the effect of pressure on the elastic shear constant C'. As Fig. 2 shows, the composition dependence is linear and high, just as was the composition dependence of the stiffness itself. In terms of dlnC'/dP or dlnC'/dlnr the pressure effect is huge for the alloys of lower thallium content. For this constant the sign of the pressure effect is also anomalous in the sense that a negative dC/dP is seldom encountered. Two examples of materials exhibiting anomalous pressure effects are cadmium sulfide(13) and several species of the sodium chloride structure (e.g. RbI(6)). In both of these cases there appears to be a connection, albeit indirect, with a pressure transformation to another structure. As Fig. 2 shows, C' decreases with pressure for all concentrations less than about 40% thallium, and the magnitude of the change increases as the f.c.c.-f.c.t. phase boundary is approached. The consequences of this behavior are described in the next section.

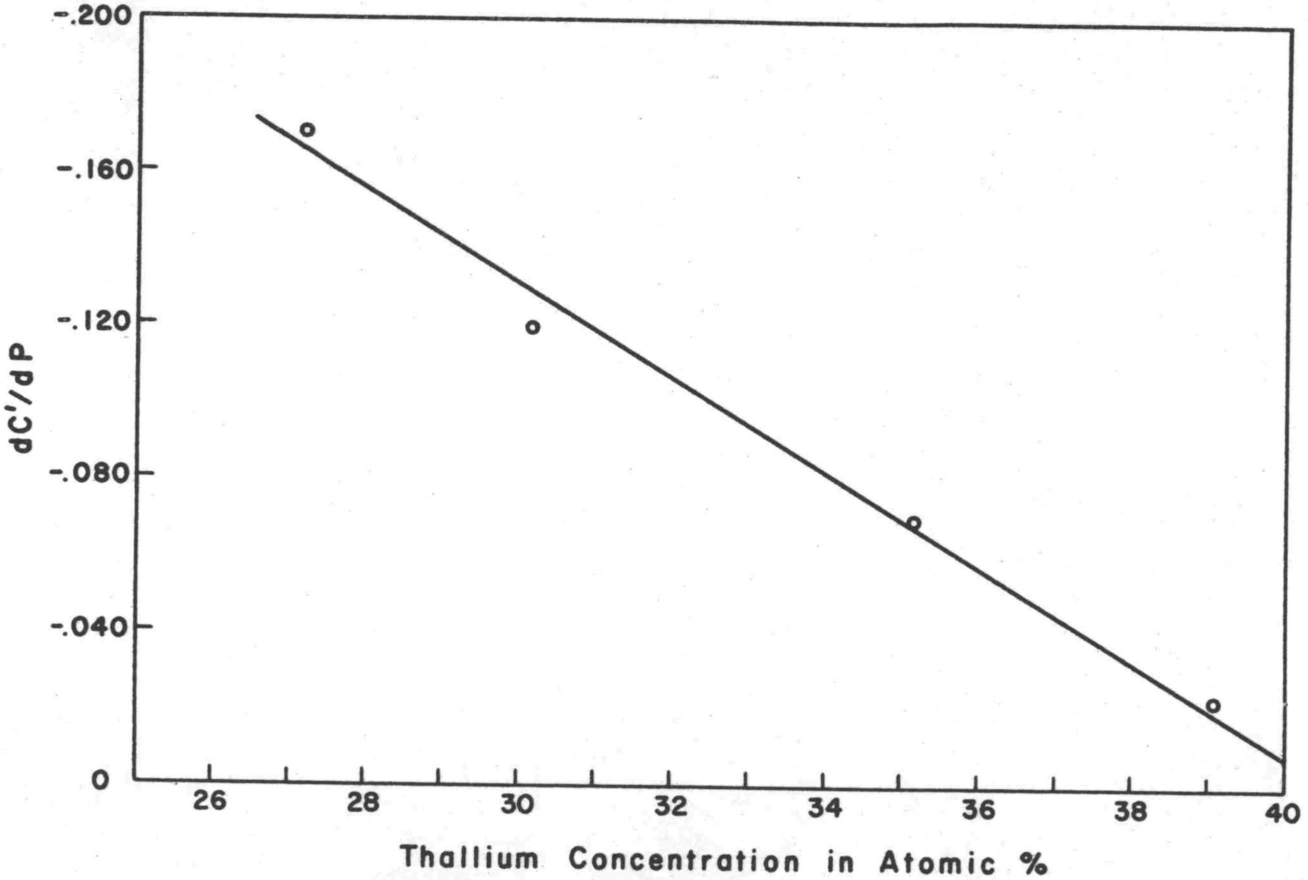

Fig. 2. The pressure derivative of the C' shear stiffness vs. alloy composition.

