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Ultrasonic study of phonon mode softening and melting in indium-thallium alloys

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Measurements of ultrasonic wave velocities have been made between room temperature and the melting point in single crystals of indium, the fct 11.5-at.%-Tl and 15-at.%-Tl alloys and the fcc 27-at.%-Tl alloy. The object has been to test Ida's theory of melting on the basis of lattice instability and also suggestions that melting may take place by a phonon-mode-softening process. Contrary to the predictions of the both these hypotheses, it is found that for these materials longitudinal-acoustic modes stiffen somewhat near the melting point, while transverse modes exhibit no measurable premelting effects. The temperature dependence of the elastic stiffness tensor components of each material have been obtained. For the fct crystals the modulus $(C_{11}-C_{12})/2$ decreases as the temperature is raised: the [110], $\vec{q}\parallel[1\bar{1}0]$ acoustic-phonon mode in these fct crystals is softening in the vicintiy of the Brillouin zone center, a result which is consistent with an incipient martensitic transition, although the crystals melt before such a transition can occur. In the 15-at.%-Tl alloy, which at its melting point is very close to the fcc-fct phase boundary, $(C_{11}-C_{12})/2$ is very small: the [110], $\vec{q}\parallel[1\bar{1}0]$ mode is particularly soft. In all the fct crystals studied the modulus $(C_{11}-C_{12})/2$ tends to zero not at the melting point but at a higher temperature; this convergence above the melting point is also found in the elastic-constant pairs (C_{11} and C_{33}) and (C_{44} and C_{66}) (in a cubic crystal $C_{11}=C_{33}$ and $C_{44}=C_{66}$). It is concluded that acoustic-mode softening is not a prelude to melting in the way that it is to the martensitic transition in these indium-thallium alloys.

I. INTRODUCTION

A number of mechanisms have been proposed for melting. So far none has received general acceptance. Laws and mechanisms of wide scope and generality have yet to be framed. This aim in itself may not prove possible: melting processes may depend on the detailed structure of crystals or on the nature of the interatomic binding forces; if this is so, a diversity of laws and mechanisms must be expected.[1] One approach to the problem stems from the Lindemann[2] proposal that vibrational instability of solids leads to melting. The Lindemann relation

$$T_m = c_L m V^{2/3}\omega_E^2 \qquad (1)$$

(where V is the molar volume, m is the molecular weight, and C_L is a constant) between the vibrational melting point T_m and the characteristic Einstein frequency[3,4] ω_E (or in another formulation the Debye frequency ω_D) corresponds to the onset of melting when the mean square amplitude of atomic vibration about the equilibrium positions reaches a certain critical fraction of the atomic separation.[4] The disappearance of low-frequency shear modes in the liquid prompted Born[5] to suggest that melting ensues when a solid becomes unstable to a long-wavelength shear mode. The temperature dependence of $\frac{1}{2}(C_{11}-C_{12})$ in rocksalt ($B1$) structure halides supports[6] the hypothesis[7] that in these ionic crystals melting arises from instability of the [110] acoustic shear mode vibrating in the $[1\bar{1}0]$ direction. In CsCl ($B2$) structure halides it is softening of the [110], $\vec{q}\parallel[001]$ acoustic shear mode (which is manifested as a decrease in C_{44}) that is associated with approach towards the melting point.[8] Recently, Jackson and Liebermann[9] have used the temperature and pressure dependence of elastic moduli to calculate critical temperatures $(T_{cr})_{P=0}$ and their pressure derivatives $(\partial T_{cr}/\partial P)_{P=0}$ for the alkali halides and have employed their results in an assessment of the instability criteria for melting, namely, $C_{11}\rightarrow C_{12}$ for the $B1$ structure and $C_{44}\rightarrow 0$ for the $B2$ structure. They have verified that the critical parameters $(T_{cr})_{P=0}$ and $(\partial T_{cr}/\partial P)_{P=0}$ correlate well with the melting temperatures $(T_m)_{P=0}$ and the derivative $(\partial T_m/\partial P)_{P=0}$, respectively. Evidence is strong for the hypothesis that melting occurs when the alkali halides lose elastic resistance to shearing stress. From an application of molecular-dynamics techniques to a Lennard-Jones solid Dickey and Paskin[10] found that at high temperatures as the amplitude of the transverse [111] mode is increased, the frequency decreases. They proposed a model for fusion based on shear instability; when a fluctuation in the distance between atoms is large enough, planes of atoms slide past each other—the solid becomes unstable to shear and melts.

Ida[11] has also presented a lattice instability theory of melting. He proposes that on account of anharmonicity the energy of thermal vibrations cannot exceed a critical value and that the lattice becomes unstable at a corresponding critical temperature identified with the melting point. To include the effect of anharmonicity he introduces an effective elongation of the interatomic distance a; this "vibrational elongation" Q is the time average of the fractional increase of the interatomic distance. Ida's condition for melting is that the vibrational elongation cannot exceed a critical limit and he uses it to develop expressions for the critical temperature of instability in terms of atomic volume, elastic constants, and the Grüneisen parameter γ. His sound velocity V dependence upon temperature is

$$V = V_0 \exp\{-b[(a-a_0)/a_0 + Q]\} ,$$

where a_0 is the lattice spacing at $T=0$, $p=0$, $(a-a_0)/a_0$ is the thermal expansion and the parameter b is approximately 3γ. Thus the velocity of sound should decrease as the temperature rises and the rate of decrease should increase markedly as the melting point is neared. Ishizaki, Bolsaitis, and Spain[12] have reformulated the critical condition for melting in terms of the dependence of the elastic wave velocity v on the temperature and have shown that Ida's theory leads to the requirement that either

