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Alloy Fermi-Surface Topology Information from Superconductivity Measurements under Pressure*

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A modified BCS gap equation is used to obtain an approximate solution for the pressure derivative of the superconducting transition temperature, dT_c/dp, at values of the Fermi energy E_F near critical points in the density of states. dT_c/dp is a functional of the energy derivative of the density of states, and therefore reflects strong structure at values of E_F near the van Hove singularities in the density of states associated with a Fermi-surface topology change. The model is extended to include the case of a dilute random alloy system in which impurity scattering broadens the singularities. A Lorentzian spectral distribution is assumed, and an analytic equation is obtained for the broadened van Hove-singularity contributions to the density of states. The model is applied to the case of indium doped with cadmium, the rate of change of the Fermi energy with concentration being estimated from a free-electron formula, and the rate of change of the lifetime estimated from the residual resistivity. A qualitative fit between the model calculation and the structure of available dT_c/dp data requires the existence of two singularities: an electron saddle point disconnecting at 0.9 at.% Cd, and an electron sphere vanishing at about 1.6 at.% Cd. A quantitative calculation is made of the variation of dT_c/dp with alloy concentration, assuming only the empirically determined singular points, and deriving all other quantities from available indium Fermi-surface information on the third-band ring. The model calculation gives surprising quantitative agreement with the data, suggesting that valuable information on the Fermi-surface topology of dilute alloys can be obtained from measurements of dT_c/dp as a function of concentration.

INTRODUCTION

THE problem of the electron energy-band structure of a random alloy has been of interest ever since the discovery that many features of alloy phase diagrams and other physical properties are correlated with the number of conduction electrons available to fill energy bands.[1] Although some of the correlations were later found to be accidental,[2] spurious,[3] or inconsistent[4] with recent direct Fermi-surface (FS) measurements in pure metals, the extent to which conduction electron concentration determines physical properties in an alloy remains of interest. The problem is essentially how to modify the Bloch representation in a disordered lattice, since most metallic properties (except those strongly influenced by impurity scattering) are not greatly altered by the lack of a perfect lattice.

Direct methods to measure FS geometry in pure metals[5] have become refined to the point where they serve as stringent tests for refining energy-band calculations.[6] With pure-metal band structures well understood, progress in alloys has been renewed on firmer ground. In alloy theory, several authors[7-9] have applied Green's-function techniques to modify the Bloch representation to take proper account of impurity scattering. Theoretical progress has been accompanied by a search[10] for measurements which give unambiguous information about alloy electronic structure.

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* Research supported by the National Science Foundation and by the Research Corporation.

[1] For a review, see W. Hume-Rothery, *Atomic Theory for Students of Metallurgy* (Institute of Metals, London, 1962), 3rd ed.

[2] T. B. Massalski and C. S. Barrett, Trans. AIME **209**, 455 (1957).

[3] W. J. Helfrich and R. A. Dodd, Acta Met. **12**, 667 (1964).

[4] W. Hume-Rothery and D. J. Roaf, Phil. Mag. **6**, 55 (1961).

[5] See, e.g., *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (Wiley-Interscience, Inc., New York, 1960).

[6] See, e.g., W. A. Harrison, *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, Inc., New York, 1966).

[7] H. Jones, Phys. Rev. **134**, A958 (1964).

[8] P. Soven, Phys. Rev. **151**, 539 (1966).

[9] Edward A. Stern, Phys. Rev. **168**, 730 (1968).

[10] R. G. Chambers, in *The Simon Fraser University Lectures on Solid State Physics*, edited by J. F. Cochran and R. R. Haering (Gordon and Breach, Science Publishers, Inc., New York, 1968), Vol. 1.

Some progress has been made[11–14] in extending direct FS measurements such as the de Haas–van Alphen (dHvA) effect into dilute alloys, using high magnetic fields and sensitive measurement techniques to overcome the amplitude reduction caused by impurity scattering. (The effect requires $\omega_c\tau > 1$, where ω_c is the cyclotron frequency eH/m^*c, and τ is the lifetime of an electron in a cyclotron orbit between scattering events.) But, since direct FS measurements in alloys are difficult, an alternative measurement is desirable to select interesting alloy systems. If one's concern is with alloy FS topology, the measurement should be unambiguously related to the electronic density of states; hence it should show structure due to van Hove singularities as the Fermi energy E_F is varied with alloy composition. One promising candidate is considered below: the precise measurement of superconducting transition temperature T_c and especially the pressure derivative dT_c/dp. In Sec. I, a simple model based on the BCS theory is developed which shows that dT_c/dp is essentially proportional to the energy derivative of the electronic density of states $dN(E_F)/dE_F$; hence in a system with no scattering dT_c/dp would show strong singularities ($\propto E^{-1/2}$) at critical points in the energy spectrum. The essential features of alloy electronic structure are incorporated by allowing a state of energy E to be broadened by $\hbar/\tau$, where the lifetime τ is estimated from residual resistance measurements. This feature produces a major modification in the density of states near critical points, and results in substantial broadening of the structure in dT_c/dp versus alloy composition.

The model is applied in Sec. II to In doped with Cd. This system was chosen because reproducible T_c[15,16] and dT_c/dp[16] data exist and show strong composition dependence below 2 at.% Cd. Considerable speculation exists that anomalies in this and other physical properties[17] at this composition indicate a change in the In FS topology. Reliable information about singularities in the alloy density of states may also prove useful in understanding the phase change[18] from face-centered tetragonal to fcc which occurs at about 4 at.% Cd (at 25°C), especially since In is a nearly-free-electron-like metal for which pseudopotential methods are applicable. In the present paper, it is shown that, within the framework of the model developed in Sec. I, there is an unambiguous quantitative agreement with the dT_c/dp data.[16] The data are consistent with the disappearance of an electron saddle point at about 0.9% Cd and suggest the disappearance of an electron pocket at about 1.6% Cd. Impurity broadening effects play an important role in providing a quantitative fit to the data. The interpretation is consistent with a recent band calculation for In.[19] However, since In is borderline between a weak coupling (BCS) and strong coupling superconductor, as discussed in the Appendix, the simple theory of Sec. I may not be precisely applicable. But the model has the virtue of intuitive simplicity, and since it predicts FS topology changes at a low enough composition for direct dHvA measurements, there exists a direct way of testing the general validity of the model and its applicability to In alloys.

