Superconductivity and the fct-fcc transformation in indium-thallium alloys as a function of pressure

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The pressure dependence of the superconducting transition temperature (T_c) has been determined up to $\sim$2.5 GPa for solid-solution In-Tl alloys with compositions between 31.5 and 36.5 at. % Tl. The cusp in T_c as a function of composition, that has been associated with the fcc-fct phase boundary at zero pressure, is found to move to higher thallium concentrations with increasing pressure. This is interpreted as a pressure-induced stabilization of the fct phase resulting from changes in the Fermi surface–Brillouin zone boundary overlap.

I. INTRODUCTION

Indium and thallium form a continuous range of disordered fct solid-solution alloys with up to 31 at. % Tl (Refs. 1–3) with the fct phase forming directly from the melt for compositions with less than approximately 15 at. % Tl. At higher thallium concentrations the alloys solidify with the fcc structure and then transform martensitically to the fct structure on cooling. The martensitic transformation temperature, T_M, varies strongly with composition and extrapolates to 0 K at the compositional limit for the fct phase.

The vanishing of the c' $[=\frac{1}{2}(c_{11}-c_{12})]$ shear modulus as the transformation is approached from both the fct and the fcc sides of the phase boundary has stimulated considerable interest in the elastic[4] and phonon[5] properties for the transforming alloys.

The role of electronic effects in determining the c/a ratio for In-Tl alloys was first suggested by Tyzack and Raynor.[6] Svechkarev[7] has proposed that the electronic energy for indium alloys is minimized through changes in the axial ratio to maintain contact between the Fermi surface and the Brillouin zone corners. Yonemitsu[8] explained the stability of the fct and fcc phases in terms of the internal energies calculated within the nearly-free-electron model. Brillouin zone boundary overlap at the Fermi surface was linked to the soft shear mode.[9] Gunton and Saunders[10] have investigated the effect of a distortion on the total energy for In-Tl alloys in calculating the phonon spectrum. They concluded that the soft-mode behavior and the stability of the crystal structure were determined by the balance between the change in the electrostatic and band-structure energies resulting from the distortion.

Evidence for the connection between the fcc-fct boundary and the electronic density of states has been inferred from the peak in the superconducting transition temperature, T_c versus composition, which occurs at 31 at. % Tl.[2] More direct support is found in the variation of the band-structure density of states for In-Tl alloys, derived from low-temperature specific-heat measurements.[11]

Low-temperature thermal expansion measurements for indium[12] and fct In-Tl alloys[13] reveal that as $T\rightarrow 0$ K the tetragonality increases. Moreover, the effect is significantly enhanced as the Fermi surface comes closer to a corner of the Brillouin zone boundary as the alloy phase boundary is approached.

The application of hydrostatic pressure up to $\sim$10 GPa increases the c/a ratio for indium and In-Tl alloys containing 5.9 and 12.0 at. % Tl.[14] However, surprisingly little is known about the effect of pressure on the fct-fcc transformation with the only direct measurements being those of Polovov and Ponyatovskii[15] for a 20 at. % Tl alloy and Brassington and Saunders[4] for a 23 at. % Tl alloy. The reported values for dT_M/dP are 0 ± 5 K GPa^{-1} and 170 K GPa^{-1}, respectively.

The value of dT_M/dP reported by Brassington and Saunders[4] was derived from elastic constant measurements made as a function of hydrostatic pressure up to 0.2 GPa. They also report that the pressure derivative, dc'/dP, at room temperature is negative for fcc alloys containing less than 30 at. % Tl and positive for fct alloys. Thus, hydrostatic pressure promotes the instability of the fcc phase and stabilizes the fct phase. Brassington and Saunders[4] also conclude from an extrapolation of their measurements of dc'/dP for fcc alloys beyond the maximum composition of 30 at. % Tl that the pressure derivative is positive for alloys containing more than 31 at. % Tl. They conclude that these alloys would not be expected to transform under pressure.