$$\left(\frac{\partial v}{\partial T}\right)_P \to -\infty \tag{2}$$

or

$$v \to 0 . \tag{3}$$

The second condition turns out to be the same as that given by Born[5] and thus to that pertaining to softening of an acoustic-phonon mode near the zone center. These conditions are tested directly here by measurement of the ultrasound wave velocities. There have been no previous measurements of sufficient accuracy and reliability of the ultrasound velocities in metals and alloys sufficiently near the melting point to provide an adequate examination of vibrational theories of melting in materials with metallic bonding. Here we present the results of measurements of ultrasound velocities between room temperature and the melting point in single crystals of indium-thallium alloys and indium. Particular emphasis has been placed on accurate determination of the temperature dependence of the ultrasound velocity, as it is this property which evidences acoustic-mode softening. Thus by determination of the ultrasound wave velocity dependence upon temperature near to T_m, we have been able to test the predictions of the vibrational theories of melting.

Indium and its disordered alloys with thallium are convenient sources of such data, for not only do they possess just one atom per unit cell—thus the problem is not obscured by the presence of optic-phonon modes—but also the property that a soft acoustic-mode phase transition[13–16] can occur at a temperature set by the composition. This fcc (high-temperature) to fct (low-temperature) martensitic transformation takes place in alloys containing between 15.5- and 31-at. % Tl, with the transition temperature T_c varying approximately linearly between 425 K (just below T_m) in the 15.5-at. %-Tl alloy and $\simeq 0$ K for the 31-at. %-Tl alloy.[17,18] A 22.5-at. %-Tl alloy transforms at room temperature. The existence region for solid and liquid-indium-rich thallium alloys is narrow and the solidus and liquidus are rather flat and therefore T_m is well defined and does not depend upon the rate of warming. As a consequence of the way in which, by adjustment of the alloy composition, soft-mode effects can be introduced at any temperature, we have been able to determine with some confidence the effects to be expected if mode softening were to occur near to the melting point. A comparison between the ultrasound velocities near T_m in alloys in which it is known that there are no mode-softening effects due to a martensitic transition and those in which there are such effects reveals the extent to which mode softening is responsible for melting. The compositions used in this investigation were as follows: (i) In–27-at. %-Tl. This alloy transforms at 127 K,[16] so that near to T_m there is no softening of the [110], $\vec{q} \parallel [1\bar{1}0]$ mode due to an incipient martensitic transition. (ii) In–15-at. %-Tl. This alloy does not transform: it is always fct but near T_m it is very close to the martensite-austenite phase boundary. Thus an approach towards the melting point necessarily involves a mode softening due to the nearing of T_c. (iii) In–11.5-at. %-Tl. This is another fct alloy right up to T_m. However, the mode softening due to the incipient martensitic transition will be less pronounced than that for the 15-at. %-Tl alloy. The results from the 15-at. %-Tl alloy are used to determine the effects of an extant soft mode on the measured ultrasound velocities near the melting point. We then look to alloys (i) and (iii) to see whether soft-mode characteristics are reflected in ultrasound-velocity measurements near T_m. Now the mode which softens at the fct-to-fcc phase transition is that polarized $[1\bar{1}0]$ for a wave vector along [110] and manifests itself in the tending to zero at T_c of the elastic modulus $\frac{1}{2}(C_{11}-C_{12})$.[13–16] Although $\frac{1}{2}(C_{11}-C_{12})$ is the elastic modulus of particular interest, in looking for a mode softening that could give rise to melting, we must also consider the possibility that other modes might soften either instead of or in addition. Consequently, it has been necessary to make ultrasound-velocity measurements of a number of modes as a function of temperature up to the melting point for indium and each alloy.

II. EXPERIMENTAL TECHNIQUES

Single crystals of 11.5 and 27 at. % indium-thallium alloys have been grown by the horizontal zone method starting from 99.999% pure indium and thallium.[16] Each as-grown boule was a crystal of size about $3.5\times1.6\times0.8$ cm^3. Back-reflection Laue photographs showed well-defined, unsplit spots, indicating little strain and no twinning. Of particular interest in this respect was the lack of twinning in the 15-at.%-Tl alloy crystals. Doubt has surrounded the form of the phase diagram in the region where the fcc-fct phase boundary meets the solidus; the diagram given in Hansen[18] shows a small temperature range over which the 15-at.%-Tl alloy is cubic, whereas that of Pollock and King[17] indicates that this alloy is always fct. The present work substantiates that of the latter workers. The lattice parameters at room temperature, obtained by the Nelson-Riley extrapolation on Debye-Scherrer powder photographs, were $a=4.67\pm0.02$ Å, $c=4.92\pm0.02$ Å, $c/a=1.05$ for the 11.5-at.%-Tl alloy and $a=4.72\pm0.02$ Å, $c=4.91\pm0.02$ Å, $c/a=1.04$ for the 15-at.%-Tl alloy.