I. STRUCTURE IN dT_c/dp DUE TO IMPURITY-BROADENED VAN HOVE SINGULARITIES IN THE DENSITY OF STATES

If, under pressure, the FS topology of a pure metal changes, there is a van Hove singularity in the density of states which is reflected in many physical properties.[20] This approach has been generalized to include the properties of nonsuperconducting impure metals.[21] Anomalies in the superconducting transition temperature of *pure* metals under pressure have been treated[22] by a modification of the BCS equation, which separates off a small singular part of the density of states from the slowly varying background. In the treatment below, we find an explicit, though approximate, solution to the integral equation developed in Ref. 22. We find the structure in T_c as a function of Fermi energy near singular points to be broadened in energy by about kT_c in pure metals ($kT_c \cong 3\times10^{-4}$ eV for In). The predominant broadening mechanism in alloys is impurity broadening of the van Hove singularities in the density of states ($\cong 5\times10^{-3}$ eV in the case considered in Sec. II). An explicit form for the impurity-broadened density of states is developed which is applicable to the four most typical topology changes.

In the calculation below, the Fermi energy is viewed as a parameter which can be varied experimentally either by alloying or by external pressure p. Therefore, measurement of dT_c/dp as a function of impurity concentration X is essentially a modulation or derivative technique, which enhances fine structure in $T_c(X)$.

The solution of the BCS gap equation for T_c must be modified when the Fermi energy E_F is near a singular point in the density of states $N(E)$ of the normal metal,

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[11] R. J. Higgins and J. A. Marcus, Phys. Rev. **141**, 553 (1966).

[12] J. P. G. Shepherd and W. L. Gordon, Phys. Rev. **169**, 541 (1968).

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[17] I. V. Svechkarev, Zh. Eksperim. i Teor. Fiz. **47**, 960 (1964) [English transl.: Soviet Phys.—JETP **20**, 643 (1964)]; B. I. Verkin and I. V. Svechkarev, *ibid.* **47**, 404 (1964) [English transl.: *ibid.* **20**, 267 (1964)].

[18] Theo Heumann and Bruno Predel, Z. Metallk. **53**, 240 (1962).

[19] N. W. Ashcroft and W. E. Lawrence, Phys. Rev. **175**, 938 (1968).

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[22] V. I. Makarov and V. G. Bar'yakhtar, Zh. Eksperim i Teor. Fiz. **48**, 1717 (1965) [English transl.: Soviet Phys.—JETP **21**, 1151 (1965)].

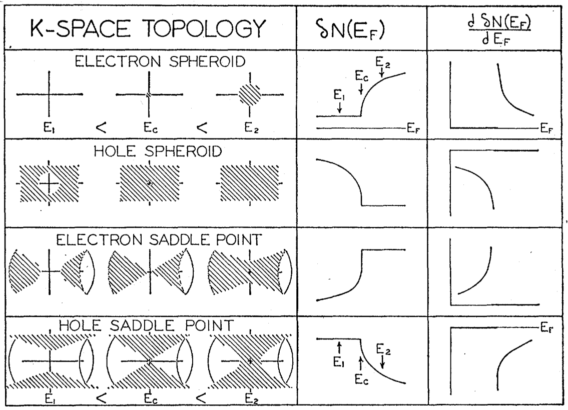

FIG. 1. FS topology changes and the associated van Hove singularities in the density of states and its energy derivative. The notation is that of Eq. (1), where δN is normally a small fraction of the total density of states in a multiband metal.

since the assumption that $N(E)$ is constant over an energy range $E_F \pm k\Theta_D$ (where Θ_D is the Debye temperature) is no longer valid. It is convenient to break up $N(E_F)$ into two parts,

$$N(E_F)=N_0(E_F)+\delta N(E_F), \tag{1}$$

where $N_0(E_F)$ is essentially constant over energies within $k\Theta_D$ of E_F, and $\delta N(E_F)$ contains any rapid variation due to van Hove singularities. $\delta N(E_F)$ may correspond to the least occupied band in a multiband metal, but its precise definition is irrelevant since the final result involves only the slope $d[\delta N(E_F)]/dE_F$. The four possible (barring band degeneracy) van Hove singularities in the density of states are shown in Fig. 1. Their algebraic form is

$$\delta N(E_F)=(\sqrt{2}/\pi^2\hbar^3)(m_1m_2m_3)^{1/2}(E_F-E_c)^{1/2} \tag{2}$$

for energies $E_F > E_c$, and zero for energies $E_F < E_c$. Appropriate permutations in the sign of δN and of the energy generate the four classes of singularity shown in Fig. 1. The $m_i (i=1\text{–}3)$ are the effective-mass components in a quadratic expansion of $E(k)$ very near any of the singular points E_c in the density of states.

In order to extract the main qualitative features necessary to explain the dT_c/dp data,[16] the calculation is carried out within the framework of the BCS one-parameter model; e.g., electron-phonon coupling is constant within $\pm k\Theta_D$ of E_F and zero outside that range. The further assumption will be made that the electron-phonon coupling is unchanged within the range of alloy compositions of interest (up to 4% impurity). None of the essential conclusions is changed as long as the coupling constant is slowly varying compared to $\delta N(E_F)$.