We report here a study of the pressure-induced fcc$\rightarrow$fct transformation for In-Tl alloys with compositions between 31.5 and 36.5 at. % Tl, based upon measurements of their superconducting transition temperatures as functions of pressure.

II. EXPERIMENTAL DETAILS

A. Sample preparation

Ingots of the required compositions were prepared by melting the required quantities of indium and thallium in an evacuated Pyrex tube over a gas flame. The solidified

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ingot was removed by carefully breaking the tube. An approximately 1-mm^3 sample was cut from each ingot using a razor blade and the samples were heat treated at 120 °C in a dynamic vacuum for typically 5 days. One tegragonal phase alloy (In-30 at. % Tl) was prepared. The other eight alloys studied had compositions of 31.5, 32.0, 33.0, 34.0, 35.0, 35.5, 36.0, and 36.5 at. % Tl and were in the cubic phase at zero pressure. These are the nominal compositions for the alloys. The scatter in the values of T_c, measured at zero pressure, implies that the uncertainty in these nominal compositions is of order ±0.25 at. %.

B. Measurements of superconducting transition temperature

The measurements of T_c as a function of pressure were made in a high-pressure clamp in which hydrostatic pressure up to 2.5 GPa is applied at room temperature and then the clamp is transferred to a liquid-helium bath. The technique has been described in detail earlier[16] with one notable change in the present measurements being the installation of the coil system used to detect the superconducting transition inside the pressure capsule.

The detection-coil system consisted of three approximately 1.4-mm-diam secondary coils surrounded by a common primary coil of 4.3-mm diameter. The primary and secondary coils were wound with 20 turns of #40 gauge copper wire and glued with "five-minute" araldite. The coils were attached to #36 gauge copper wires which pass through an epoxy seal in the beryllium-copper (Be-Cu) end piece of the 0.64-cm ($\frac{1}{4}$") diam Teflon, high-pressure capsule.[17]

This arrangement, although requiring more time to set up and being more susceptible to failure under pressure than one in which the detector coils are outside the high-pressure cylinder, did provide an unambiguous identification of the superconducting transition for each sample. This was an important consideration as it was found in earlier measurements, in which the superconducting transitions were detected by coils mounted outside the high-pressure cylinder, that overlap of the transition curves resulting from the change in T_c with pressure, made an accurate determination of the change in T_c, ΔT_c, impossible.

A 350-Hz voltage was fed to the primary coil and output signals from the secondary coils were individually switched to the input of a lock-in amplifier, the dc output of which was fed to the Y axis of an X-Y recorder. The X axis of the recorder was driven by the voltage across a germanium thermometer. All the measurements were made below 4.2 K while the temperature of the liquid-helium bath was slowly lowered by pumping. Temperatures determined from the vapor pressure over the helium bath were recorded at regular intervals on the recorder trace and served to calibrate the temperature (X) axis.

The pressure medium was a 1:1 mixture of n-pentane and iso-amyl alcohol. The pressure in the pressure capsule at low temperature was derived from the superconducting transition of a tin manometer placed in one of the coils.[18] Two alloy samples were placed in the other two coils. Measurements were generally made with pressure increasing up to the maximum pressure (~2.4 GPa) with the zero-pressure T_c being determined at the start and finish of the sequence. For some of the samples pressure was cycled and not necessarily increased monotonically from one measurement of T_c to the next. From these checks it was proven that the sequence of pressure changes had no influence on the overall trend for the variation of ΔT_c with pressure.

III. RESULTS

A typical record of a superconducting transition curve is shown in the inset to Fig. 2. The value for T_c is defined from the midpoint of the extrapolated linear portion of the transition curve. This extrapolation, which is shown by the dashed lines in the inset, also defines the transition width shown as bars on the plotted data points.

