Influence of Fermi Surface Topology on the Pressure Dependence of T_c for Indium and Dilute Indium Alloys*

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The pressure dependence of the superconducting transition temperature for In, In–Cd (to 3.5 at. %), and In–Pb (to 12 at. %) has been determined to 24 kbar. A small deviation from a linear dependence of T_c on volume compression is found for indium. Alloying with Cd and Pb modified this nonlinear contribution, which is interpreted as arising from changes in the Fermi surface topology. In all, four transitions are identified and their possible origins, based upon the known Fermi surface of indium, are discussed.

1. INTRODUCTION

The development of sophisticated and sensitive techniques for examining the Fermi surface has led to a considerable and detailed knowledge of the shapes of the Fermi surface for many of the pure metals.[1] These techniques have also been successfully applied to a number of well-ordered compounds and some very dilute solid solutions, but their requirement of a long electron mean free path inhibits their application to more disordered systems. Thus, the study of the effects of alloying on the Fermi surface has necessitated recourse to the more indirect and much cruder information which may be inferred from such observations as the change in lattice parameters, the optical properties, the low-temperature heat capacity, and the transport properties in general.

By virtue of its dependence on the density of electron states at the Fermi surface, the superconducting transition temperature T_c should, in principle, provide a relatively sensitive indication of modifications to the Fermi

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surface. Thus, abrupt changes of the rate of variation of T_c with alloy composition, found in a number of systems,[2-5] have been associated with the interaction of the Fermi surface with a plane of the Brillouin zone boundary. Furthermore, singularities in the Fermi surface produced by the application of hydrostatic pressure or uniaxial stress should also be reflected in the variation of T_c.[6,7]

Measurements of the pressure dependence of T_c for thallium[8,9] and rhenium[10] and a number of their solid solutions have shown anomalous contributions which have been interpreted in terms of changes in their Fermi surface topologies. Although corroborating evidence for such transitions has still to be obtained in these cases, de Haas–van Alphen measurements provide a strong indication that a change in the Fermi surface topology is responsible for the very marked anomaly at 6 kbar in the variation of T_c with pressure for the ordered compound $AuGa_2$.[11]

Changes in the Fermi surface topology are also considered to be the source of the anomalous variations in the initial pressure dependence of T_c for dilute indium alloys which have been reported by Makarov and Volynskii.[12] While there is only indirect evidence available, based upon observations of other physical properties,[13-19] to support the existence of these suggested changes, it nevertheless provides an overall description which is quite convincing.

This paper reports a detailed investigation aimed at examining the form of the anomalous contributions to the pressure dependence of T_c for In and In alloys at pressures greater than the ~1.7 kbar limit of Makarov and Volynskii.[12] Accordingly, measurements of T_c have been made as a function of hydrostatic pressure to 24 kbar for In, In–Cd, and In–Pb alloys for concentrations up to 3.5 and 12.0 at. %, respectively.

2. EXPERIMENTAL DETAILS

The alloys were prepared in sealed, evacuated Pyrex tubes, by melting the appropriate amount of lead or cadmium (American Smelting and Refining Corp. 5N material) with Johnson–Mathey spectroscopic grade indium. The constituents were mixed in the molten state by continuously rotating the capsule for several hours at 300°C. The rotation was then stopped and the alloys were slow cooled to 140°C, at which temperature they were annealed for 1 to 2 weeks. The tubes were then allowed to cool to room temperature in air and the alloy ingots (~3 mm diam, ~1 cm long) were carefully removed. The superconductivity measurements were made on roughly cubic samples of an approximately 1.5 mm side which were cut with a razor blade from the center of the ingots.

The experimental procedure, which has been described in detail previously,[20] permitted up to four samples and a tin manometer to be studied simultaneously.

3. RESULTS

3.1. Zero Pressure

The initial zero-pressure T_c values as a function of alloy composition are presented in Figs. 1 and 2. The transition curves were sharp having widths of ~ 3 mdeg for the In–Cd alloys and a maximum of 20 mdeg for the higher concentration In–Pb alloys. T_c is taken to be the temperature at the midpoint of the transition curve. The sharpness of the transition curves and the reversibility of the magnetic behavior, as evident in the strong differential paramagnetic effect displayed by all of the In–Cd alloys and the In–Pb alloys with compositions less than 7 at.%, are taken to indicate a high degree of homogeneity for the samples.

T_c data from some previous investigations[3,4,21] are also included in Figs. 1 and 2, and the overall agreement with the present measurements is seen to be good. The straight lines have been drawn through the two sets of data
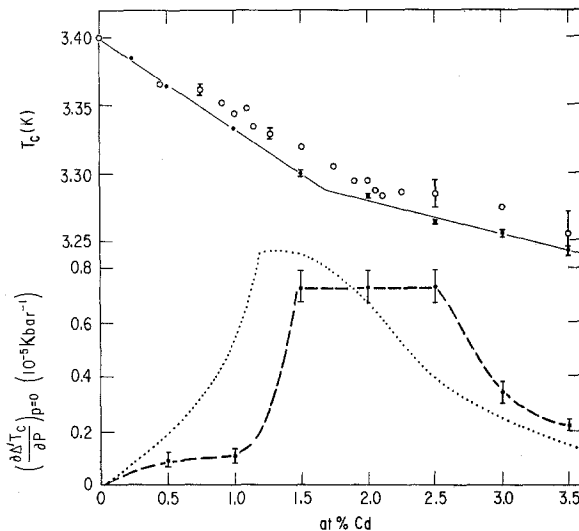