Following Ref. 22, Eq. (1) is inserted into the BCS gap equation. The result is an integral equation for T_c;

$$T_c=T_c^0 \exp\frac{F[\delta N(E_F),T_c]}{2N_0(E_F)}, \tag{3}$$

where

$$T_c^0=1.13\Theta_D \exp[-1/\mathcal{V}N_0(E_F)] \tag{4}$$

and

$$F[\delta N(E_F),T_c] = \int_{-k\Theta_D}^{k\Theta_D} \frac{\tanh(|E|/2kT_c)}{|E|}\,\delta N(E_F-E)\,dE. \tag{5}$$

Here Θ_D is the Debye temperature, $\mathcal{V}$ is the electron-phonon pairing potential, T_c is the superconducting transition temperature to be determined, and T_c^0 is the transition temperature in the pure metal at atmospheric pressure.

It is easily shown that

$$dT_c/dp \cong \frac{\partial T_c}{\partial E_F}\frac{dE_F}{dp}+\frac{\partial T_c}{\partial \mathcal{V}}\frac{d\mathcal{V}}{dp}, \tag{6}$$

provided that the alloy band gaps vary slowly with impurity concentration (see the Appendix). In what follows we consider only the first term in Eq. (6), which will show structure due to FS topology changes. The second term is larger in magnitude, but is not likely to vary rapidly with alloying, since the fine details of FS topology affect the phonon spectrum and the electron-phonon coupling only slightly.[23] The first term in Eq. (6) may be evaluated from Eq. (3), using a first-order iteration of Eq. (5) which is valid provided that $N_0(E_F) \gg \delta N(E_F)$ (see the Appendix). The result is

$$\frac{dT_c}{dp}=T_c^0\frac{dE_F/dp}{2N_0(E_F)}\frac{dF[\delta N(E_F),T_c^0]}{dE_F}, \tag{7}$$

where

$$\frac{dF[\delta N(E_F),T_c^0]}{dE_F} = \int_{-k\Theta_D}^{k\Theta_D} \frac{\tanh(|E|/2kT_c^0)}{|E|}\frac{d}{dE_F}\delta N(E_F-E)\,dE. \tag{8}$$

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[23] Strongly impurity-dependent terms due to the response in $\mathcal{V}$ to singular points in the electronic density of states are of higher order than the first term in Eq. (6), because two successive averages are involved. Using the formalism of Ref. 38 [Eqs. (5), (15), (19), and (23)], the BCS $N_0\mathcal{V}$ is closely related to the average electron-phonon coupling constant λ (they are equal in the weak-coupled limit). Now λ is an average over the phonon spectrum of the phonon density of states $F(\omega_q)$ times the square of the electron-phonon interaction averaged over the Fermi surface $\alpha^2(\omega_q)$ with a weight factor ω_q^{-1}. Although the electronic structure affects the phonon spectrum ω_q, even so gross a feature as the FS itself produces a minor disturbance (the Kohn anomaly) in ω_q. The fraction of the FS which contributes to the singular points in question is really quite small (<0.1% of the FS area in the case of In). Subtle topological features in the FS could affect ω_q, but they are averaged twice in obtaining λ: once in obtaining $F(\omega_q)$ and a second average over ω_q in the integral for λ. Furthermore, that integral is weighted towards low-frequency phonons by the factor ω_q^{-1}, which weighs against phonons influenced by the electron FS. Thus, a single derivative of the second term in Eq. (6) is unlikely to bring out structure due to singular points in the electronic density of states.

Therefore, the shape of dT_c/dp as a function of impurity composition reflects the energy dependence of the *slope* of the singular part of the density of states $[\propto (E-E_c)^{-1/2}]$. The effect of the convolution integral in Eq. (8) is to broaden the structure by an amount of order kT_c^0, so that dT_c/dp does not diverge at critical points E_c.

In the alloy systems of interest, however, the van Hove singularities in the density of states are blurred by impurity scattering; this broadening will be shown to be far more important than the kT_c broadening discussed above. The algebraic form of the singularities written in Eq. (2) is correct only when E is an eigenstate of wave vector k. In an impure system, there is scattering, and the amplitude to be in a state k decays with time. This may be represented by a complex energy

$$E(k) \rightarrow E(k)+\Sigma(k)+i\Gamma(k), \tag{9}$$

where $E(k)$ is the quasiparticle dispersion relation in the pure system, and $\Sigma(k)$ and $\Gamma(k)$ are the real and imaginary parts of the self-energy change due to the added impurities.[24] In what follows, it is assumed that $\Sigma(k)$ and $\Gamma(k)$ are dependent only on E (surfaces of constant energy unchanged in shape by alloying, and relaxation-time isotropic on any energy surface). This allows us to absorb $\Sigma(k)$ into $E(k)$ for computational simplicity[25]; note that the location of the critical points E_c in alloys does not locate critical points in the pure metal density of states until $\Sigma(E)$ has been determined. As is well known for the impurity problem,[24] E and k are now connected by a spectral distribution function

$$\delta[E'-E(k)] \rightarrow \frac{1}{2\pi}\frac{\Gamma}{[E'-E(k)-\Sigma]^2+(\frac{1}{2}\Gamma)^2}. \tag{10}$$

Physically, a quasiparticle in an alloy in state k does not have a uniquely defined energy, since a state which had energy E_F in the pure system now has a finite lifetime $\hbar\tau = /\Gamma(E_F)$. This broadens the van Hove singularities; the square-root density of states [Eq. (2)] is convoluted with a Lorentzian:

$$\delta N(E_F-E_c,\Gamma) = \frac{\Gamma}{2\pi}\frac{\sqrt{2}(m^*)^{3/2}}{\pi^2\hbar^3} \times \int_{E_c}^{\infty} \frac{(E-E_c)^{1/2}dE}{(E_F-E_c-E)^2+[\frac{1}{2}\Gamma(E_F)]^2}. \tag{11}$$

This integral may be evaluated analytically[26]:

$$\delta N(E_F-E_c,\Gamma) = (\tfrac{1}{2}\sqrt{\Gamma})\frac{(m^*)^{3/2}}{\pi\hbar^3} \times [(1+\epsilon^2)^{1/4}\sin(\tfrac{1}{4}\pi-\tfrac{1}{2}\tan^{-1}\epsilon)]^{-1}, \tag{12}$$

where energy dependence is measured in units of the linewidth:

$$\epsilon = (E_F-E_c)/\Gamma(E_F). \tag{13}$$

The impurity-broadened density of states is shown in Fig. 2(a). Note that this is a universal curve valid whenever the spectral distribution function is Lorentzian, and involves no assumptions about how Γ and E_F vary with alloying. Equation (12) approaches $(E_F-E_c)^{1/2}$ as E_F approaches infinity, and approaches $\frac{1}{4}\Gamma(E_F-E_c)^{-1/2}$ for E_F far below E_c, where there were no states in the pure system.