The crystals were aligned by Laue back-reflection to within $\pm\frac{1}{2}°$ of the required crystallographic direction and cut by spark erosion. End faces on the ultrasonic specimens were spark planed to a parallelism better than 3×10^{-4} rad X- and Y-cut quartz transducers operated at their fundamental frequency (10 Mhz) were used to generate and receive the ultrasound; they were bonded to the alloy crystals with either a silicone oil of viscosity 6000 centistoke or Nonaq vacuum grease. Ultrasound wave transit times were measured by the pulse superposition method: the repetition rate of the rf pulses applied to the transducer is increased until the time between pulses has been reduced to a small multiple of the ultrasound double transit time. The pulse repetition frequency is set by a stable (1 in 10^8) frequency synthesizer, and since the coincidence of a received ultrasound pulse with the transmission of the next rf pulse can be determined to an accuracy of better than 1 part in 10^5, it is possible to determine changes in sound velocity with a similar precision. This is important as it is these velocity changes which can be used as evidence for or against mode softening. A detailed description of the errors involved in the system has been given elsewhere.[19,20] The data were taken with the sample immersed in a thermostatically controlled (± 0.1 °C) oil bath. To enable corrections to be made for changes in the sample length with temperature, the components α_{11} and α_{33} of the thermal expansion tensor of each fct sample were measured as a function of temperature by a strain-gauge method. Indium was found to become very soft at high temperatures, a problem which has caused us to reduce the emphasis on the element during the course of the work. Fortunately the alloys did not exhibit this drastic material softening; and the [110], $\vec{q}\parallel[1\bar{1}0]$ transverse acoustic mode is softer in the fct alloys than in indium at any temperature: for the present purposes the alloys are the more important materials to study.

III. EXPERIMENTAL RESULTS

Indium and its alloys with less than 15-at.%-Tl, having the point group $4/mmm$, belong to the $4/mmm$ Laue group and hence their elastic properties can be described by six independent elastic constants, while cubic crystals require only three. In Voigt notation the matrix forms are

$$\overset{\text{Cubic}}{\begin{pmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{pmatrix}} \quad \overset{\text{Tetragonal}}{\begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{pmatrix}} . \tag{4}$$

To determine the elastic constant set, it is necessary to measure the velocities of a sufficient number of modes; the solutions of the Christoffel equations

$$(L_{ik}-\rho v^2\delta_{ik})u_{0k}=0 \quad (i=1,2,3) \tag{5}$$

for the chosen propagation directions ([100], [110], [001], and [011]) are listed in Table I. All the constants except C_{13} can be determined from velocity measurements for waves propagated along the first three of these directions for which the modes are pure. C_{13} can be obtained by propagation in any direction for which the direction cosine n_3 and either n_1 or n_2 are not zero. There is an accidental pure mode direction, which depends upon the elastic constant values of the material in

TABLE I. Relations between elastic stiffness constants and ultrasound wave velocities together with the measured velocities at room temperature for the tetragonal crystals.

Propagation direction	Polarization direction	Relationships between velocities and elastic constants	15-at. %-Tl alloy, 290 °K Ultrasound velocity (10^5 cm sec^{-1})	15-at. %-Tl alloy, 290 °K ρv^2 (10^{11} dyn cm^{-2})	11-at. %-Tl alloy, 290 °K Ultrasound velocity (10^5 cm sec^{-1})	11-at. %-Tl alloy, 290 °K ρv^2 (10^{11} dyn cm^{-2})	Indium, 300 °K Ultrasound velocity (10^5 cm sec^{-1})	Indium, 300 °K ρv^2 (10^{11} dyn cm^{-2})
[100]	[100]	$\rho v_1^2 = C_{11}$	2.283	4.200	2.34	4.265	2.504	4.57
[100]	[010]	$\rho v_2^2 = C_{66}$	1.149	1.062	1.161	1.050	1.285	1.20
[100]	[001]	$\rho v_3^2 = C_{44}$	0.956	0.736	0.931	0.675	...	...
[001]	[001]	$\rho v_4^2 = C_{33}$	2.281	4.180	2.325	4.155	2.450	4.46
[001]	x-y plane	$\rho v_5^2 = C_{44}$	0.950	0.727	...	...	...	...
[110]	[110]	$\rho v_6^2 = \frac{1}{2}(C_{11} + C_{12} + C_{66})$	2.488	4.983	2.557	5.093	...	...
[110]	[1$\bar{1}$0]	$\rho v_7^2 = \frac{1}{2}(C_{11} - C_{12})$	0.39	0.122	0.48	0.18	0.577	2.424
[110]	[001]	$\rho v_8^2 = C_{44}$	0.948	0.723	0.935	0.681	0.946	0.65
[011]	[100]	$\rho v_9^2 = \frac{1}{2}(C_{44} + C_{66})$	1.046	0.881	0.94	0.688	...	...
[011]	ϕ[a]	$\rho v_{10}^2 = \frac{1}{2}[A + (A^2 - B + C^2)^{1/2}]$[b]	2.445	4.812	2.44	4.637	2.620	4.99
[011]	$\phi + \frac{1}{2}\pi$	$\rho v_{11}^2 = \frac{1}{2}[A - (A^2 - B + C^2)^{1/2}]$[b]	0.36	0.104	0.88	0.603	0.540	2.12

[a] ϕ is an angle which depends upon the values of the elastic constants and is measured from [001] in the (100) plane.

[b] $A = C_{44} + \frac{1}{2}(C_{11} + C_{33})$, $B = (C_{11} + C_{44})(C_{33} + C_{44})$, $C = C_{13} + C_{44}$.