Fig. 1. Variation of T_c (upper plot) and $(\partial \Delta' T_c / \partial P)_{P=0}$ (lower plot) for indium–cadmium alloys. (O) T_c data taken from Merriam[4]; (●) from the present work. The dotted curve in the lower plot represents the data of Makarov and Volynskii.[12]
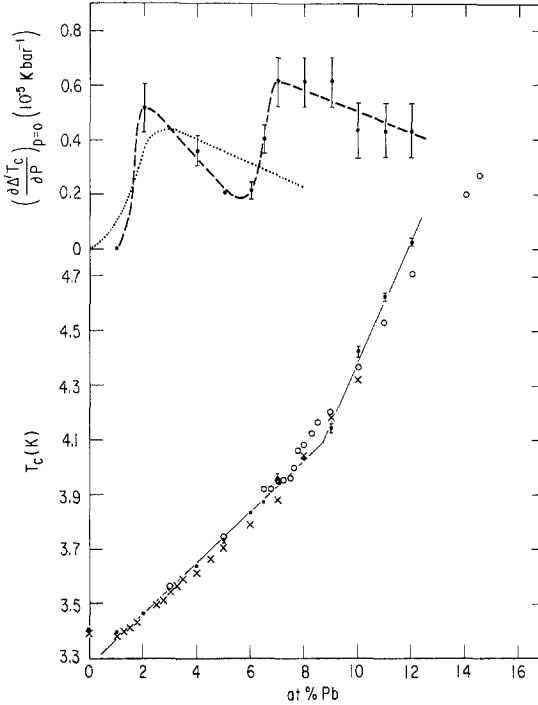
Fig. 2. Variation of T_c (lower plot) and $(\partial \Delta' T_c/\partial P)_{P=0}$ (upper plot) for indium–lead alloys. (○)T_c data taken from Merriam[3]; (×) from Gygax[21]; (●) from the present work. The dotted curve in the upper plot represents the data Makarov and Volynskii.[12]

to emphasize the previously noted[3,4,15,21] abrupt changes in the composition dependence of T_c which occur at ~ 7 at. % Pb and ~ 1.7 at. % Cd. It is not intended to imply that the concentration dependence of T_c for either system strictly consists of two linear regions.

3.2. High Pressure

The shape and width of the transition curves measured at high pressure were unaltered from those determined at zero pressure. No significant distortion of the samples was found after release of the pressure.

The data for the indium and the alloys are a combination of up to three quite independent series of pressure cycles. In addition to the initial zero-pressure transition curve, a number of the transitions were also redetermined after release of the pressure to test for reversibility and reproducibility.

Zero-pressure T_c values determined in any particular series agreed within 2 mdeg and from series to series on the same sample by 5 mdeg.

The high-pressure T_c data for the indium and the alloys will be described separately, with particular attention being given to the details of the indium data, since this will constitute the quite considerable background against which the alloy data will be compared.

3.2.1. Indium

Two samples of indium were used, and the combined data for the change in T_c, ΔT_c, as a function of volume compression are shown in Fig. 3. This particular form of presentation, rather than a plot as a function of pressure, has been selected as being the more physical and also providing the best means for resolving any possible contribution to ΔT_c due to a change in the Fermi surface topology. This follows from the theoretical expectation of a near-to-linear dependence of T_c upon volume for the present range of pressure, in the absence of any abrupt changes in the pairing interaction between the electrons.

The low-temperature volume compression appropriate to the applied pressure was calculated from the Murnaghan relationship using a bulk modulus of 462.5 kbar, derived from the low-temperature elastic data of Chandrasekhar and Rayne[22] and the pressure derivative of 5.24 obtained by
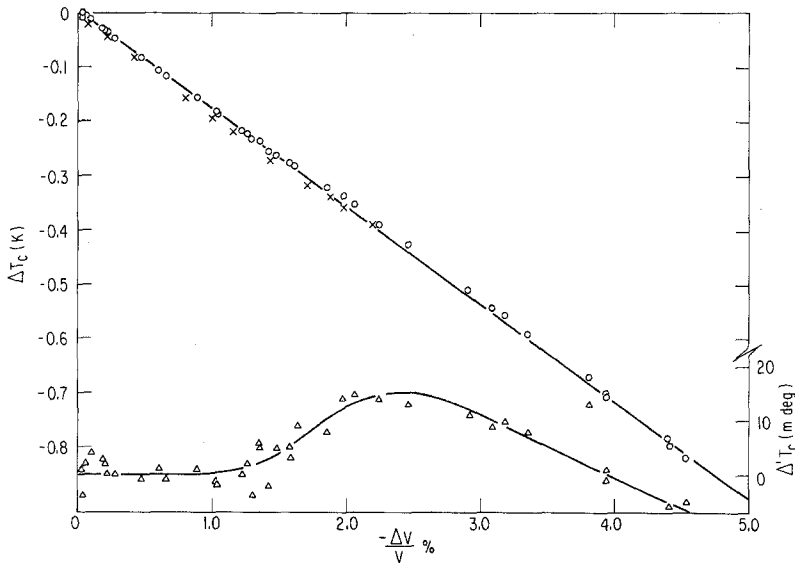
Fig. 3. ΔT_c as a function of $\Delta V/V$ (upper plot). (◯) ΔT_c data from present work; (×) from Jennings and Swenson.[8] The lower plot shows the nonlinear contribution to ΔT_c.

TABLE I

Parameters Derived from Least-Squares Fits of ΔT_c to $\alpha \Delta V/V + \beta$ for Indium

σ,[a] mdeg	α, deg	σ_α, deg	β, mdeg	σ_β, mdeg	$(\partial T_c/\partial P)_{P=0}$, 10^{-5} K·bar^{-1}	σ, 10^{-5} K·bar^{-1}	Max pressure, kbar
6.4	17.69	0.48	—	—	3.83	0.10	24.3
7.2	18.30	1.10	—	—	3.96[b]	0.24	10.9
2.0	17.64	0.72	—	—	3.81	0.15	6.1
1.5	17.96	0.13	3.07	1.09	3.88	0.03	6.1
1.7	18.98	0.92	—	—	4.10[b]	0.20	5.6
0.9	18.70	0.10	−2.44	0.71	4.04[b]	0.02	5.6

[a]Overall standard deviation for the fit.
[b]Data of Jennings and Swenson.[8]

Vaidya and Kennedy[23] from their room-temperature compressibility measurements.

As may be seen from Fig. 3, ΔT_c quite closely follows a linear variation with $-\Delta V/V$, but a linear least-squares fit revealed a small systematic deviation which suggested that there was a nonlinear contribution for $-\Delta V/V \geq 1.2\%$ (~ 6 kbar). Consequently, linear fits of ΔT_c to $\Delta V/V$, restricted to the data taken at pressures less than 6 kbar, were also made. Both a zero and a nonzero intercept for ΔT_c were considered, and the various parameters derived from these fits are listed in Table I.

When values of ΔT_c, calculated from the linear fit to $\Delta V/V$, are compared with the directly measured ΔT_c for data beyond the range of the fit, a small, but clearly resolved, nonlinear difference $\Delta' T_c$, is found. This is demonstrated in Fig. 3 for the case of the fit with a nonzero intercept for ΔT_c.