MACROSCOPIC APPLICATIONS

The elastic constants and their composition, temperature and pressure derivatives lead directly to three macroscopic applications. These are:

a. Determination of the motion of the f.c.c.-f.c.t. phase boundary with pressure.

b. Determination of the constant volume temperature coefficients of the elastic constants, $(d\ln C/dT)_V$, quantities of theoretical interest.

c. Values of the "elastic" Debye temperature and of the low and high temperature Gruneisen constants, leading to estimates of the coefficient of thermal expansion at temperatures low and high with respect to the Debye temperature.

The position of the f.c.c.-f.c.t. boundary in these alloys has been correlated with the vanishing of the C' shear stiffness leading to an absolute thermodynamic instability of the f.c.c. phase. Consequently, the behavior of C' with pressure and temperature determines the motion of the phase boundary with these variables. The temperature behavior has already been determined, showing that the boundary moves toward lower thallium concentration with increasing temperature. The analysis for pressure is straightforward. Let x_o be the concentration at which $C' = 0$ for zero pressure. Then if the pressure increases by a small amount, P, the change in concentration required to keep $C' = 0$ is Δx, and is given by

$$\Delta x = -P \frac{\left.\frac{\partial C'}{\partial p}\right)_{p=0,x=x_o}}{\left.\frac{\partial C'}{\partial x}\right)_{p=0,x=x_o}}$$

From Table 4, we see that ($\partial C'/\partial P$) is negative and from Fig. 1, ($\partial C'/\partial x$) is positive. Then for increasing pressure, the boundary moves to higher concentrations of thallium. Extrapolating ($\partial C'/\partial P$) to 21.7 at.% thallium ($C' = 0$) on Fig. 2 one obtains -0.216, and from Fig. 1 ($\partial C'/\partial x$) = 0.45 kbar/%. The shift of the phase boundary is then given by $\Delta x = 0.48P\%\ \mathrm{kbar}^{-1}$. For the 27.1 at.% thallium alloy at 300°K, the transition should occur at 11.3 kilobars, a readily available pressure.

The temperature dependence of the elastic stiffness at constant volume is obtained from an easily derived thermodynamic relation,

$$\left.\frac{d\ln C}{dT}\right)_P = \left.\frac{d\ln C}{dT}\right)_V - \beta B_T \left.\frac{d\ln C}{dP}\right)_T . \qquad (3)$$

The left hand side is the observed temperature coefficient and has been taken from Novotny and Smith(3). The second term on the right represents the portion of the total stiffness change owing to thermal expansion (not small), and the term $(d\ln C/dT)_V$ is called the intrinsic effect of temperature. Table 5 contains computed values of the intrinsic coefficient.

It is seen that for B_s this coefficient is positive even though the constant pressure coefficient is negative. This behavior has been observed for many metals and non-metals. The magnitude is normal, being of the order of, but larger than, the thermal expansion coefficient $\beta \sim (1 \times 10^{-4}\ \mathrm{deg}^{-1})$ as is found in most materials. For the shear stiffness C the constant volume coefficient is negative as is usual and of normal magnitude, except for the lowest thallium composition.

The shear constant C' as might be expected is anomalous, but in a peculiar way. The negative sign is that usually encountered but the magnitudes are very large compared with β and increase rapidly with thallium concentration. The constant volume coefficient extrapolates to zero in the general vicinity of the f.c.c.-f.c.t phase boundary at ∿21.5 at.% thallium. This behavior is in some contrast to the constant pressure coefficient(3) which goes through zero in the neighborhood of 30 at.% thallium, being positive at lower composition.

Table 5. Temperature coefficients of the elastic constants at constant volume and 300°K. Units are 10^{-4} deg^{-1}.