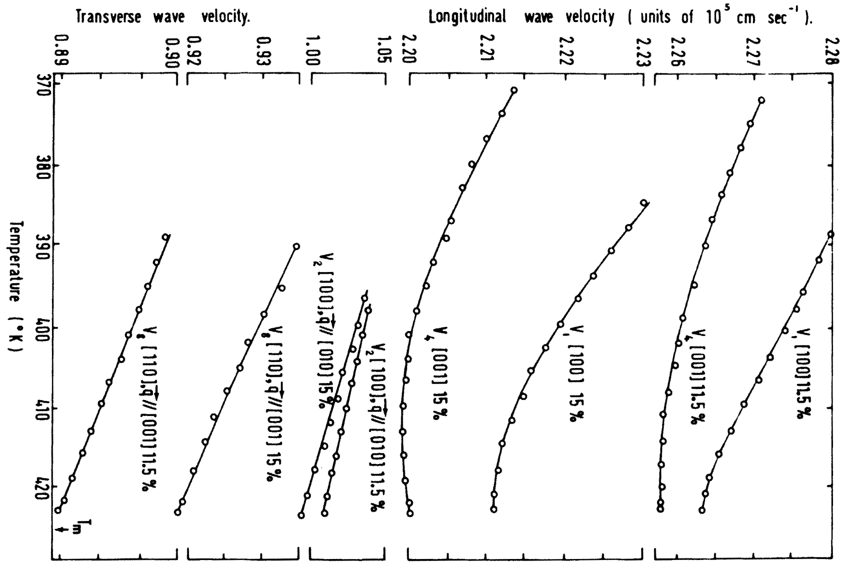

FIG. 1. Ultrasonic wave velocities in the fct 11.5-at. %- and 15-at. %-Tl alloys at temperatures near the melting point.

question, in the (001) plane. For the indium-thallium alloys, with a c/a ratio of nearly 1.0, this accidental pure mode direction turns out to be about 43° from the z axis, close to the [011] direction. All the quantities in the expressions for v_{10} and v_{11} (Table I) are known except C^2. Thus two values result for C_{13}, one positive and one negative, whose moduli differ by $2C_{44}$. Only one of these solutions leads to the observed polarizations for tetragonal materials [Dr. J. M. Farley (private communcation)].

In the case of the fct crystals under discussion it also happens that the other possible value (a small negative one) of C_{13} violates the Born stability criterion $C_{33}(C_{11} + C_{12}) > 2C_{13}^2$ and is physically unreal. The measured velocities at room temperature are collected in Table I.

The measurements of the temperature dependences of velocity of ultrasonic waves propagating in the fct alloys at high temperature are shown in Fig. 1 and those for indium in Fig. 2. The velocities above room temperature of the fcc 27-at. %-Tl alloy are given in Fig. 3; these results complement those obtained previously below room tem-

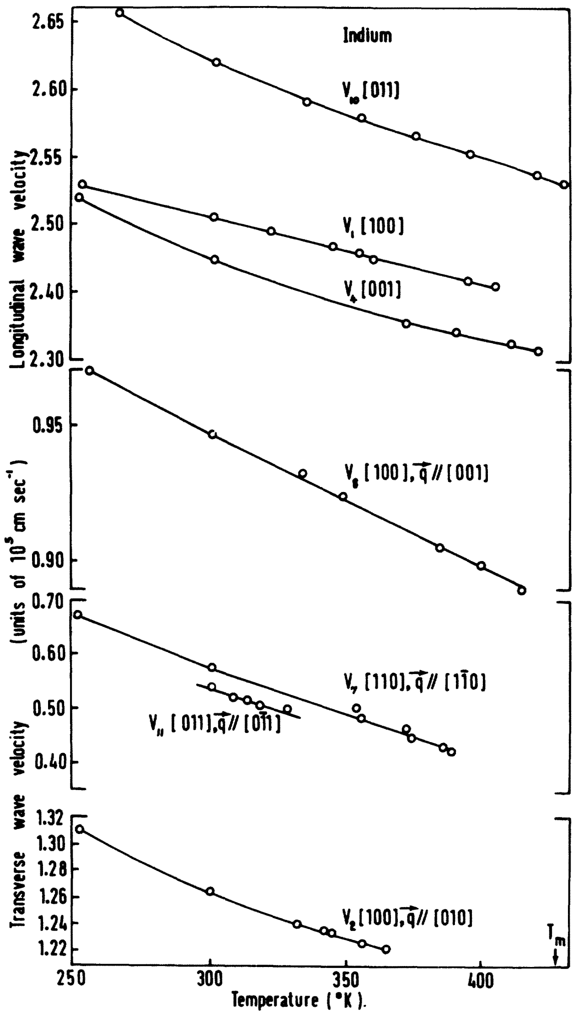

FIG. 2. Ultrasonic wave velocities at higher temperatures in indium single crystals.

perature when the objective was to study the martensitic transition in that alloy.[16] It has proved possible to measure directly the velocity of the $[1\bar{1}0]$ polarized, transverse mode propagating in the [110] direction. For the 11.5-at. %-Tl alloy this was achieved up to 423 K (melting point 427 K) but in the case of the 15-at. %-Tl material a direct measurement could only be made up to 390 K; these results, together with those for the fcc 25 and 27-at. %-Tl alloys are given in the form of the modulus $\frac{1}{2}(C_{11} - C_{12})$ in Fig. 4. The pulse-superposition method used here measured ultrasound velocity changes with considerable precision. This is the reason for the very small scatter in the velocity data presented in Figs. 1–3, and 5 and in the elastic constant data in Figs. 4 and 6–8. The absolute accuracy of each elastic constant determination is better than 1% (except for C_{13} since this modulus must be calculated by difference methods) and is indicated by the error bars. The inherent inaccuracies involved in ultrasonic pulse techniques preclude more accurate measurements of elastic constants than this.