The zero-pressure values for T_c, recorded prior to the pressure measurements, are plotted as a function of thallium composition in Fig. 1. The data of Luo, Hagen, and Merriam[2] are shown for comparison. The overall agreement is satisfactory. As noted above, the scatter in the

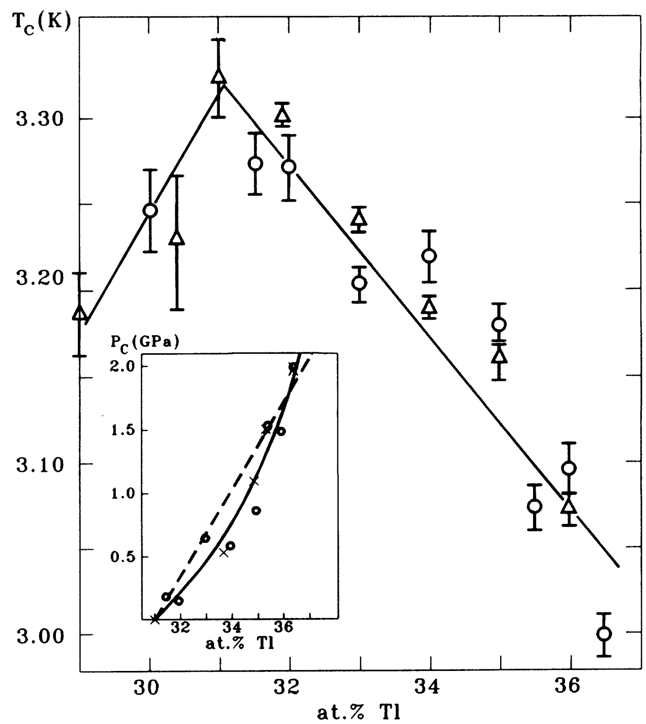

FIG. 1. Superconducting transition temperature, T_c, as a function of thallium concentration for In-Tl solid-solution alloys. The error bars indicate the widths of the superconducting transitions, as illustrated in the inset to Fig. 2. (○) are the present data and (△) are those of Luo, Hagen, and Merriam (Ref. 2), for comparison. In the inset, values of P_c, the pressure required to induce the fcc→fct transformation, as a function of thallium concentration, are shown. In this inset (○) are values derived from ΔT_c's as functions of pressure and (×) are values derived from isobars of T_c versus concentration. The dashed line represents the value of $\Delta P_C/\Delta C$ derived from expression (1).

present data implies an uncertainty in alloy composition of order ±0.25 at. % Tl.

The notable feature in the zero-pressure T_c data is the maximum in the vicinity of 31 at. % Tl. This maximum is more well defined in the previously reported data[2] which cover a wider range of thallium concentration, and is identified with the fct-fcc phase boundary. Representative plots of ΔT_c as functions of pressure for tetragonal phase In-30 at. % Tl and cubic phase In-35.5 at. % Tl are presented in Fig. 2. In the case of the In-30 at. % Tl alloy, T_c decreases smoothly with pressure in the same way as for indium.[19] For the In-35.5 at. % Tl there is a distinct cusp in ΔT_c as a function of pressure at around 1.5 GPa. Similar cusps were found for the ΔT_c versus pressure plots for the other alloys examined, with the pressure at which the cusp occurs varying with composition.

In order to emphasize the cusplike behavior, a linear background represented by $-0.35P$ K, where the pressure, P, is in GPa, has been subtracted from ΔT_c to give $\Delta T_c'$, i.e.,

$$\Delta T_c' = \Delta T_c + 0.35P \text{ K} .$$

This background is shown in Fig. 2. The resulting values of $\Delta T_c'$ as functions of pressure are presented in Fig. 3. Consistent with the deviation from the straight line used as background in the raw data for In-30 at. % Tl (Fig. 2), $\Delta T_c'$ versus P for this alloy shows a shallow minimum around 1.2 GPa.

The data for the In-35.5 at. % Tl, where the pressure was cycled, as indicated by the numbering of the data points in Fig. 2, demonstrated the reproducibility of the measurements. Similar reproducibilities for ΔT_c versus P were also demonstrated by cycling pressure for the 35.0, 36.0, and 36.5 at. % Tl samples. Furthermore, the two independent sets of data that are presented for In-36.5 at. % Tl taken on different samples cut from the same ingot are in excellent agreement. The solid lines drawn through the data points on all figures are "by-eye" best fits.