The evaluation of dT_c/dp via Eq. (7) involves the energy derivative of Eq. (12), shown in Fig. 2(b). The strong $E^{-1/2}$ singularity is removed by impurity scattering, but the sign and shape of the curve still determine a unique correspondence with the type of van Hove singularity, as in the pure system (Fig. 1).

II. APPLICATION TO INDIUM DOPED WITH CADMIUM

A. Density-of-States Information from dT_c/dp Measurements

The general results of Eqs. (7), (8), and (12) are applied in this section to the example of In-Cd alloys. Fermi-energy changes (measured from the bottom of the first band) are estimated from the free-electron

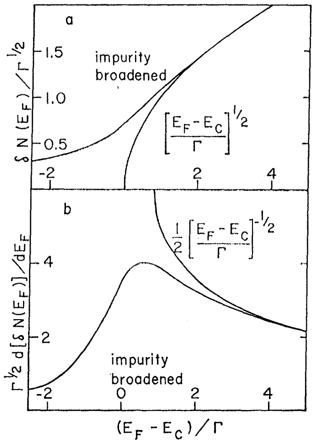

FIG. 2. Impurity-broadened density of states (a) [Eq. (12)] and its energy derivative (b) near a singular point E_c, when the spectral distribution function connecting k and E is Lorentzian. The curves are plotted in appropriate units so that they are functions only of the dimensionless energy (measured in units of the imaginary part of the self-energy, or scattering linewidth). For comparison, the familiar square-root density of states and its energy derivative are also plotted in the same units. Impurity scattering is seen to remove the singularity in slope at E_c and to produce below E_c a nonvanishing density of states, which decreases as $(E_c-E_F)^{-1/2}$.

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[24] L. P. Kadanoff and G. Baym, *Quantum Statistical Mechanics* (W. A. Benjamin, Inc., New York, 1962), p. 28.

[25] Relaxing the isotropy restriction on Σ would allow the effective-mass parameters in Eq. (2) to change, which affects only the amplitude of the result and not the energy dependence. Anisotropy in $\Gamma(k)$ would further smear the structure in dT_c/dp.

[26] We are indebted to Professor J. W. McClure for carrying out this integral. Although the form of the result is quite different from that used earlier (Ref. 21), we find the two to be numerically identical.

formula, as is justified by the recent band-structure calculation,[19] which found a value of E_F within 1% of the free-electron value, and by the successful use of changes in the free-electron Fermi energy to interpret recent FS measurements[14] in this alloy system. For the conduction-electron concentration, we take 3.00 for In and 2.00 for Cd, which is consistent with the pure-metal band structures and the existing alloy FS measurements.[14] In evaluating the imaginary part of the self-energy, perturbation theory is not valid (charged impurities), and, rather than perform a detailed phase-shift analysis or Green's-function calculation, we prefer to rely on experiment and estimate Γ from the measured[15] residual resistance ratio as a function of composition. The value of Γ obtained is likely to be an underestimate, since small-angle scattering events which shorten the lifetime of the state do not affect the resistivity. The estimates which result are

$$dE_F/dX = -0.0051 \text{ eV/(at.\% Cd)},$$
$$d\Gamma/dX = +0.0039 \text{ eV/(at.\% Cd)}.$$

In evaluating the rate of change in E_F, changes in conduction-electron concentration, volume, and axial ratio have been taken into account.[14] In evaluating the rate of change in Γ, a free-electron conductivity expression with free-electron mass has been used, justified by the band-structure calculation,[19] which shows an average band mass near the free-electron value. Relaxation-time isotropy has been assumed. The numbers quoted above are precise but not necessarily accurate, because of these assumptions. What matters is the ratio of the two numbers which will be treated as a parameter for comparison with experiment. It is convenient to vary only $d\Gamma/dX$, with $d\Gamma_\sigma/dX$ being the value quoted above.

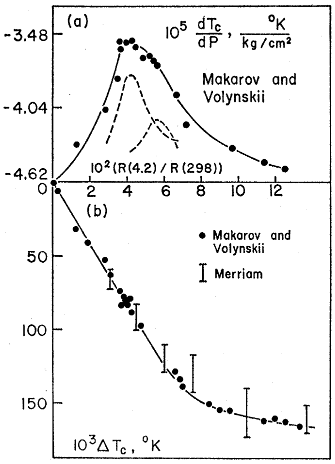

FIG. 3. Superconductivity data of Makarov and Volynskii (Ref. 16) for In alloys. (a) Pressure derivative of the superconducting transition temperature as a function of atomic percent Cd. The initial data, plotted as a function of residual resistance ratio, has been converted to impurity composition using $R(4.2\text{ K})/R(300\text{ K}) = 0.042$/at.% Cd (Ref. 16). The dashed curves were suggested by Makarov and Volynskii in interpreting their data. (b) Zero pressure change in the superconducting transition temperature, confirming Merriam's earlier work (Ref. 15) which led to the suggestion of a FS topology change in this system.