The values for α ($= \partial T_c/\partial \ln V$) listed in Table I, when divided by the bulk modulus, give values for $\partial T_c/\partial P$ in the zero-pressure limit, and this quantity is also included in Table I. Although the nonlinear contribution to ΔT_c and the choice of intercept significantly influence the quality of the least-squares fit, as evident from the variations in the standard deviations, their effect upon the value of $(\partial T_c/\partial P)_{P=0}$ is relatively small. However, since both $\Delta' T_c$ and a nonzero intercept for ΔT_c are considered to be significant contributions to ΔT_c, $-3.88 \pm 0.06 \times 10^{-5}$ K·bar^{-1} is considered to be the most appropriate value for $(\partial T_c/\partial P)_{P=0}$, where the uncertainty has been taken to be twice the standard deviation from the fit and does not include any absolute errors.

Figure 3 also includes data* taken to ~ 11 kbar by Jennings and Swenson,[8] for which least-squares fits of ΔT_c to $\Delta V/V$ have also been made; the parameters are given in Table I. The present value for the initial pressure dependence of T_c is 4% smaller than that derived from the corresponding fit

*These data have been corrected for the 3% error in the pressure scale used in Ref. 8.[24]

TABLE II
Values of $(\partial T_c/\partial P)_{P=0}$ for Indium

$(\partial T_c/\partial P)_{P=0}$ 10^{-5} K·bar^{-1}	$(\partial H_c/\partial P)_{T_c}$ 10^{-3} G·bar^{-1}	Pressure range, kbar	Reference
-3.95 ± 0.3^a	not given	0–0.1 liquid He	25
-4.04 ± 0.04^b		0–5.6 solid H	8
-4.34 ± 0.3		0–0.1 liquid He	26
-4.24 ± 0.3^a	-6.6 ± 0.3^c	0	27
-4.3 ± 0.4^d		0	27
-4.35 ± 0.05^a	-6.78 ± 0.05	0–1.0 solid He	28

^{a}Derived from $(\partial H_c/\partial P)_{T_c}$ using $(\partial H_c/\partial T)_{T_c} = -155.8 \pm 1.0$ G·deg^{-1}.^{25}
^{b}Derived from present fit to data of Jennings and Swenson^8 (see Table I). Error limits given are twice the standard deviation from the least-squares fit.
^{c}Derived from the volume difference between the normal and superconducting states.
^{d}Derived from Ehrenfest's relationship using the discontinuities in the thermal expansion coefficient and the specific heat at T_c.

to the data of Jennings and Swenson, which is regarded as being quite reasonable agreement. However, when compared with the more comprehensive listing of values from a number of other previous investigations, given in Table II, the agreement is not so good. With the exception of the value given by Muench,[25] which compares well with the present work, the other determinations give $(\partial T_c/\partial P)_{P=0} \sim -4.3 \pm 0.3 \times 10^{-5}$ K·bar^{-1}.

An obvious source of this disagreement between the present and previous determinations of the initial pressure dependence of T_c for indium could lie with the pressure scale[29] employed in the present work, which assumes a knowledge of the pressure dependence of T_c for tin. This has been taken from the measurements of Jennings and Swenson[8] and is therefore related to their absolute scale, which would account for the more reasonable agreement with their value of $(\partial T_c/\partial P)_{P=0}$ for In. Nevertheless, it is strictly a measure of the *relative* change of T_c for tin and indium which the present measurements give, and therefore it is more appropriate to compare this quantity with that expected from previous measurements of their initial pressure dependences. Since the values which have been reported[8,25,26,30] for $(\partial T_c/\partial P)_{P=0}$ of tin range from* -4.3 to -4.7×10^{-5} K·bar^{-1}, the difference $\Delta T_c(\text{In}) - \Delta T_c(\text{Sn})$ would be anticipated to be quite small. However, it may be seen from Fig. 4 that the measured difference, given as a function of $\Delta T_c(\text{Sn})$, lies well outside the shaded region, which represents the limits of the variation based upon the initial pressure dependences. Kan et al.[26] noted a similar discrepancy in measurements made to ~ 1.7 kbar in an ice bomb, which they concluded was due to an

*It may be noted that the present pressure scale is based upon a value of -4.67×10^{-5} K·bar^{-1}.
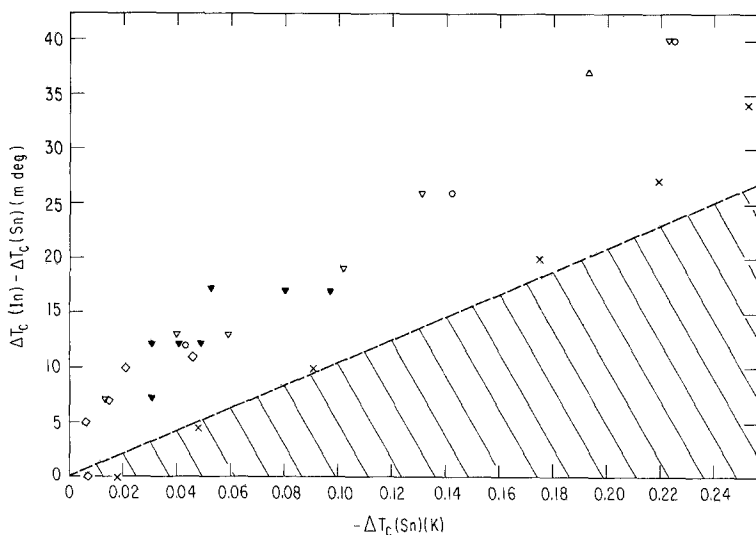
Fig. 4. The relative change of T_c for indium and tin as a function of ΔT_c for tin. The shaded area represents the limits of the difference calculated from previous determinations of their initial pressure dependences of T_c. Open symbols, different runs in the present measurements; closed symbols, data of Kan et al.[26]; crosses, data of Jennings and Swenson.[8]

abrupt change of slope in $T_c(P)$ for tin. On the other hand, the data of Jennings and Swenson[8] show no indication of any such discontinuity in slope. Swenson[24] has suggested that the origin of the discrepancy may be the larger relative thermal expansion between tin and ice, compared with indium and ice, resulting in higher local pressure around the tin.