As in the case of the zero-pressure T_c data, the cusp in $\Delta T_c'$ is taken to indicate the transformation from the fcc to the fct phase induced by pressure. In most of the alloys there was a noticeable broadening of the supercon-

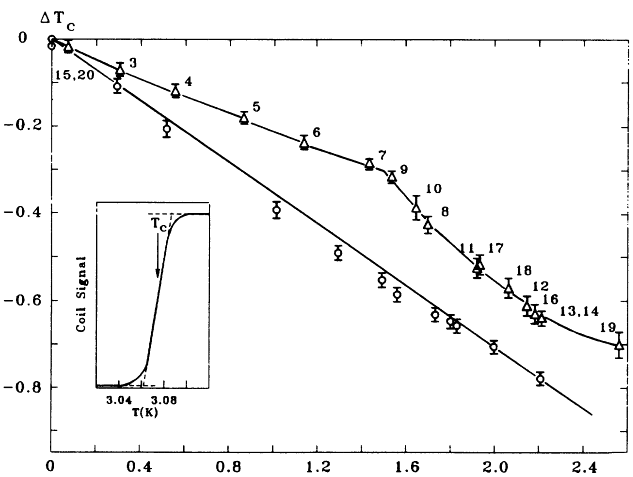

FIG. 2. The change in superconducting transition temperature ΔT_c as a function of pressure for In-30 at. % Tl (○) and In-35.5 at. % Tl (△). The "error" bars indicate the widths of the superconducting transition curves, as illustrated in the inset. The data for the In-35.5 at. % Tl points are identified by the order in which they were collected. The straight line represents the linear background $-0.35P$ K referred to in the text.