Composition at.% thallium	$\left.\frac{\partial \ln C'}{\partial T}\right)_V$	$\left.\frac{\partial \ln C}{\partial T}\right)_V$	$\left.\frac{\partial \ln C_{11}}{\partial T}\right)_V$	$\left.\frac{\partial \ln B_s}{\partial T}\right)_V$
27.1	- 7.6	+ 1.6	+ 3.3	+ 3.4
30.15	-13.8	- 2.4	+ 1.8	+ 2.0
35.15	-19.1	- 3.4	+ 2.1	+ 2.6
39.06	-28.6	- 3.8	+ 1.6	+ 2.4

The significance of these anomalies is not immediately apparent but it is clear that a theory of the temperature dependence of the elastic constants is better cast in terms of $(d\ln C/dT)_V$ which is free of large thermal expansion effects.

The anharmonic character of the crystal can be expressed by a single dimensionless parameter, the Gruneisen constant. This is found from thermodynamics and statistical mechanics with the assumption that the crystal can be viewed as an assembly of masses connected by slightly non-linear springs. As shown in standard texts, then the Gruneisen constant is related to experiment by,

$$\gamma = \beta B_T \frac{V}{C_V} , \qquad (4)$$

with

$$= \frac{\sum_i c_i \gamma_i}{\sum_i c_i} , \qquad (5)$$

and

$$\gamma_i = \frac{d\ln\omega_i}{d\ln V} . \qquad (6)$$

The sum is over the normal modes of the system and the c_i are the mode specific heats. The natural frequencies, ω_i, are assumed to be only volume dependent, not functions of temperature. This amounts to saying that any change in spring constant with temperature is cancelled by a change in spring length due to thermal expansion.

Two limiting versions of Eq. (5) can be considered with the available data, namely, when temperature is high or low compared to the Debye temperature. Schuele and Smith(14) describe the derivation of equations for γ_i and the sum for both temperatures. Essentially, three elastic constants and their pressure derivatives are found for 192 directions in the cubic unit triangle. The low temperature, denoted $\overline{\gamma}_L$, is then found by a numerical integration. Assuming the γ_i are constant over the entire dispersion curve, a high temperature approximation, $\overline{\gamma}_H$ is also found. The values of the elastic constants alone leads to an elastic Debye temperature. A computer program was developed by Schuele and Smith to perform these operations and was used in this work.

Fig. 3 shows the elastic stiffnesses ($C_i = \rho v_i^2$) as functions of direction around the boundary of the unit triangle for the alloy with lowest thallium content. C_1 is the lower shear stiffness, C_2 the higher shear stiffness, and C_3 the longitudinal stiffness. The data for the other alloys is quite similar. First, it is obvious that the alloys are highly anisotropic, even more so than indium itself. Aluminum, which is also trivalent, is almost isotropic so that a theoretical model which fits both these alloys and aluminum must be flexible indeed. As has been noticed for indium(15), the ratio of the longitudinal to average shear stiffness is also remarkably high, being the order of 7. Orindary b.c.c. and f.c.c. metals have values around 2 to 3.

Fig. 4 shows the mode gammas, γ_i, as a function of direction around the unit triangle for the lowest thallium content alloy. γ_1 is associated with the slow shear wave, γ_2 with the fast shear wave, and γ_3 with the longitudinal wave. The unusually large negative value for γ_1 in the [110] direction is associated with the large negative pressure derivative of C' as was the predicted motion with pressure of the f.c.c.-f.c.t. phase boundary. The data for the other alloys is similar; with the two minima in γ_1 becoming shallower, the smaller being about -1 in the highest thallium content alloy.