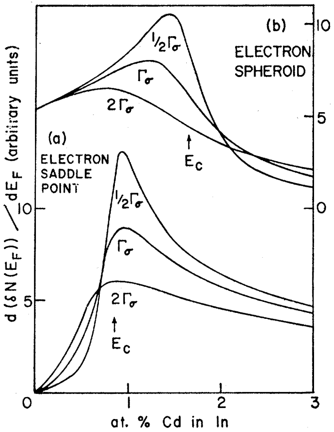

FIG. 4. Impurity-broadened density-of-states derivative as a function of Cd impurity content in In. The dT_c/dp data (Fig. 3) are consistent with an electron saddlepoint opening up at 0.9 at.% Cd and an electron spheroid disappearing at 1.6 at.% Cd. Starting from this postulate, the impurity-broadened density of states was calculated by computer from the derivative of Eq. (12), using a rate of change of Fermi energy E_F and linewidth Γ with impurity content estimated as described in the text. In order to check the estimates against experiment, curves were also calculated using values of Γ half and twice as large as that estimated from residual resistivity (Γ_σ in this figure). (a) Electron saddlepoint opening up at 0.85 at.% Cd ($\Delta E_F = -4.25 \times 10^{-3}$ eV). Arrows labeled E_c locate the critical points in the unbroadened density of states. (b) Electron spheroid disappearing at 1.65 at.% Cd ($\Delta E_F = -8.25 \times 10^{-3}$ eV).

The dT_c/dp data[16] which are to be interpreted is shown in Fig. 3(a). The predominant structure is a sharp, asymmetric positive peak, rising above a negative background.[27–29] The results of Sec. I show that singularities in the density of states are located by the *shoulders* or points of steep slope in dT_c/dp rather than by the peaks. Taking the data at face value, there is a pronounced shoulder at about 0.9% Cd, and a less pronounced shoulder at 1.6 at.% Cd. The sign and shape of the shoulder at 0.9 at.% Cd are consistent with the disappearance of an electron saddle point at this composition. This assignment may be made more quantitative by evaluating the impurity-broadened density of states [Eq. (12)] for such a topology change using the E_F and Γ values estimated above. The most striking aspect of the result [plotted in Fig. 4(a)] is that the

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[27] The observation that T_c decreases with increasing pressure is a common observation in the polyvalent metals (Ref. 28) and has to do with the electron-phonon coupling becoming weaker (lattice stiffer) more rapidly than the density of states $N(E_F)$ increases. This gross feature is described by the second term in Eq. (6), and is outside the scope of the theory of Sec. I. We will also not discuss the atmospheric-pressure variation of $T_c(X)$ [Fig. 3(b)] since the structure in that measurement is complicated by a rapid variation with composition (anisotropy effect; see Ref. 29), which, however, contributes only to the nearly constant background in dT_c/dp.

[28] J. L. Olsen and H. Rohrer, Helv. Phys. Acta 33, 872 (1960).

[29] D. Markowitz and L. P. Kadanoff, Phys. Rev. 131, 563 (1963).

curve does not fall to the $(E_F-E_c)^{-1/2}$ shape for compositions above the critical point. This is because Γ varies nearly as fast as E_F, so that the asymptotic limit of Fig. 2(b) is reached very slowly. Because of this, the model calculation requires that a second singularity must be added to fit the data. The more diffuse shoulder at 1.6 at.% Cd is consistent with the disappearance of an electron spheroid at that composition. The diffuseness makes the assignment less certain than for the saddlepoint at 0.9 at.% Cd, since the impurity broadening is nearly a factor of 2 larger. The appropriate derivative density-of-states curve for such a singularity is shown in Fig. 4(b). Here the asymptotic $E^{-1/2}$ limit of Fig. 2(b) is reached on the low-composition side, but the simultaneous changes in E_F and Γ skew the shape of the curve from that of Fig. 2(b). It is clear that the sum of such density of states derivatives (Fig. 4) has the right shape to account for the structure in dT_c/dp [Fig. 3(a)], and that the use of a lifetime determined from resistivity ($\Gamma=\Gamma_\sigma$) is in reasonable agreement with the experimental broadening.

B. Quantitative Estimate of dT_c/dp and the FS of Indium Alloys

Section II A demonstrated that the structure in dT_c/dp data is remarkably close to the shape of the energy derivative of an impurity-broadened density-of-states curve, using postulated topology changes in as yet unspecified bands and simple estimates of the rate of change of Fermi energy and Bloch-state lifetime due to alloying. We now show that the postulated topology changes are *the only ones* consistent with what is known about the FS of pure In, and the magnitude of the calculated dT_c/dp anomaly is in quantitative agreement with the data, with *no free parameters* except the concentrations at which topology changes are inferred.

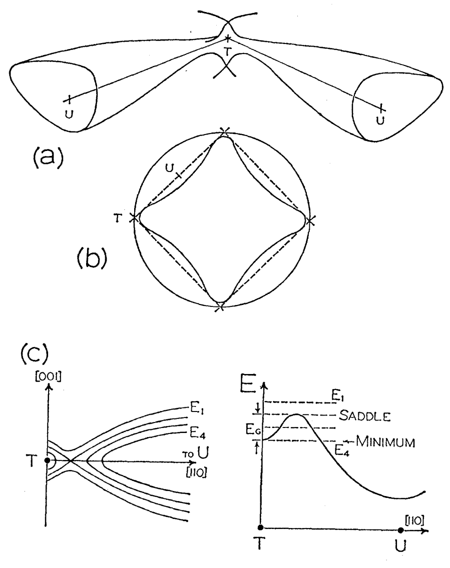

FIG. 5. Geometry of the third-band electron ring in In. (a) Perspective view looking towards the corner at T, showing the bulge in the [001] direction predicted by the band-structure calculation (Ref. 19). (b) View of the ring lying in the (001) plane. The T-U line is in the [110] direction. (c) Schematic equal-energy contours for a cross section perpendicular to the [110] direction, and dispersion relation in the T-U direction consistent with Fig. 5(a).