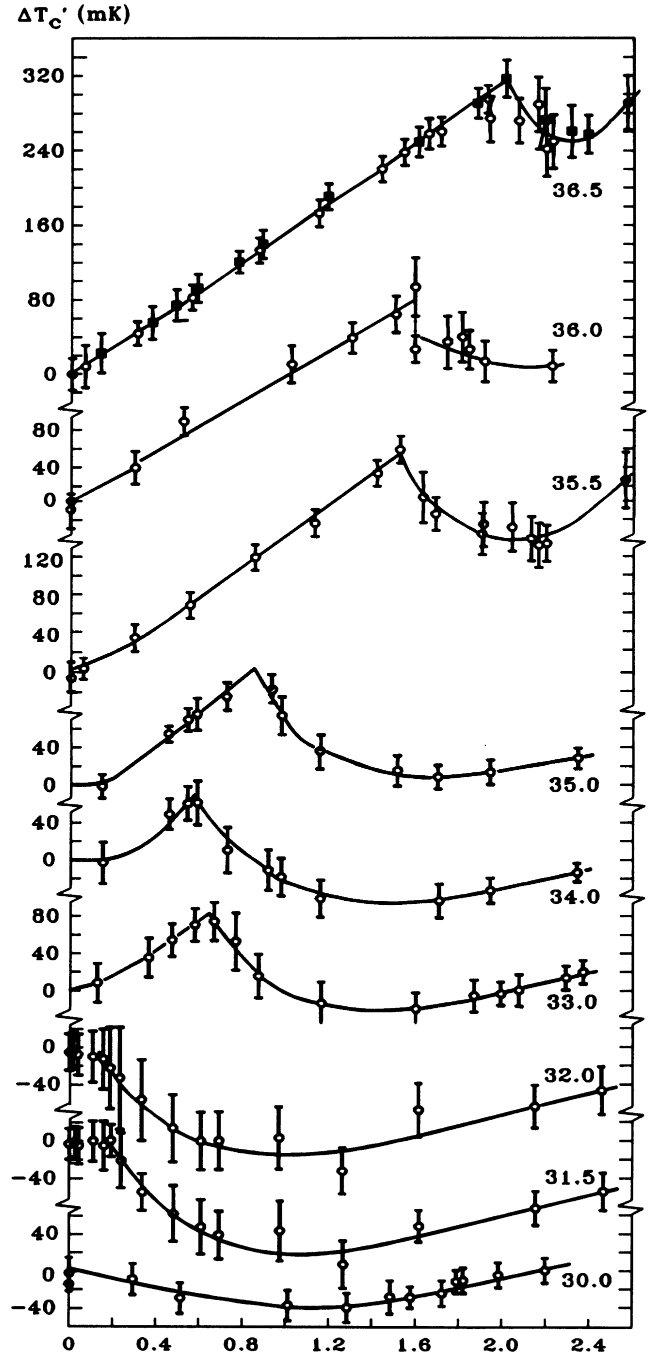

FIG. 3. The pressure dependence of $\Delta T_c'$, as defined in the text, for In-Tl solid-solution alloys. The individual curves are identified by the thallium concentration in at. %. The "error" bars indicate the widths of the transitions, as illustrated in the inset to Fig. 2. For In-36.5 at. % Tl, data from a second sample cut from the same ingot are indicated as (■).

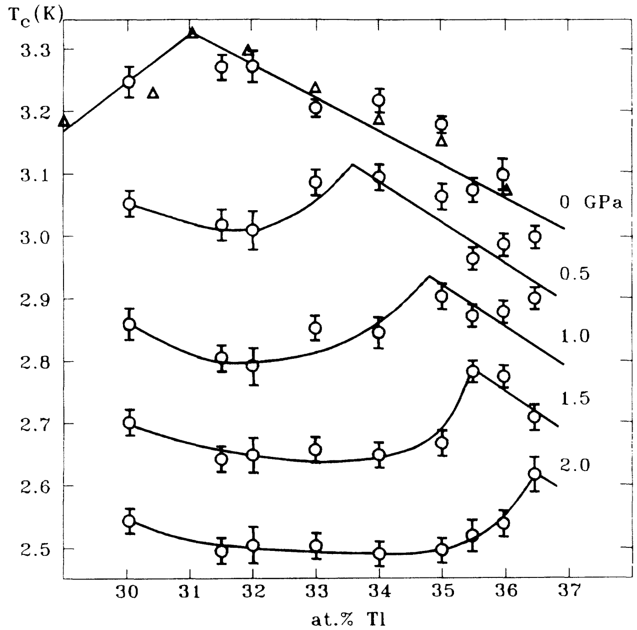

FIG. 4. Isobars for T_c as a function of thallium concentration, derived from the variation of $\Delta T_c'$ with pressure. The individual curves are identified by the pressure in GPa. The "error" bars indicate the widths of the superconducting transition curves, as illustrated in the inset to Fig. 2. The data points represented by (△) at zero pressure are from Luo (Ref. 2).

ducting transition curve, as indicated by the bars on the data points, on passing through the transformation. This broadening is consistent with the inhomogeneous strain distribution to be expected in a polycrystalline sample following the tetragonal distortion. In the case of the In-36.0 at. % Tl there was very significant broadening of the transition curve with evidence of a double transition at the maximum in $\Delta T_c'$. This suggests a two-phase region at the transformation.

The variations of T_c as functions of thallium concentration for various values of pressure, derived from the $\Delta T_c'$ plots, are shown in Fig. 4. The cusp is clearly defined and the shift of the cusp in T_c to higher thallium concentrations with increasing pressure is clear. Values of P_C, the pressure required to induce the fcc→fct transformation as a function of thallium concentration, C, derived from these cusps in T_c are displayed in the inset to Fig. 1. The inset also includes values of P_C derived directly from the cusps in $\Delta T_c'$ as a function of pressure. From this plot it appears that P_C increases nonlinearly with C and progressively higher pressure is required to induce the transformation as the thallium content increases.