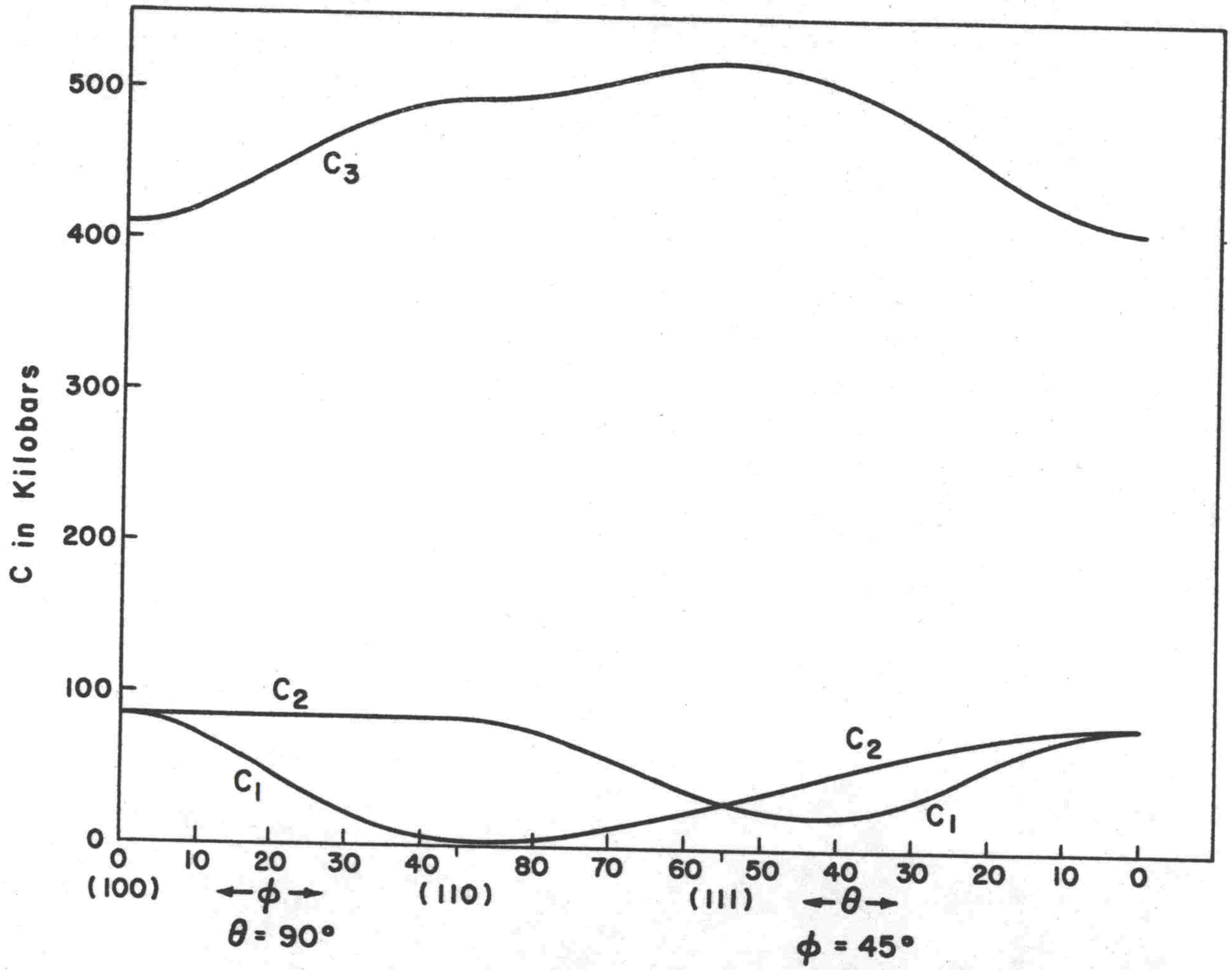

Fig. 3. Illustration of the elastic anisotropy of the 27.1 atomic % thallium alloy. Roots of the secular equation $C = \rho v^2$ are plotted as a function of direction around the periphery of the cubic unit triangle.