The FS of pure In consists of a full first band, a large second-band surface of holes, and a ring of electrons in the third band.[19] There may be small regions of contact of the second-band surface with the Brillouin zone,[19] though evidence for this is not consistent, and the feature may be removed by spin-orbit coupling.[30] This question is not relevant to the In-Cd system, since, if the contact exists in pure In, it would show up as a singularity in dT_c/dp data only with impurities of higher valence. The third-band electron ring, which is of most interest here, is shown in Fig. 5. The dominant effect with decreasing Fermi energy would be a decrease in size of the corners of the ring at T, followed by a pinching off of the ring into four disconnected ellipsoidal pieces.[31] This corresponds to an electron saddlepoint singularity in the density of states, as required in Sec. II A to explain the dominant shoulder in the dT_c/dp data at 0.9 at.% Cd. Moreover, recent measurements[14] of the ring cross-sectional area at U in In doped with up to 2 at.% Cd give a rate of change of area which is entirely consistent with this interpretation.[32]

In addition, the band-structure results[19,30] obtained from fitting FS data give a slight bulge in the corner of the ring at T [Fig. 5(a)]. No direct evidence exists for this bulge, which would show up only with the applied field **H** very near [100]. Unfortunately, the published dHvA measurements[30] were made with a torsion balance, and with this technique the amplitude of this dHvA oscillation vanishes at [100]. Our interpretation of the dT_c/dp data (Sec. II A) requires more than a simple saddlepoint, and the nature of the electron bulge at the corners of the ring is consistent with the density-of-states anomaly suggested by the weak shoulder in dT_c/dp at 1.6 at.% Cd. There are three reservations in this conclusion, all of which may be clarified by further work. First, the existence of a bulge at the corner of the ring is as yet unproven in pure In. Second, density-of-states evidence from alloy measurements need not correspond directly to the energy dependence of the density of states in the pure system, because of our neglect of the real part of the self-energy change in alloys [Eq. (9)]. This is especially true for fine details of topology such as this which are quite sensitive to the band gaps. Third, the form of the van Hove singularities

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[30] J. P. G. Shepherd, J. Phys. C (to be published), and references therein.

[31] Further geometry changes come from the decrease in the axial ratio c/a with Cd impurity. The effect is to accelerate the rate of change in size of the third-band ring (Ref. 14).

[32] Scaling the results and interpretation of Ref. 14 to the small orbit at the corner of the ring predict its disappearance at well below 1% Cd. No precise statement will be made at present, because the details in this case are extremely sensitive to the pseudopotential form factor and its change with alloying.

used in Secs. I and II A is valid only within the energy range for which a quadratic expansion of the electron-dispersion law is valid. For the corner of the third-band ring, the simplest dispersion relation which can give both a saddlepoint and a bulge is shown in Fig. 5(c). It is clear that quadratic expansions such as Eq. (2) are valid only for energies small compared to the energy gap E_G in Fig. 5(c). Use of Eq. (2) should give the shape of the shoulders but is likely to distort the peak in dT_c/dp, for instance. However, since impurity broadening is likely to smear all structure except that very near critical points, it is of interest to carry out the dT_c/dp calculation within the framework of the simple density-of-states model. Refinements in the density-of-states model will be shown to produce only minor changes in the result.

A calculation of dT_c/dp [Eq. (7)] has been carried out, using the impurity-broadened density of states curves (Fig. 4) for the postulated topology changes, and performing the convolution integral [Eq. (8)] numerically. There are no free parameters, except the location of the singular points as determined by inspection of the dT_c/dp data. The numerical quantities involved are

$$\frac{dE_F}{dp}=\frac{dE_F}{dV}\frac{dV}{dp}\cong\frac{2}{3}\frac{E_F}{V}\frac{dV}{dp}$$

$$=-\tfrac{2}{3}\kappa E_F=1.2\times10^{-5}\frac{\text{eV}}{\text{kg/cm}^2}, \qquad (14)$$

where the first equality is correct only if band-gap changes with pressure affect E_F negligibly, and the second equality follows from the free-electron Fermi-energy formula. The calculated[19] Fermi energy $E_F=8.7$ eV and the compressibility $\kappa=-2.2\times10^{-3}$ kbar^{-1} measured[33] at 4.2°K have been used. For the over-all density of states, it is convenient to write

$$N_0(E_F)=\left(\frac{N_0(E_F)}{N_0^0(E_F)}\right)N_0^0(E_F), \qquad (15)$$

where $N_0^0(E_F)$ is the free-electron density of states. The quantity in large parentheses has been calculated by Ashcroft and Lawrence.[19] Note that a density-of-states term appears in both the numerator and denominator of Eq. (7), so that electron-phonon enhancement of the normal metal density of states cancels to first order.[34] However, there is substantial anisotropy in the electron-phonon enhancement in indium,[27] and we choose to account for this by using the measured cyclotron mass[30] (phonon-enhanced) $m^*=0.15m_0$ in calculating the density of states δN at the third-band corner, and the specific-heat mass[19] (phonon-enhanced) $m^*=1.6m_0$ in evaluating $N_0(E_F)$.

The dT_c/dp results are shown in Fig. 6. The zero on the y axis has been shifted to give optimum matching of the curves, since this calculation does not attempt to give the (monotonic) shift in T_c which is observed when a lattice is compressed.[27,28] The resistivity linewidth has been used (curves marked Γ_σ in Fig. 4) since this value of $\Delta E_F/\Delta\Gamma_\sigma$ gave density-of-states curves in reasonable correspondence with dT_c/dp data. This choice seems well justified by the excellent correspondence in the size of the calculated dT_c/dp peak with experiment. Curve a makes use of the density-of-states curves presented in Fig. 4. Curves b and c are attempts to incorporate a more realistic model which recognizes that the two singularities are not likely to be in separate bands but are both from the third band (Fig. 5). Curve b assumes that the electron spheroid can continue to expand with increasing E_F in two directions after the electron saddlepoint has made contact. Curve c allows the spheroid to expand only in one direction after the saddlepoint makes contact, which is the present prediction of the band-structure calculation[19] for pure In [Fig. 5(a)]. It appears that more realistic models [Fig. 6(b) and 6(c)] go in the right direction to improve the agreement with experiment, and that *if* the monotonic (lattice stiffness) part of dT_c/dp is slowly varying, curve b is the most consistent with experiment. No attempt has been made