A notable feature of Fig. 4 is the nonzero intercept for $\Delta T_c(\text{In}) - \Delta T_c(\text{Sn})$ when extrapolated to zero $\Delta T_c(\text{Sn})$. While this might be taken to imply an abrupt change in the pressure dependence of T_c for tin, or indium, around 0.1 kbar it is probably more reasonable to adopt Swenson's[24] suggestion and assume that it is the consequence of a small pressure differential between the tin and the indium arising from the differences in their thermal expansions. The local pressure difference necessary to account for the ~ 5 mdeg intercept would only amount to ~ 0.1 kbar. It is for this reason that the least-squares fit allowing a nonzero intercept for ΔT_c is preferred.

However, even if the data in Fig. 4 were arbitrarily displaced by 5 mdeg, they would still fall outside of the shaded area. Thus, it is concluded that, irrespective of any systematic error which may be associated with the measurement of the pressure, the relative change of T_c for indium and tin is significantly smaller than would be expected from previous low-pressure determinations of the initial pressure dependences.

Fortunately, this problem associated with the correct *absolute* pressure dependence of T_c for indium does not enter into the investigation of the nonlinear contribution to ΔT_c and its change upon alloying since this may be treated as being a *relative* effect. Consequently, the changes in $(\partial T_c/\partial P)_{P=0}$ and the nonlinear contribution $\Delta' T_c$ due to alloying have been resolved by subtracting a pure indium "background," given by $\Delta T_c = 17.96\Delta V/V$, from the measured ΔT_c. It will be noted that the 3 mdeg intercept has not been included in this "background." It was felt that it was more appropriate to omit this contribution to ΔT_c in view of its most likely origin being a small difference in the pressure experienced by the indium and the tin manometer and there being no reason to suppose that the same pressure differential would exist for the alloys.

Unfortunately, since the required information on the compressibilities of the alloys is not available, it has been necessary to present the data for their $\Delta' T_c$ as a function of pressure instead of volume compression.

3.2.2. Indium–Cadmium Alloys

The $\Delta' T_c$ for the indium–cadmium alloys are shown in Fig. 5. With the exception of three of the data points for the 0.5 at. % alloy the scatter in the data is similar to that for pure In (2–3 mdeg). Only the data for the 1.0 at. % alloy extrapolate to a significant nonzero intercept at zero pressure (although the scatter in the low-pressure data for the 0.5 at. % alloy may mask a possible nonzero intercept here also), which would suggest that the pressure differential between the sample and the tin is no longer present, or is at least reduced.

Clearly, both $(\partial T_c/\partial P)_{P=0}$ and $\Delta' T_c$ are altered from that of indium by alloying with the cadmium. The change in the initial pressure dependence of T_c, given by $(\partial \Delta' T_c/\partial P)_{P=0}$, is seen to be small for the addition of 0.5 and 1.0 at. % Cd, but shows a marked increase for additions of 1.5, 2.0, and 2.5 at. %. This dependence of $(\partial \Delta' T_c/\partial P)_{P=0}$ upon cadmium concentration is displayed in Fig. 1, where it may be compared with the form of the variation* reported by Makarov and Volynskii.[12] Apart from a slight horizontal shift, the overall agreement in the shape and magnitude of the change in the initial pressure dependence of T_c is good.

Returning to Fig. 5, it can be seen that the peak in $\Delta' T_c$ for In is displaced towards higher pressure in the alloys with 0.5, 1.0, and 1.5 at. % Cd, and a second peak appears at lower pressure. At 2.0 at. % Cd the double peak

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*Makarov and Volynskii give values of $(\partial T_c/\partial P)_{P=0}$ which were usually obtained from a single pressure measurement made at ~ 1.7 kbar. Since they determine $(\partial T_c/\partial P)_{P=0}$ for In to be -4.55×10^{-5} K·bar^{-1}, their data have been normalized to the present value of $(\partial T_c/\partial P)_{P=0}$ before making the comparison of the changes produced by alloying.
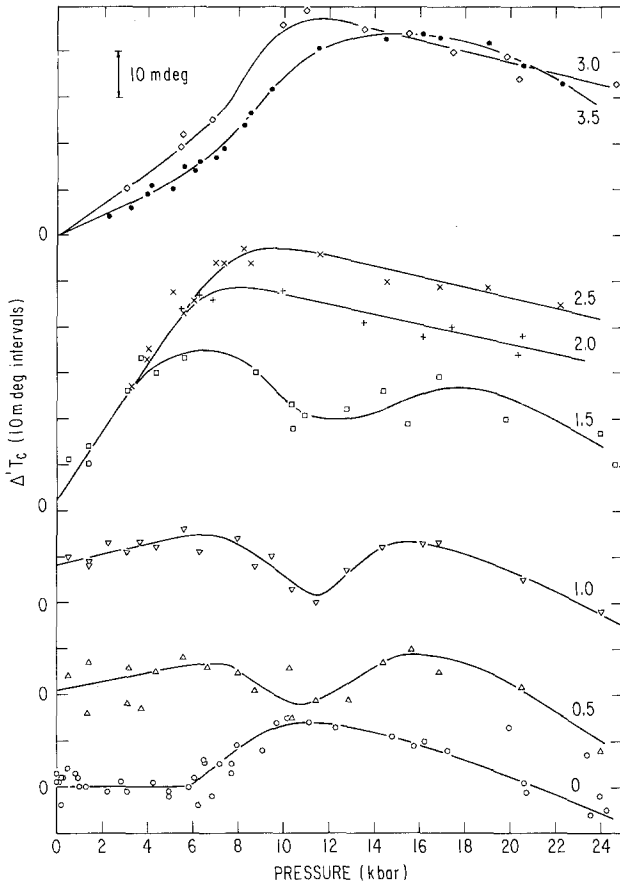
Fig. 5. Nonlinear contribution to ΔT_c as a function of pressure for In–Cd alloys. Numbers refer to the cadmium content in atomic percent.

structure is replaced by a more pronounced single peak, which moves to higher pressure as the cadmium content is increased.