It is worth stressing, however, that the conclusions reached on mode softening depend directly on the ultrasound velocity and in particular on the temperature dependence of velocity. The velocities of a number of modes have been measured to 4.2 K. High attenuation levels at low temperature precluded measurements by the pulse-superposition technique for all the modes studied. However, just one result need be presented here (Fig. 5) to illustrate the fact that away from the vicinity of either T_c or T_m the temperature dependence of sound velocity is that usually found in crystalline solids: the slope $(\partial v/\partial T)_P$ tends to zero as the temperature T approaches 0 K and is almost linear above about 20 K. The slopes $(\partial v/\partial T)_P$ also vary with orientation and mode of propagation. For the 11.5-at. %-Tl alloy, $(\partial v/\partial T)_P$ ranges between 3.45×10^2 cm sec^{-1} K^{-1} for the shear wave velocities (v_3, v_5, v_8) which depend solely on C_{44} and 1.88×10^3 cm sec^{-10} K^{-1} for the slow shear mode (v_7); for the 15-at. %-Tl alloy the corresponding gradients are 2.85×10^2 and 2.0×10^3 cm sec^{-10}K^{-1}, respectively. The slope $(\partial v/\partial T)_P$ reflects the anharmonicity in the binding forces appropriate to the particular mode. The finding that v_7 (the velocity of the soft mode) has the steepest slope indicates that the atomic displacements associated with this mode are those most

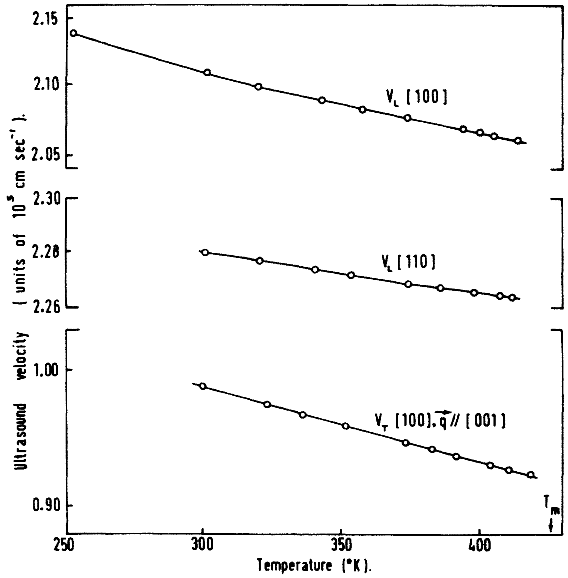

FIG. 3. Ultrasonic wave velocities between room temperature and the melting point in the fcc 27-at. %-Tl alloy.

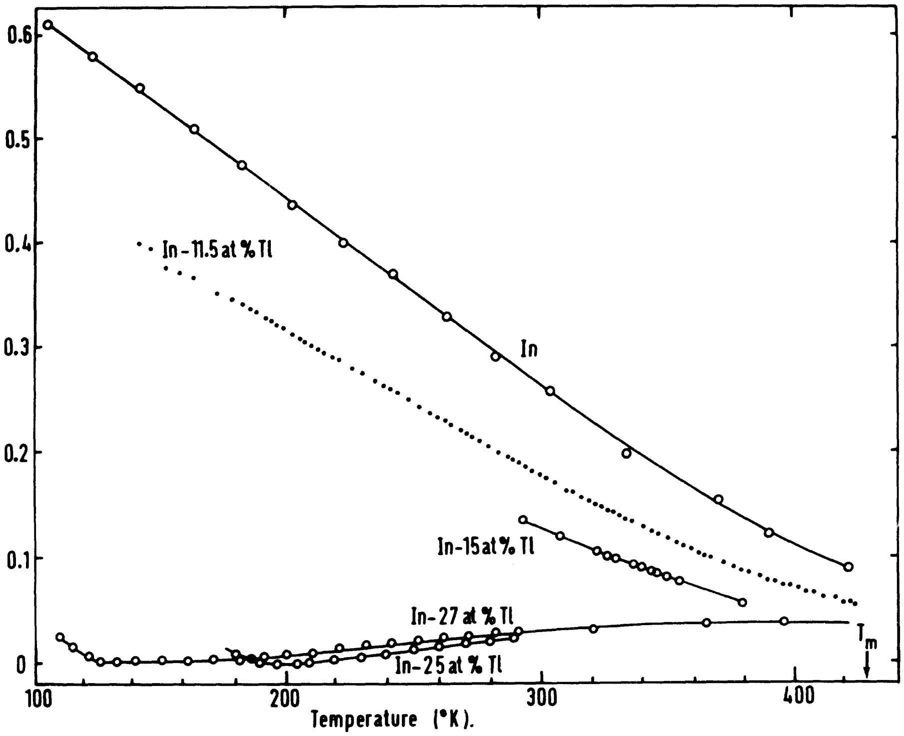

FIG. 4. Soft-mode elastic constant $\frac{1}{2}(C_{11}-C_{12})$ as a function of temperature in indium and its thallium alloys.

subject to anharmonic forces. The elastic stiffness constants of indium are compared in Table II with those given at room temperature by other workers.

The attenuation in indium has been measured near the melting point (Fig. 9). The general behavior observed is that the attenuation begins to rise as T_m is approached. This effect has been