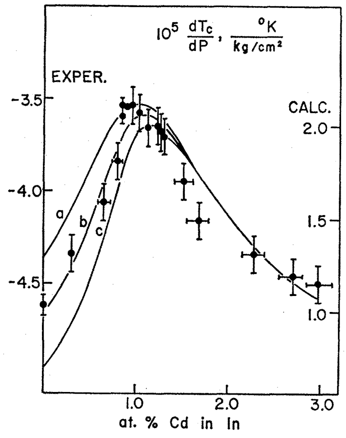

FIG. 6. Computed dT_c/dp for In doped with Cd compared with experiment (Ref. 16). The experimental error bars have been estimated by us based on the precision in composition and the breadths of the superconducting transition quoted in Ref. 16. The calculated curves have been shifted vertically to meet the experimental peak, since this calculation attempts only to determine size and shape of the rapid-composition-dependent peak (FS topology effect) superposed on a larger but slowly varying background (lattice-stiffness effect). Curve a shows impurity-broadened density of states of Fig. 4 ($\Gamma=\Gamma_\sigma$) used in Eq. (8), assuming independent bands. Curves b and c are attempts to recognize the likely structure of the third band (Fig. 5) by allowing the spheroid to expand in two directions and one direction, respectively, after the saddlepoint makes contact.

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[33] B. S. Chandrasekhar and J. A. Rayne, Phys. Rev. **124**, 1101 (1961).

[34] The electron-phonon effective-mass enhancement factor in In is of order 1.6–1.8 (Ref. 19), so that use of the band mass rather than the quasiparticle mass in evaluating $N_0(E_F)$ would result in an error of more than a factor of 2 in dT_c/dp. On the other hand, if it is the band mass (no electron-phonon enhancement) which should be used in Eq. (7), the amplitude calculated for dT_c/dp would be reduced by 25%, because our calculation takes electron-phonon enhancement anisotropy (Ref. 19) into account.

to make a minimum error fit by varying critical-point energies, etc., since it is our intention to emphasize the physical information which can be extracted from such measurements using a very simple model for dT_c/dp and the impurity-broadened density of states. The appeal of the model is that it results in predictions which may be tested by direct FS measurements, using the dHvA effect or related techniques.

III. CONCLUSIONS

(1) A modified BCS gap equation has been formulated, following Ref. 22, to take into account the rapid variation in the density of states $N(E_F)$ near an energy at which the FS topology changes. An approximate solution has been found for the pressure derivative of the superconducting transition temperature, dT_c/dp. This quantity reflects structure proportional to the energy derivative of the density of states, which varies as $(E_F-E_c)^{-1/2}$ near critical points, convoluted with a broadening factor of width kT_c.

(2) In a random-alloy system, sharp van Hove singularities in the density of states are not expected because impurity scattering limits the lifetime of a state k and hence broadens the energy associated with that state. An exact expression has been evaluated for the broadened van Hove singularities, assuming a Lorentzian line shape for the spectral distribution function relating k and E, and neglecting relaxation-time anisotropy at a given energy. The broadened density of states approaches the usual square-root form above the singular point, is smeared in slope at the singular point, and falls off as $\Gamma/(E_c-E_F)^{1/2}$ below the singularity.

(3) This general model for dT_c/dp in an alloy has been applied to explain existing data[16] on In doped with Cd. The rate of change of Fermi energy with impurity concentration was estimated from a free-electron formula. The rate of change of lifetime was estimated from residual resistivity. The ratio of these quantities gives qualitatively good agreement with the curve of dT_c/dp versus concentration, with an electron saddle-point opening up at 0.9 at.% Cd and an electron spheroid vanishing at 1.6 at.% Cd being the only topology changes consistent with the data.

(4) The numerical calculation of the structure in dT_c/dp versus concentration is in quantitative agreement with the data. The calculation involves no free parameters aside from the empirically determined singular points mentioned above, but makes use of available information on the portion of the FS (the third-band ring) believed to be responsible for the structure in dT_c/dp.

(5) The theory is a simple one, whose primary advantage is the intuitive connection between dT_c/dp and density-of-states anomalies. Though agreement with experiment is excellent, many estimates are involved, and in fact the validity of the BCS model for In is uncertain. However, a direct test of the model and its applicability to In is possible, since the composition of the postulated FS anomalies is low enough for direct measurement, using the dHvA effect. Such a test is now in progress.[35]

ACKNOWLEDGMENTS

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APPENDIX

A. Validity of the BCS Gap Equation for In Doped with Cd

Pure In is borderline between a weak-coupling superconductor, for which the BCS model is valid, and a strong-coupling superconductor, for which a more complex theory is required. This is seen by the value of the interaction strength $N(E_F)\mathcal{V}$,[36] and by the value of $2\Delta/kT_c$ which is close to the BCS value of 3.53.[37]

Metal	Al	Sn	In	Hg	Pb
$N(E_F)$	0.18	0.25	0.30	0.35	0.39
$2\Delta/kT_c$	3.3	3.5	3.6	4.6	4.6

Moreover, tunneling $I-V$ curves for In are well fitted by a BCS expression,[38] and do not show the obvious structure typical of a strong-coupling superconductor such as Pb. Recently, McMillan[39] has evaluated an expression for the critical temperature of strong-coupling superconductors. In that formulation, the quantity $\lambda-\mu^*$ plays the role of $N(E_F)\mathcal{V}$ in the BCS limit, where λ is the electron-phonon coupling constant and μ^* is the Coulomb pseudopotential. For small μ^*, the expression for T_c is

$$T_c/\Theta_D = e^{-(1+\lambda)/\lambda}. \tag{A1}$$

The factor $1+\lambda$ is the electron-phonon renormalization factor which appears in the cyclotron mass, the specific heat, and other properties.[40] For $\lambda<1$, by associating λ with the BCS $N(E_F)\mathcal{V}$, the additional $1+\lambda$ in Eq. (A1) *removes* the electron-phonon enhancement from the density of states, so that the expression for T_c depends on the band-structure density of states rather than the phonon-enhanced density of states. But since this enhancement cancels to first order in our theory [see discussion below Eq. (15)], the strong-coupling theory does not appear to change the physical nature of our results,[34] as long as $\lambda<1$ ($\lambda\cong0.7$ for In).