3.2.3. Indium–Lead Alloys

The $\Delta' T_c$'s for the In–Pb alloys are shown in Fig. 6, where it may be seen that alloying has again changed the behavior from that for In. However, the changes are less complicated than for the cadmium. The peak in $\Delta' T_c$ is displaced towards lower pressure and then gradually broadens almost to the point of disappearing by about 6 at. %, only to rapidly reappear as further lead is added. The corresponding variation of $(\partial \Delta' T_c/\partial P)_{P=0}$ with lead content, shown in Fig. 2, has two rather abrupt changes at ~ 2 and ~ 7 at. %.
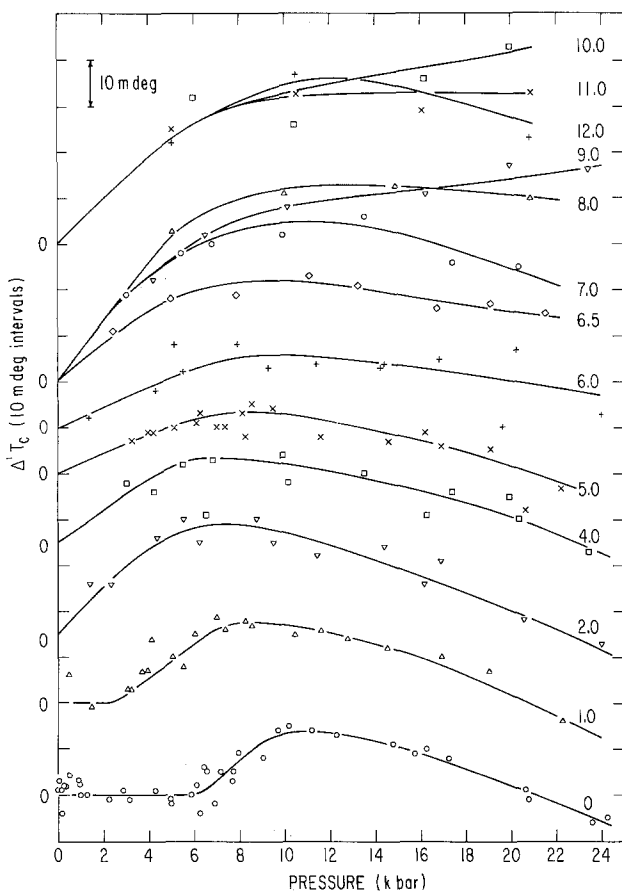
Fig. 6. Nonlinear contribution to ΔT_c as a function of pressure for In–Pb alloys. Numbers refer to the lead content in atomic percent.

On comparing this behavior with that reported by Makarov and Volynskii,[12] good agreement is found for the alloys with less than 6 at. %, but there is no indication of the second increase in their data, which extends to 8 at. % Pb.

Measurements of the pressure dependence of T_c have been previously made[31] to 15 kbar for a number of In–Pb alloys with concentrations up to 10 at. % Pb. Unfortunately, the data are not sufficiently detailed to provide a comparison with those given in Fig. 6, and the presented values for $(\partial T_c/\partial P)_{P=0}$ follow a rather erratic variation with alloy composition, which only loosely approximates the changes shown in Fig. 2.

4. DISCUSSION

It is evident from Figs. 1, 2, 5, and 6 that the change of T_c with pressure for In, dilute In–Cd, and In–Pb alloys includes a number of admittedly small, but quite distinct features. In the following discussion it will be assumed that these features are the result of changes in the Fermi surface topology, and they will be used to characterize the general nature of the changes responsible. The interpreted behavior will then be discussed in relation to the known Fermi surface and a calculated band structure for indium.

The contributions to T_c and $\partial T_c/\partial P$ due to the passage of the Fermi energy E_f through critical points in the energy spectrum were first discussed by Makarov and Bar'yakhtar[6] and later by Higgins and Kaehn.[7] The appropriate expressions, taken from the paper by Higgins and Kaehn, are

$$T_c = T_{c0} \exp \{F[\Delta N(E_f), T_c]/2N_0(E_f)\} \tag{1}$$

where

$$F[\Delta N(E_f), T_c] = \int_{-k\theta_D}^{k\theta_D} [\tanh(|E|/2kT_c)/|E|]\Delta N(E_f - E)\, dE \tag{2}$$

and

$$\partial T_c/\partial P = [(T_{c0}\partial E_f/\partial P)/2N_0(E_f)](dF/dE_f)[\Delta N(E_f), T_{c0}] \tag{3}$$

where

$$(dF/dE_f)[\Delta N(E_f), T_{c0}] = \int_{-k\theta_D}^{k\theta_D} [\tanh(|E|/2kT_{c0})/|E|]d/dE_f)\Delta N(E_f - E)\, dE \tag{4}$$

T_{c0} is the transition temperature of the pure metal at zero pressure, $N_0(E_f)$ is the "background" density of states, which is taken to be constant over the energy range $\pm k\theta_D$ about the Fermi energy E_f, and $\Delta N(E_f)$ is the rapidly varying part of the density of states due to the singularity. With a simple quadratic approximation for the form of the electron dispersion at the singularity energy E_c, $\Delta N(E_f)$ is given by

$$\Delta N(E_f) = (\sqrt{2}\pi^2\hbar^3)^{-1}(m_1 m_2 m_3)^{1/2}(E_f - E_c)^{1/2} \tag{5}$$

for $E_f > E_c$ and zero for $E_f < E_c$, where the m_i are the effective mass components on the electron surface involved in the transition. The four possible types of critical point, not counting band degeneracy, are associated with saddle points of indices 1 and 2 and a local minimum or a local maximum in $E(k)$. The respective contributions to the density of states are given by the appropriate combination of the sign of $\Delta N(E_f)$ with that of the energy difference $E_f - E_c$. Thus, if E_f increases relative to E_c to pass through a local minimum (maximum) a new surface is formed (destroyed), while passage through a saddle point of type $S_2(S_1)$ results in the formation (disruption) of a "neck," i.e., the transition from a closed to an open section of Fermi

surface (or vice versa). For E_f decreasing relative to E_c, the reverse transitions will occur.