IV. DISCUSSION

This study of the fcc-fct transformation in In-Tl alloys as a function of pressure clearly shows that the transformation boundary moves to higher thallium concentration under pressure and exceeds the 31 at. % limit inferred by Brassington and Saunders.[4] If it is assumed that pressure induced a constant displacement of the boundary in concentration (see Fig. 5), it is possible to compare the measured variation of P_C with C with the value of $\Delta P_C/\Delta C$ derived from the pressure and concentration dependences of the transformation temperature, T_M. Referring to Fig. 5, we may write

$$\Delta T_M = -\Delta C \frac{dT_M}{dC} \approx \Delta P \frac{dT_M}{dP}$$

and hence

$$\frac{\Delta P}{\Delta C} \approx -\frac{dT_M/dC}{dT_M/dP} . \tag{1}$$

Substituting $dT_M/dC \simeq -56$ K (at. % Tl)$^{-1}$ (as at 30 at. % Tl in the phase diagram[3]) and $dT_M/dP \simeq 170$ K GPa^{-1} [at 23 at. % Tl (Ref. 4)] into (1) gives $\Delta P/\Delta C \simeq 0.33$ GPa (at. % Tl)$^{-1}$. This coefficient can be inferred to give the dependence of P_C on concentration and is shown as the dashed line in the inset to Fig. 1. It is seen to be in satisfactory agreement with that measured directly from the raw data for ΔT_c versus P or from the isobaric plots of T_c versus composition.

As noted above, the cusp in T_c as a function of composition has been identified with the crossing of the fcc-fct phase boundary in the superconducting state.[2] The observation of soft-mode elastic behavior in the vicinity of the phase transformation raises the question of whether this is directly responsible for the increase of T_c.[20,21] The superconducting tunneling measurements of Dynes[20] show no discernible effect of the soft mode on the overall

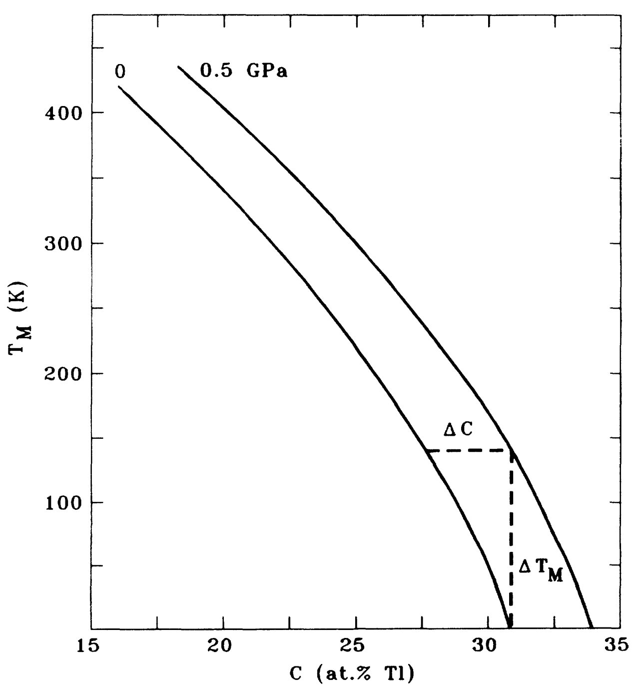

FIG. 5. Variation of the fcc-fct transformation temperature, T_M, as a function of concentration for zero and 0.5 GPa. The zero-pressure boundary is taken from Ref. 3. The 0.5-GPa boundary assumes a constant pressure-induced shift in concentration, ΔC, as derived from the plot of P_C versus concentration (inset to Fig. 1).

effective phonon distribution (the product of the electron-phonon parameter and the phonon density of states as a function of frequency) although there is a minimum in the average phonon energy at about 31 at. % Tl. Analysis of the T_c data does suggest that the maximum is due to a peak in the density of electron states,[21] a view that is supported by low-temperature specific-heat measurements.[11]