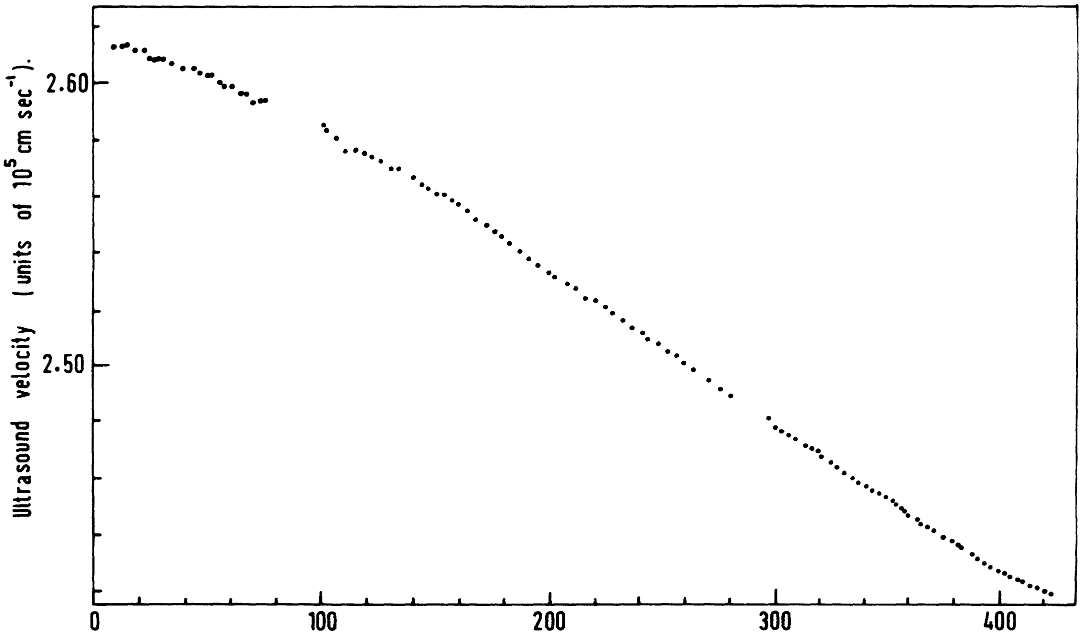

FIG. 5. Velocity between 4.2 °K and the melting point of the longitudinal ultrasonic wave propagated in the [110] direction in In–15-at. %-Tl alloy.

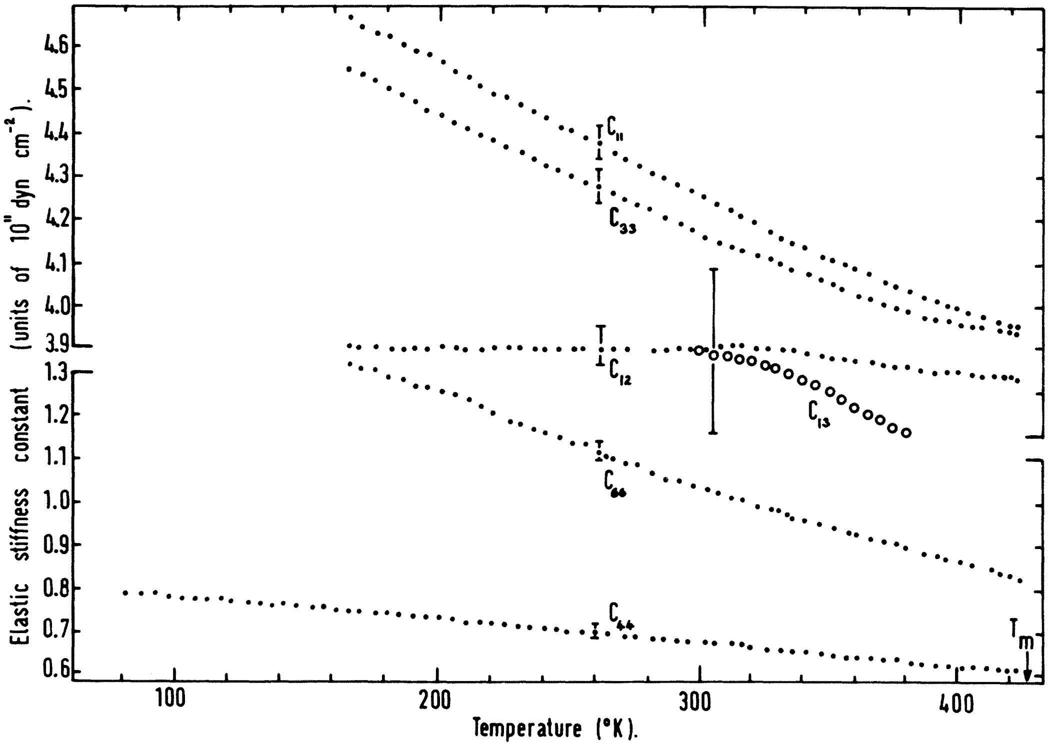

FIG. 6. Temperature dependences of the elastic constants of In-11.5-at. %-Tl alloy single crystals. The absolute error on each set of points indicated by the bars.

noted before in In_2Bi and for that material has been attributed to enhanced phonon interactions ensuing from increased anharmonicity.[23]

IV. DISCUSSION

Inspection of the phase diagram[17,18] indicates that as the temperature is raised the fct alloys and indium get closer to the fcc-fct boundary; these materials melt and do not transform to the fcc phase although the elastic stiffness moduli change with temperature in a way which suggests that a transformation would take place if it were not for the prior melting. This behavior is ramified in two ways:

(i) While a TI tetragonal crystal has six elastic constants, a cubic crystal has three; the relationship between the moduli which correspond to these two symmetries can be seen from the matrix representations (4). The data for the fct alloys in Figs. 6 and 7 demonstrate that the moduli converse in pairs (C_{11} with C_{33}; C_{44} with C_{66}) as T_c is approached—in a cubic crystal the members of

TABLE II. The elastic stiffness constants in units of 10^{11} dyn cm^{-2} in single-crystal indium.