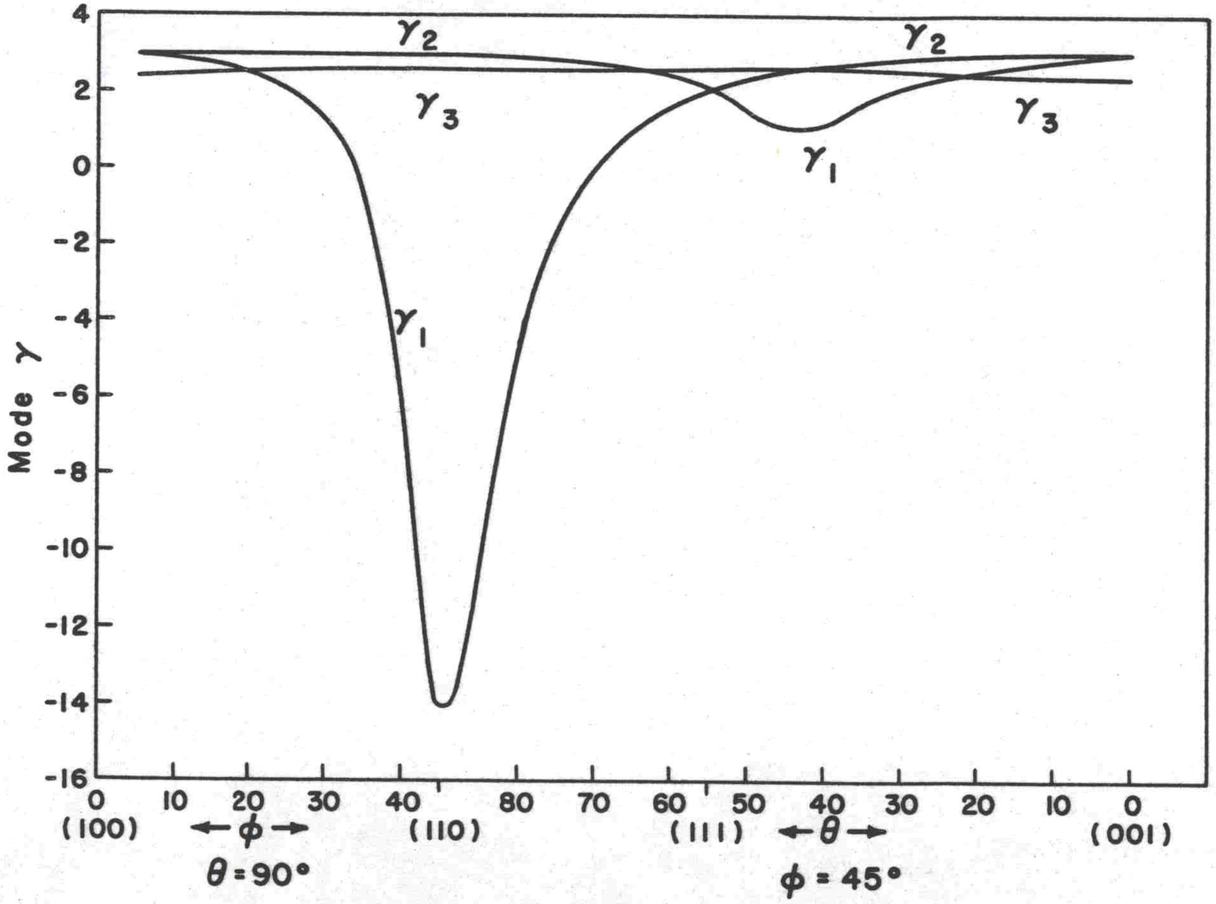

Fig. 4. Mode Gruneisen parameters for the 27.1 atomic % thallium alloy as a function of direction in the crystal. Values are shown for directions around the periphery of the cubic unit triangle.

The computer program calculates the integral

$$I = \sum_{i=1}^{3} {}_{\Omega} C_i^{-3/2} d\Omega$$

over the unit triangle. This leads to the elastic Debye temperature through the relation

$$\theta_D = \frac{h}{k}\left(\frac{3N}{4\pi V}\right)^{1/3} \rho^{-1/2} I^{-1/3}$$

Here h is Planck's constant, k is Boltzmann's constant, V/N is the atomic volume and ρ is density. Fig. 5 shows θ_D as a function of thallium concentration for the alloys along with the values for pure indium and thallium(16). The circles are the computed values and the solid curve is a parabolic fit with least deviation. The zero value at 21.7% thallium reflects the vanishing of C' at that point. At concentrations near that value, C' will still be small and dominate the sum. Since C' is linear in concentration, θ_D will vary about as the square root of concentration above 21.7%, hence the parabolic fit.