The Fermi surface for indium consists of a closed second-zone hole surface and interconnected third-zone electron arms around the [110] Brillouin zone edges in the {001} plane.[22] The tetragonality of indium has a significant effect on the third-zone overlap and it has been proposed that it is this overlap which is responsible for the distortion from a cubic structure.[8,13] Very little is known about the influence of pressure upon the indium Fermi surface. The only direct measurements are those of O'Sullivan, Schirber, and Anderson[23] derived from the pressure dependence of the de Haas–van Alphen frequency. They find that the cross-sectional area of the electron arms increases with pressure, which indicates increased overlap of the Fermi surface into the third zone at the {001} plane. More circumstantial evidence for the pressure-induced overlap of the Fermi surface into the third zone has been deduced from measurements of the superconducting transition temperature as a function of pressure for indium solid-solution alloys.[19]

Thus, limited as it is, the information on the pressure dependence of the Fermi surface for indium is consistent with the picture of the increase in the tetragonal distortion under pressure being electronically driven. Furthermore, the present measurements demonstrate that the tetragonal distortion can also be induced by the application of pressure in the cubic phase.

V. CONCLUSION

It is concluded from the reported measurements of the superconducting transition temperature as a function of pressure for In-Tl solid-solution alloys in the composition range 31.5–36.5 at. % Tl that pressure stabilizes the fct phase and displaces the fcc-fct phase boundary to higher thallium concentration. It is proposed that the fcc-fct transformation is driven by the overlap of the Fermi surface with the Brillouin zone boundary.

[1]R. W. Meyerhoff and J. F. Smith, Acta Met. **11**, 529 (1963).

[2]H. L. Luo, J. Hagen, and M. F. Merriam, Acta Met. **13**, 1012 (1965).

[3]J. T. A. Pollock and H. W. King, J. Mater. Sci. **3**, 372 (1968).

[4]M. P. Brassington and G. A. Saunders, Proc. R. Soc. London Ser. A **387**, 289 (1983).

[5]T. R. Finlayson, M. Mostoller, W. Reichardt, and H. G. Smith, Solid State Commun. **53**, 461 (1985).

[6]C. Tyzack and G. V. Raynor, Trans. Faraday Soc. **50**, 675 (1954).

[7]I. V. Svechkarev, Zh. Eksp. Teor. Fiz. **47**, 960 (1964) [Sov. Phys. JETP **20**, 643 (1965)].

[8]K. Yonemitsu, J. Phys. Soc. Jpn. **21**, 1231 (1966).

[9]D. B. Novotny and J. F. Smith, Acta Met. **13**, 881 (1965).

[10]D. J. Gunton and G. A. Saunders, Solid State Commun. **12**, 569 (1973).

[11]L. V. Munukutla and R. L. Cappelletti, Phys. Rev. B **21**, 5111 (1980).

[12]J. G. Collins, J. A. Cowan, and G. J. White, Cryogenics **7**, 219 (1967).

[13]M. Liu, T. R. Finlayson, and T. F. Smith, Aust. J. Phys. **46**, 695 (1993).

[14]R. W. Vaughan and H. G. Drickamer, J. Phys. Chem. Solids **26**, 1549 (1965).

[15]V. M. Polovov and E. G. Ponyatovskii, Zh. Eksp. Teor. Fiz. **64**, 937 (1973) [Sov. Phys. JETP **37**, 476 (1973)].

[16]T. F. Smith, in *High Pressure Science and Technology,* Proceedings of the 6th AIRAPT Conference, edited by K. D. Timmerhaus and M. S. Barber (Plenum, New York, 1979), Vol. 1, p. 309.

[17]K. S. Kim, Rev. Sci. Instrum. **41**, 1102 (1970).

[18]T. F. Smith, C. W. Chu, and M. B. Maple, Cryogenics **9**, 53 (1969).

[19]T. F. Smith, J. Low Temp. Phys. **11**, 581 (1973).

[20]R. C. Dynes, Phys. Rev. B **2**, 644 (1970).

[21]T. F. Smith and T. R. Finlayson, Contemp. Phys. **21**, 265 (1980).

[22]P. W. Holtham, J. Phys. F **6**, 1457 (1976).

[23]W. J. O'Sullivan, J. E. Schirber, and J. R. Anderson, Solid State Commun. **5**, 525 (1967).