The integrals (2) and (4) have been evaluated numerically using a free-electron approximation for $N_0(E_f)$ and assuming isotropic electron masses, i.e., $m_1 = m_2 = m_3 = m^*$. The resulting forms for $\Delta'T_c$ and $\partial\Delta'T_c/\partial E_f$ as a function of E_f for $T_{c0} = 3.0$ K, $\theta_D = 200$ K, and $m^*/m = 0.2$ (m is the average electron mass) are shown in Fig. 7. Makarov and Bar'yakhtar,[6] in a schematic representation of these curves, show the broadening of the divergent singularity in $\partial\Delta'T_c/\partial E_f$ to be of order $2k\theta_D$, presumably based upon the effective range of the electron–phonon interaction, whereas, in fact, due to the rapid variation of $(\tanh|E|/2kT_c)/|E|$ with energy, the calculation reveals a considerably smaller broadening of order several kT_c, as noted previously by Higgins and Kaehn.[7] These latter authors have pointed out that, in alloys, the impurity scattering of the electrons will constitute a far more important source of broadening of the details in the T_c behavior. However, experimental observations[12] of $(\partial T_c/\partial P)_{P=0}$ as a function of resistance ratio for indium alloys would indicate that the effect of the
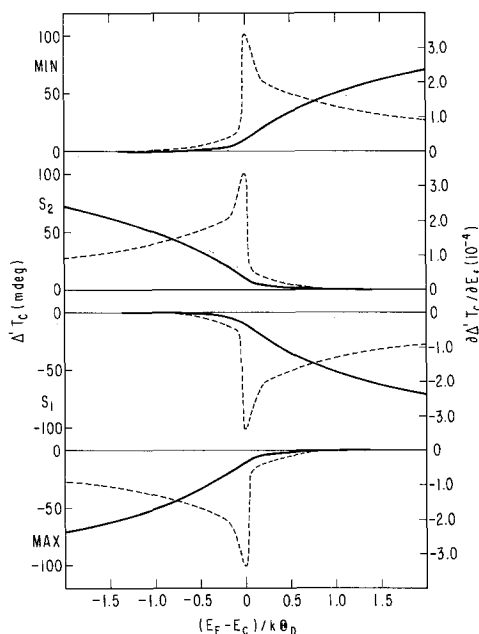

Fig. 7. Energy dependences of $\Delta'T_c$ (solid line) and $\partial\Delta'T_c/\partial E_f$ (broken line) as E_f passes through the critical point energy E_c. S_2 and MIN are contributions associated with changes to an electron surface and S_1 and MAX with changes to a hole surface.

impurity scattering is not as drastic as their theoretical model would predict. For the purpose of the present discussion, which will be of a qualitative nature, the forms shown in Fig. 7 will be regarded as being representative enough for the characterization of the experimental observations, but it should be kept in mind that broadening is to be expected. Furthermore, it will be assumed that the relative separation of the Fermi energy and a critical point energy will vary smoothly with pressure or electron concentration n such that any singularities in $T_c(P, n)$ may be associated directly with $T_c(E_f)$.

Considering first the variation of $(\partial \Delta' T_c / \partial P)_{P=0}$, Figs. 1 and 2 indicate the occurrence of singularities in the Fermi surface topology for indium alloys containing approximately 1.5 at.% Cd, 2 at.% Pb, and 7 at.% Pb. Comparing the shape of $(\partial \Delta' T_c / \partial P)_{P=0}$ for the cadmium alloys with the theoretical forms in Fig. 7 (remembering E_f is decreasing with increasing Cd content*) would point to the passage of the Fermi energy through a saddle point of the type S_2, corresponding to the breaking of an electron neck. In the case of the In–Pb alloys both transitions are identifiable with the increasing Fermi energy passing through energy minima to form two new electron surfaces.

*With the exception of the transition at ~ 7 at.% Pb, where it will be seen that $\partial E_f / \partial P \sim 0$, the assumption that pressure increases E_f relative to E_c leads to the most consistent description of the transitions. This may not always be the situation, and a choice of the appropriate sign for $\partial E_f / \partial P$ should be made on the basis of the observed behavior.
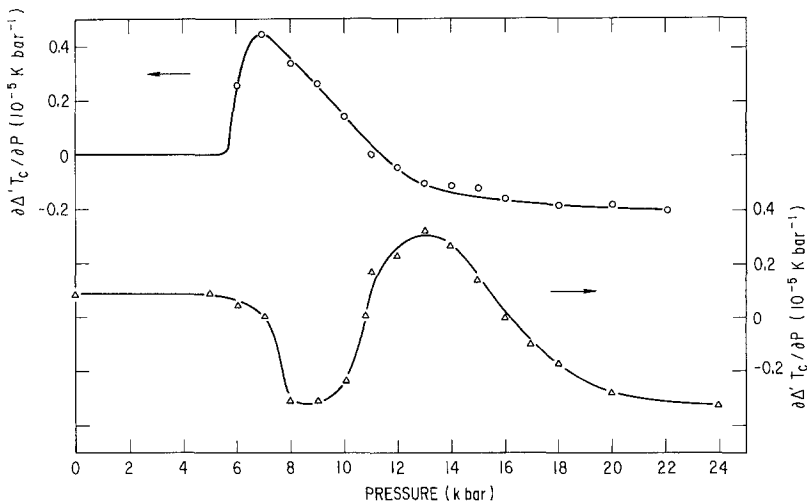

Fig. 8. $\partial \Delta' T_c / \partial P$ as a function of pressure for In (upper plot) and In–0.5 at.% Cd (lower plot) as determined graphically from the plots of $\Delta' T_c(P)$ given in Fig. 5.

Turning now to the plots of $\Delta'T_c$ as a function of pressure (Figs. 6 and 7), the situation is found to be somewhat more complex than a considera-tion of $(\partial\Delta'T_c/\partial P)_{P=0}$ alone would imply. With the addition of lead the pressure-induced transition in indium moves to lower pressure and ulti-mately gives rise to the singularity in $(\partial\Delta'T_c/\partial P)_{P=0}$ seen at 2 at. % Pb. This correspondence between the application of pressure and the addition of Pb for driving E_f through the critical energy is clearly seen by comparing the shape of $\partial\Delta'T_c/\partial P$, determined graphically from $\Delta'T_c(P)$, as a function of pressure for In shown in Fig. 8 with the form of $(\partial\Delta'T_c/\partial P)_{P=0}$ as a function of concentration shown in Fig. 2.