The computed values of $\overline{\gamma}_L$ and $\overline{\gamma}_H$ appear on Fig. 6 as functions of thallium concentration. Values of the thermal expansion gamma from Eq. (4) for pure indium and thallium are also shown. These were computed using AIP Handbook data for specific heat and thermal expansion coefficient, and Bridgman's data(17) for compressibility. The agreement of $\overline{\gamma}_H$ with these two numbers is excellent, as often happens with metals. Another point of view is that the agreement gives one confidence in the interpolated expansion coefficients of Table 2 since the specific heat will surely be nearly the Dulong and

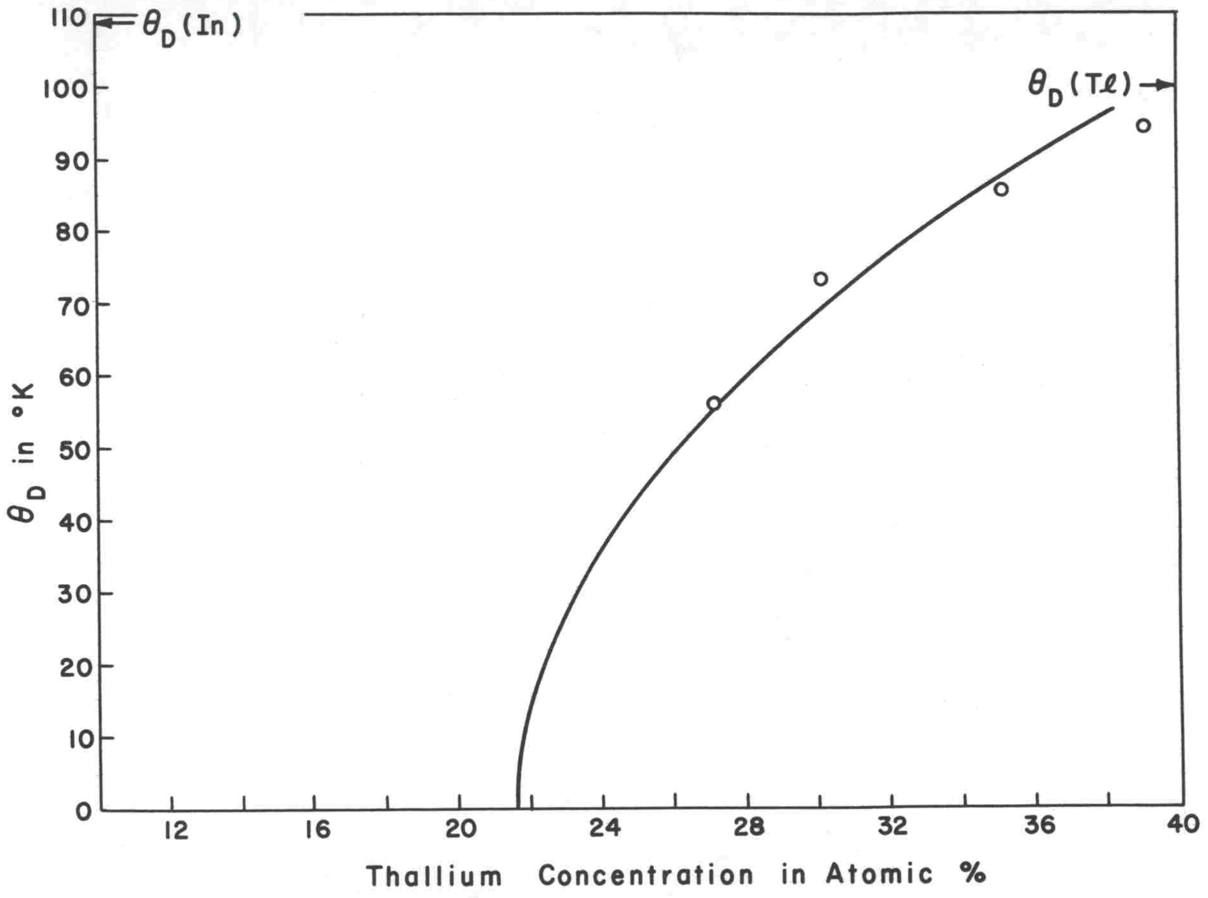

Fig. 5. Elastic Debye temperatures for indium-thallium alloys vs. alloy composition.