	Temperature (°K)				
	300 °K	300 °K	300 K	350 °K	400 °K
Elastic stiffness constant	Present work	Chandrasekhar and Rayne (Ref. 21)	Winder and Smith (Ref. 22)	Present work	Present work
C_{11}	4.57 ± 0.01	4.535	4.44	4.40	4.20
C_{33}	4.46 ± 0.01	4.515	4.43	4.27	4.07
C_{44}	0.65 ± 0.01	0.651	0.653	0.61	0.58
C_{66}	1.20 ± 0.01	1.207	1.22	1.09	0.99
C_{12}	4.07 ± 0.10	4.006	3.94	4.04	3.99
C_{13}	4.16 ± 0.15	4.151	4.04	4.14	4.17

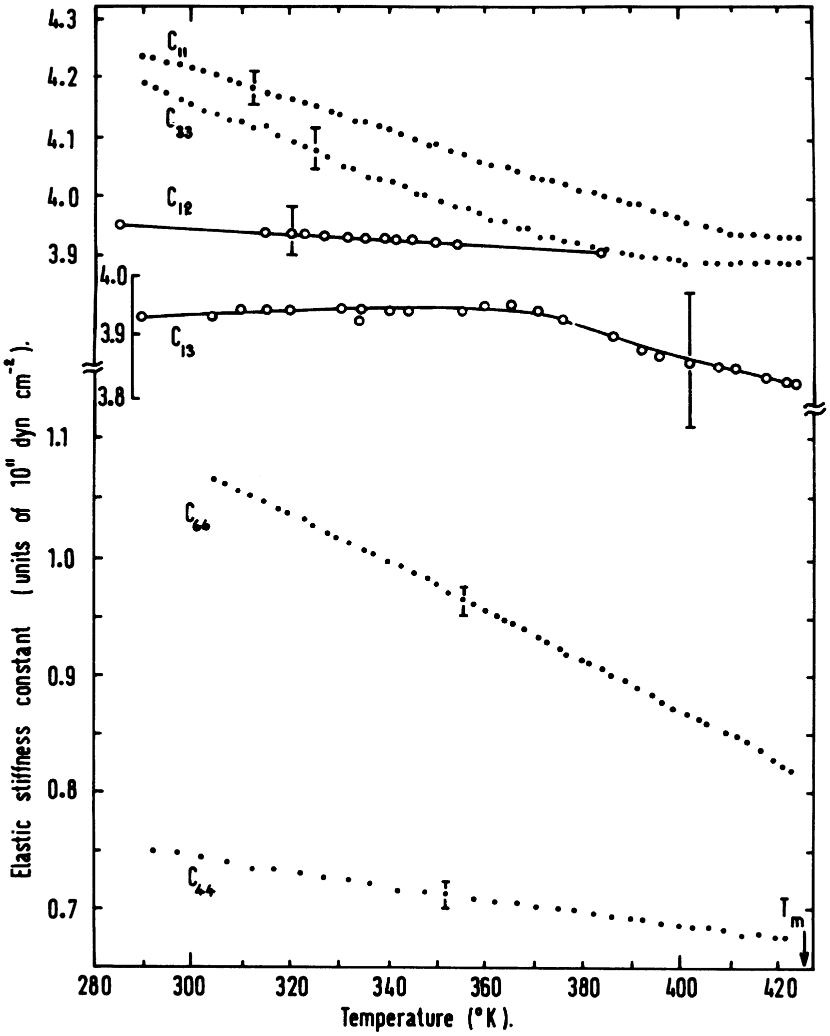

FIG. 7. Temperature dependences of the elastic constants of In-15-at. %-Tl alloy single crystals.

each pair are equal. Similarly the moduli C_{12} and C_{13} would also be expected to converge, but the large experimental error in C_{13} (which arises because differences in velocity are squared are involved in its determination) prevents any definite conclusion on this point. At a given temperature the 15-at. %-Tl alloy is closer to the phase boundary than is the 11.5-at. %-Tl; the elastic constant pairs reflect this: near the melting point the differences between C_{11} and C_{33} and also between C_{44} and C_{66} are smaller for the higher composition alloy than for that containing less thallium. Also $(C_{11} - C_{12})$ is smaller (Fig. 4). Indium also follows these general trends (Fig. 8). Since the absolute error in the elastic constants except C_{13} is less than 1%, the convergence of pairs of moduli is well established by the experimental data.

(ii) Unlike the conditions $C_{11} = C_{33}$, $C_{44} = C_{66}$, and $C_{12} = C_{13}$, equality of C_{11} and C_{12} is not required of a cubic crystal (nor for a tetragonal one). Although previous results for twinned samples of fct indium-thallium alloys are consistent with the decrease of $\frac{1}{2}(C_{11} - C_{12})$ towards zero as the martensitic transition is approached from the fct side, the present results establish for the first time this behavior of $\frac{1}{2}(C_{11} - C_{12})$ in single crystals of the fct phase. In alloys with less than 15.5-at. %-Tl and in indium itself softening of the [110], $\vec{q} \parallel [1\bar{1}0]$ acoustic-phonon mode takes place as the temperature is raised. Thus the experimental results are consistent with the soft-mode mechanism. But although the modulus $\frac{1}{2}(C_{11} - C_{12})$ does decrease as the temperature is raised (Fig. 4) for the fct indium-thallium alloys and for indium this effect is not a preliminary to fusion: the curves for $\frac{1}{2}(C_{11} - C_{12})$ do not extrapolate to zero at the melting point but at a higher temperature at which we can surmise that the crystals would have undergone the martensitic transition were they not to melt first. The elastic constant pair C_{11} and C_{33} also converge at a temperature above the melting point as do C_{44} and C_{66}. The three convergence