One further concern is the possible variation of pairing interaction as the system is made less pure. However, the variation of alloy quasiparticle lifetime does

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[35] R. J. Higgins *et al.* (unpublished).

[36] G. Rickayzen, *Theory of Superconductivity* (Wiley-Interscience, Inc., New York, 1940), p. 187.

[37] C. Kittel, *Introduction to Solid State Physics* (Wiley-Interscience, Inc., New York), 3rd ed., p. 344.

[38] I. Giaever and K. Megerle, Phys. Rev. **122**, 1101 (1961).

[39] W. L. McMillan, Phys. Rev. **167**, 331 (1968).

[40] R. E. Prange and L. P. Kadanoff, Phys. Rev. **134**, A566 (1964).

not change the strength of the pair interaction for "dirty" alloys (mean free path less than the coherence length).[41] One estimate suggests that this criterion is satisfied for Cd impurity concentrations exceeding 0.4 at.%.[15] Further, this theorem makes the BCS one-parameter model more valid in the alloys than in pure In, since anisotropy in the pair interaction in the pure system is removed as the "dirty" regime is reached.[24]

B. Validity of the First-Order Solution for dT_c/dp [Eq. (7)]

The integral equation for T_c [Eqs. (3)–(5)] has no apparent analytic solution when E_F is near a singular point in the density of states. However, in evaluating dT_c/dp, a first-order iteration can be used to arrive at Eq. (7), assuming that dT_c/dp is small. The approximation consists in holding T_c constant in Eq. (8) while differentiating with respect to E_F. Relaxing this restriction and evaluating Eq. (7),

$$dT_c/dp=(dT_c/dp)^{(1)}+\beta dT_c/dp\,, \tag{A2}$$

where superscript (1) designates the first-order solution [Eq. (8)] and the correction term β is given by

$$\beta=\frac{1}{2N_0(E_F)}\int_{-k\Theta_D}^{k\Theta_D}\operatorname{sech}^2(|E|/2kT_c^0)\times\delta N(E_F-E)\frac{dE}{2kT_c^0} \tag{A3}$$

$$<\frac{1}{2N_0(E_F)}\int_{-k\Theta_D}^{k\Theta_D}\delta N(E_F-E)\frac{dE}{2kT_c^0}\,. \tag{A4}$$

This last quantity is of order $\frac{3}{8}(m^*/m_0)^{3/2}(k\Theta_D)^{3/2}E_F^{-1/2}(kT_c)^{-1}$. For indium, the parameters used in Sec. II give an upper bound for β of less than 0.02, justifying the approximation used.

C. Pressure Modulation of the Density of States

In Sec. I, applying pressure to the system was viewed as a way of modulating the Fermi energy, and hence the density of states $N(E_F)$, through the volume dependence of the Fermi energy. This useful simplification is not strictly correct, since pressure also varies the axial ratio of tetragonal In, shifting the relative population of various bands, and in addition varies the lattice potential, further affecting the density of states. For small portions of the FS such as have been discussed in this paper, the latter two effects need not be small.[14] These effects will, of course, play a role in determining the composition at which topology changes occur, but these are not determined in our calculation. In addition, the amplitude of dT_c/dp will be affected, so that the excellent agreement between theory and experiment demonstrated by Fig. 6 may perhaps be accidental. An estimate of these corrections will now be made. A more accurate expression for the first term in Eq. (6) is

$$\frac{dT_c}{dp}=\frac{\partial T_c}{\partial E_F}\frac{\partial E_F}{\partial V}\frac{\partial V}{\partial p}+\frac{\partial T_c}{\partial N}\frac{\partial N}{\partial E_F}\times\left(\frac{\partial E_T}{\partial \alpha}\frac{\partial \alpha}{\partial p}+\sum_K\frac{\partial E_T}{\partial V_K}\frac{\partial V_K}{\partial p}\right). \tag{A5}$$

Here the first term is the one calculated in the text, and the second term contains the axial ratio α and band-gap V_K effects. N stands for $\delta N(E_F)$ associated with the third band in the region of the corner T (Fig. 5). For simplicity, a rigid-band assumption has been made, e.g., the shift in the density of states with a change in axial ratio or band gap is proportional to the derivative of the density of states at E_F times the shift in the energy E_T of the bottom of the third band at T.

Under pressure at 4.2°K, In ($c/a=1.08$) becomes *less* cubic.[42] This surprising observation is unexplained, but would result in extra population of states near the point T, resulting in a positive contribution to dT_c/dp. Under pressure, the lattice band gaps in In become smaller in magnitude,[42] which also increases the population of states near T, with an additional positive contribution to dT_c/dp. An upper bound to the quantity in parentheses in Eq. (A5) can be estimated by using data from Refs. 19 and 42 for comparison with the volume effect $(\partial E_F/\partial V)(\partial V/\partial p)$, which was estimated to be of order 1.2×10^{-5} eV (kg/cm^2)$^{-1}$ [Eq. (14)]. We find the axial ratio and lattice band gap effects to be at most 0.7×10^{-5} and 0.4×10^{-5} eV (kg/cm^2)$^{-1}$, respectively. These two corrections are therefore not negligible, and, being of the same sign as the volume effect calculated in the text, increase the size of the peak in dT_c/dp. These upper bounds are crude estimates involving rather subtle features of portions of the band structure not yet fully determined by experiment.

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[41] P. W. Anderson, J. Phys. Chem. Solids **11**, 26 (1959).

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