On the other hand, the sharp increase in the initial pressure dependence found at 7 at. % Pb would appear to be associated with the growth of a new peak in $\Delta'T_c$ as the lead content is increased, rather than a pressure-dependent transition passing through the pressure origin. This is more clearly illus-trated in Fig. 9, where isobars of $\Delta'T_c$ as a function of lead concentration have been constructed. Indeed, the transition is relatively insensitive to pressure and does not exhibit the displacement in concentration which would be expected if the application of pressure substantially changed the position of E_f relative to the critical energy. Furthermore, while the movement of the 2 at. % Pb transition with pressure is clearly seen in the isobars, there is also evidence of a small, essentially pressure-independent contribution to $\Delta'T_c$ close to this composition.
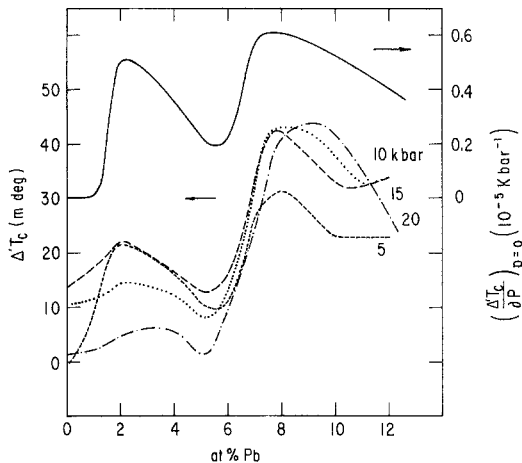
Fig. 9. Isobars for $\Delta'T_c$ for In–Pb alloys as a function of concentration generated from the plots of $\Delta'T_c(P)$ given in Fig. 6. Numbers indicate pressure in kilobars. Upper curve shows $(\partial\Delta'T_c/\partial P)_{P=0}$ for In–Pb alloys.

Alloying with cadmium moves the pressure-induced transition in indium to higher pressure and therefore compliments the behavior noted for the initial addition of lead. However, it is also seen that the addition of Cd results in the appearance of a new peak in $\Delta'T_c$ at lower pressure, indicating a further transition—evidence of which was not seen in the plot of $(\partial\Delta'T_c/\partial P)_{P=0}$. Comparing the form of $\Delta'T_c(P)$ with the curves in Fig. 7 indicates that this transition is associated with the change of a hole surface. More specifically, the shape of the derivative of $\Delta'T_c(P)$ as a function of pressure for the 0.5 at. % alloy (Fig. 8) points to the transition being of the type S_1: the breaking of a hole neck. Since there is no indication of such a hole surface transition in pure In it must be further concluded that the surface is normally closed and only becomes connected when the Fermi level is lowered by the addition of Cd. The applied pressure then depresses the newly opened band below E_f severing the connection. Furthermore, the top of this energy band, once opened, would appear to adjust in energy with the further addition of cadmium to maintain a constant separation from E_f, since the pressure required to close it is independent of the cadmium content.
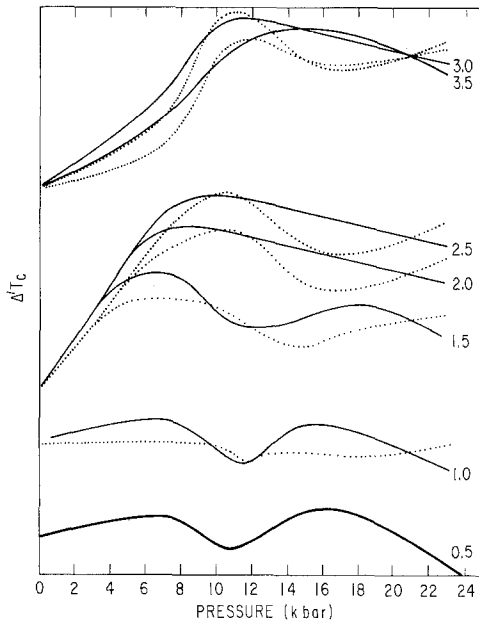

Fig. 10. Plots of $\Delta'T_c$ for In–Cd alloys (————) from which the curve for the 0.5 at. % alloy has been subtracted (·····) to show the development of the contribution to $\Delta'T_c$ at higher Cd compositions.

As the cadmium content increases beyond 1 at. %, $\Delta'T_c$ is dominated by the occurrence of the transition identified with the breaking of an electron neck. In an attempt to resolve the contribution to $\Delta'T_c$ from this transition, the smooth curve representing $\Delta'T_c$ for the 0.5 at. % Cd alloy has been subtracted from the curves drawn through the data for the higher concentrations. Although a somewhat arbitrary and far from satisfactory procedure, it does provide a clearer picture of the development of the transition, as illustrated in Fig. 10. The displacement of the transition to higher critical pressures as the cadmium content increases is quite distinct. Thus, the pressure may be regarded as effecting the "repair" of the electron neck.

To summarize, the changes in the Fermi surface topology of indium induced by alloying, pressure, or a combination of the two, which have been deduced from the measurements of T_c, are as follows.

On lowering E_f: (a) The connection of a hole surface ($\lesssim 0.5$ at. % Cd), which may be disrupted by pressure (~ 8 kbar); (b) the disruption of an open electron surface ($\gtrsim 1.5$ at. % Cd), which may be reconnected by pressure (> 5 kbar).

On raising E_f: (c) the formation of a new electron surface (~ 2 at. % Pb), which may also be formed by pressure alone (~ 6 kbar); (d) the formation of a further electron surface at 7 at. % Pb, independent of applied pressure.

The transitions (b) and (c), as produced by alloying, have been previously suggested by Makarov and Volynskii[12] from their studies of the initial pressure dependence of T_c for indium alloys. Transition (b) has also been inferred from measurements[32] of the uniaxial strain dependence of T_c for In–Cd whiskers.

Before examining to what extent these proposed transitions are consistent with the present knowledge of the band structure and Fermi surface for indium, it is appropriate to survey the additional evidence for their existence, which may be seen in other physical properties.

Irregularities in the composition dependence of the lattice spacing in solid solutions have long been recognized as indicative of the interaction and overlap of the Fermi surface at a face of the Brillouin zone.[33] Abrupt changes in the composition dependence of c/a have been reported for indium alloys at[15] ~ 8 at. % Pb and[14] ~ 2 at. % Cd. Anomalies or marked features in other physical properties which have been attributed to changes in the Fermi surface are quite numerous and include: (i) thermoelectric power close[13] to 5 and 7 at. % Pb; (ii) critical magnetic field at absolute zero, coefficient of the electronic specific heat and the Ginzburg–Landau parameter (as derived from magnetostriction and magnetization measurements) at[18,21] ~ 7 at. % Pb; (iii) magnetic susceptibility at[17] ~ 2 at. % Cd and ~ 5 at. % Pb; (iv) the anisotropy of the electrical and thermal conductivity at 3.5 and 7 at. % Pb.[16] Finally, low-temperature heat-capacity measure-
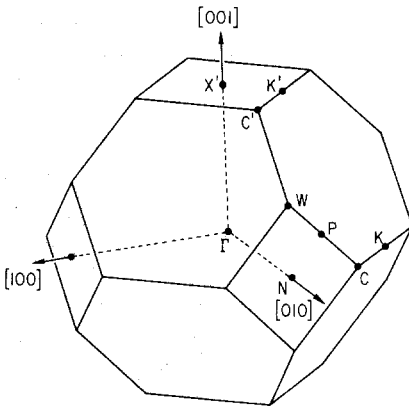
Fig. 11. Brillouin zone for indium with various symmetry points indicated.

ments[19] for a range of In–Cd and In–Sn alloys (the latter are isoelectronic with In–Pb and therefore may be expected to exhibit similar behavior) reveal abrupt changes in the electron concentration dependence of the electronic density of states consistent with sudden changes in the number of electron states at ~ 2 at. % Cd and ~ 9 at. % Sn and in the hole states close to pure indium.