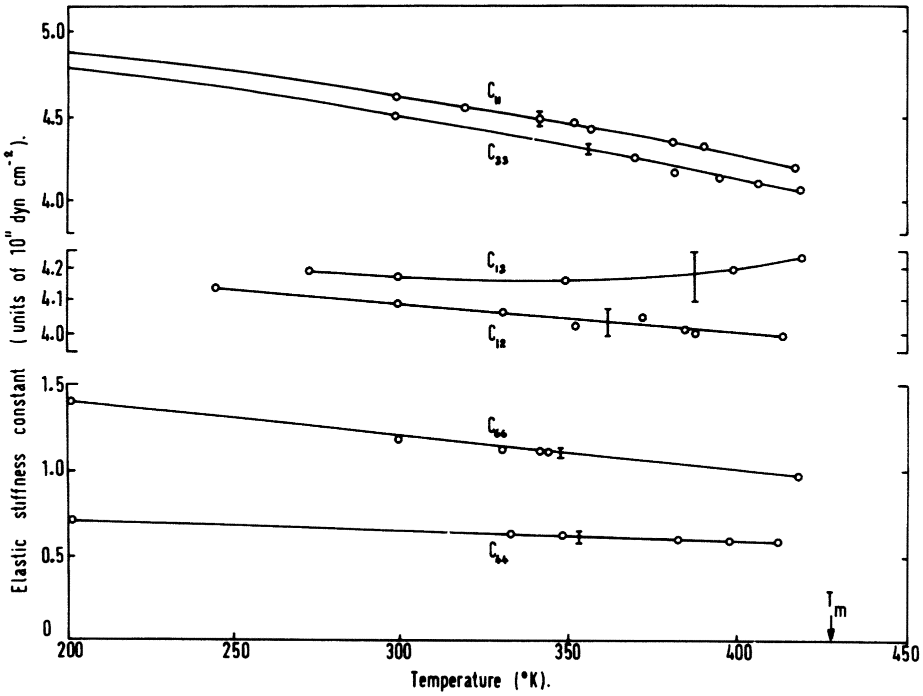

FIG. 8. Elastic constants of indium at high temperatures.

temperatures are similar. That the mode softening is not the prelude to fusion finds further confirmation in the data obtained for the cubic 27-at.%-Tl alloy (Fig. 4): $\frac{1}{2}(C_{11}-C_{12})$, which does go to zero within experimental error at the martensitic transition ($T_c = 127K \pm 2$ K), does not decrease again as T_m is neared. Consequently, the results demonstrate that in these metallic alloys a softening of a phonon mode near the Brillouin-zone center does not take place specifically near the melting point.

In none of the materials studied does any sound velocity tend to zero at the melting point: condition[11,12] (3) is not fulfilled. Figures 2.4 in Ida's paper[11] and Fig. 2 of the critical comment by Ishizaki and his co-workers[12] provide a quantitative prediction of the reduced velocity v_s/v_{s0} (where v_{s0} is the velocity of the mode s at 0 K) against the reduced temperature T/T_m. On the basis of Ida's theory even when the temperature has reached only 0.9 T_m, v_s/v_{s0} should have fallen measurably below the normal linear decrease expected of an ultrasound velocity. We have not observed such a decrease in any mode of any of the alloys discussed here [nor in In_2Bi, and intermetallic compound also under investigation, Chung and Saunders (unpublished)].

The velocity data show no tendency for $(\partial v/\partial T)_p$ to incline towards $-\infty$ as the temperature goes to within 0.995 T_m. However, there are deviations from linearity in the measured longitudinal wave velocities of the alloys near the melting point (Figs. 1 and 3). In contradiction to Ida's predictions[11] near T_m the temperature dependence of the longitudinal velocity is reduced and in some cases the slope becomes positive (Fig. 1). We may associate this with a premelting effect[1] rather than with a premartensitic effect because it is

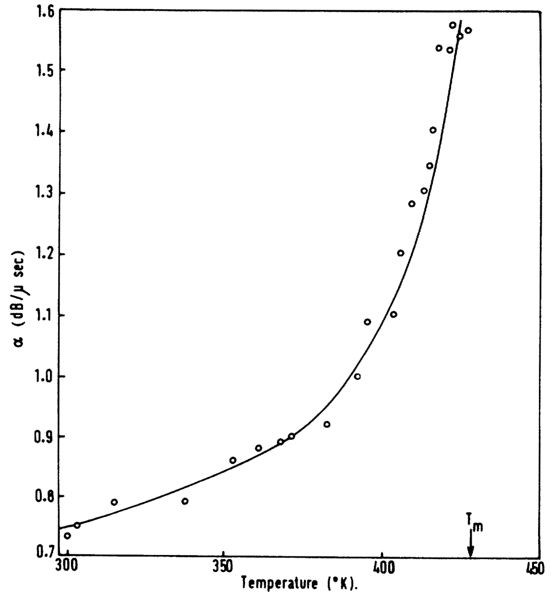

FIG. 9. Temperature dependence of attenuation of 10-MHz longitudinal ultrasonic waves propagated in the [011] direction of indium near its melting point.

seen to a similar extent in both the 11.5-at. %-Tl and 15-at. %-Tl alloys. Furthermore, the longitudinal wave propagated in the [100] direction of the 27-at. %-Tl alloy also shows a similar but not so marked decrease in $(\partial v/\partial T)_p$ with temperature. In general, the longitudinal but not the transverse modes stiffen near T_m.

V. CONCLUSION

In indium and its fct alloys with thallium as the temperature is raised the acoustic [110], $\vec{q} \parallel [1\bar{1}0]$ phonon mode softens close to $\vec{q}=0$. At a given temperature this mode is softer in a 15-at. %-Tl than in an 11.5-at. %-Tl alloy and is hardest in the element itself. Acoustic-mode softening does not play a similar role at the melting point to that which it does at the martensitic transformation or in the melting of the alkali halides.[6,7,9] It is important to note that ultrasonic experiments test acoustic-mode softening only near $\vec{q}=0$. A lattice instability near the melting point could exhibit itself as a decrease towards zero of the $\omega - q$ dispersion curve at some other point in the Brillouin zone—our experiments would not monitor such an effect. These findings apply for these particular metallic crystals and are not necessarily of wide generality or application to materials with other types of interatomic binding.

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