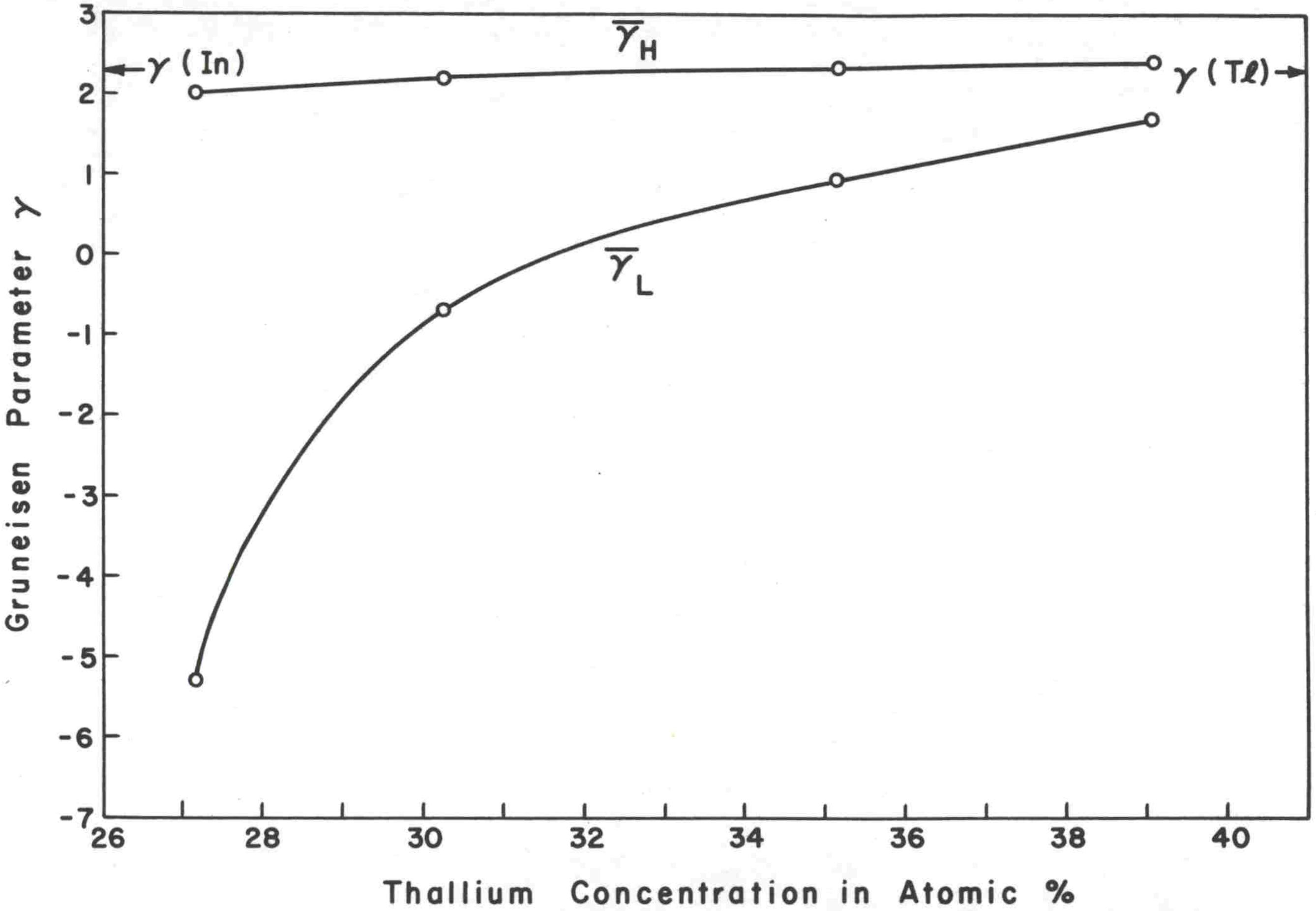

Fig. 6. Low and high temperature approximation to the Gruneisen parameter vs. alloy composition.

Petit value. The value of 2 to 2.5 is also common among metals.

$\overline{\gamma}_L$ is seen to fall from near $\overline{\gamma}_H$ at high thallium content to a large negative value for 27.1% thallium. Negative $\overline{\gamma}_L$ implies that the low temperature thermal expansion coefficient for this alloy should be negative. However, $\overline{\gamma}_L$ describes β only at temperatures of the order of $\theta_D/50$ which is 1-2°K, which makes experimental observation of the effect most difficult. Secondly, it is probable that this alloy will transform to the f.c.t. structure before that temperature is reached. Consequently, the negative $\overline{\gamma}_L$ may be interesting to contemplate, but experimentally uninteresting.

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