Although admittedly circumstantial, the accumulated zero-pressure evidence for changes in the Fermi surface in the vicinity of the alloy concentrations given for (a)–(d) is quite impressive. However, it should be noted that a variety of interpretations have been made regarding the actual areas of the indium Fermi surface responsible for the transitions, not all of which are compatible with the present viewpoint. These differences will not be specifically discussed in what follows, since they are largely a question of personal opinion and will only be decided when more information is available; but reference will be made to those instances where there is concurrence with the present description.

It now remains to check the compatibility of the proposed transitions with what is known of the Fermi surface and band structure of indium. In the free-electron approximation the Fermi sphere will overlap the Brillouin zone (Figure 11) at the corner C' and will fall just inside it at the points W and C. (Due to the tetragonal distortion of the indium lattice from cubic symmetry, the corners C and C' are no longer equivalent.) Thus, there is a first zone which is almost full, having small hole pockets at W; a second-zone hole surface multiply connected at W; a third-zone electron surface consisting of two sets of arms, denoted as α and β, lying along the [110] and [101] edges, respectively, and connected at C'; and a fourth-zone electron pocket around C'. Of course, the detailed nature of the actual Fermi surface is expected to differ from that of the free-electron model and will depend
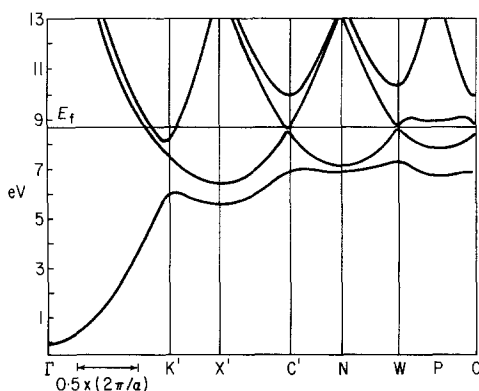
Fig. 12. Band structure for indium calculated by
Hughes and Shepherd.[34]

critically upon the position of the energy bands relative to the points C, C',
and W, the very regions most sensitive to the lattice potential. Experi-
mentally, it appears there are no holes in the first zone, nor electrons in the
fourth; the second-zone hole surface is closed, and the third-zone α arms are
absent. Several pseudopotential models have been proposed to describe the
various measured Fermi surface parameters, and the following comments
are based upon the band structure calculated by Hughes and Shepherd[34]
(Fig. 12).

The application of pressure will change the shape of the Fermi surface
for indium in two ways: by modifying the pseudopotential and thus moving
the energy bands relative to E_f (this will be particularly important at the
points C, C', and W), and by altering the distortion of the Brillouin zone
through the increase in c/a which occurs under pressure. Alloying will also
affect the shape of the Brillouin zone in addition to changing the Fermi
surface by moving the Fermi level because of the change in electron con-
centration. No appreciable shift in the relative positions of the energy bands
is expected for dilute alloys.

Referring to Fig. 12, the transitions (a)–(d) are explained as follows:
(a) is the result of the opening of the second-zone energy band W when the
Fermi level is lowered. This then requires that pressure lowers the second-
zone band relative to the Fermi level at this point. Furthermore, as noted
above, once opened the change in the axial ratio on further lowering of the
electron concentration must modify the distortion of the zone to as to main-
tain a fixed separation between the top of the band and the Fermi level. This
requirement is similar to a proposal of Svechkarev[35] in which the electronic
energy is minimized by the axial ratio adjusting to retain contact between
the Fermi surface and the zone corners. The further lowering of E_f will

result in the Fermi level falling below the third-zone band at C', causing the disruption of the β arms, which would account for the transition (b), as noted by Makarov and Volynskii.[12] It must then be assumed that pressure also depressed the third band to regain contact with the Fermi level.* Makarov and Volynskii actually associated the form for their data on $(\partial T_c/\partial P)_{P=0}$ in the In–Cd system with *two* transitions, which they described as the breaking of the β arms at ~ 1.3 at. % Cd and the destruction of small electron cavities at ~ 1.9 at. % Cd. Higgins and Kaehn[7] have identified the latter with a slight bulge at the corner of the β arms which nips off as the arms are broken. However, it is debatable whether the resolution of the data is sufficient to justify the significance which has to be attributed to the detailed shape of $(\partial T_c/\partial P)_{P=0}$ for such fine detail in its interpretation. If it is assumed that pressure will also lower the third-zone band at W (or C), overlap into the third zone could occur, which would be responsible for (c). Raising the Fermi level by the addition of electrons would decrease the pressure required to promote the transition and eventually result in overlap into the third zone at zero pressure. Further increase of E_f will ultimately produce overlap at P giving rise to (d). Since this latter transition was found to be essentially independent of pressure, it must be assumed that this is also the case for the third-zone energy band at P.

As a final comment to the above discussion it is found that to achieve reasonable agreement between the size of the calculated $\Delta' T_c$ and those observed requires values for m^*/m in the range 0.1–0.2 (cf. Figs. 5 and 6 with Fig. 7). It is therefore significant to note that Hughes and Shepherd[34] give $\sim 0.2 m_e$ for the electron mass at the junction of the β arms, which when combined with the overall average mass of $1.32 m_e$, determined from the electronic specific heat,[19] gives $m^*/m \sim 0.15$.

While it has been demonstrated that the proposed changes in the Fermi topology of indium resulting from either a change in the electron concentration by alloying or by applying pressure are consistent with the known details of its Fermi surface, this does not prove that they actually occur. To do this a more direct measure of the Fermi surface geometry is required, and it is hoped that these predictions will provide the incentive for such measurements to be undertaken.

*The growth under pressure of the cross-sectional area of the β arms at K indicates that at this point, at least, pressure lowers the energy of the third band relative to E_f.[36]

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