The Mixed State in Superconducting Thin Films*

F. E. HARPER† AND M. TINKHAM‡
Department of Physics, University of California, Berkeley, California

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Critical magnetic fields of superconducting vacuum-evaporated tin films were measured for all angles θ between the magnetic field and the film surface at temperatures from $0.4T_c$ to T_c. The experimental results were found to be consistent with Ginzburg-Landau theory provided that the original theory was modified to account for the extended temperature range and the nonlocal nature of superconducting electrodynamics. Measurements of the temperature dependence of the parallel and perpendicular critical fields supported the extensions of Ginzburg-Landau theory developed, most notably, by Maki and de Gennes. The angular dependence of the critical field for $0<\theta<\frac{1}{2}\pi$ at different temperatures was found to be in agreement with Tinkham's original formula for several sufficiently thin films, $d\ll\xi_T$; a detailed derivation of that formula is given here, with discussion of its range of validity. For thicker films the corrections found by Yamafuji *et al.* were necessary to obtain agreement with the data. The critical fields were carefully measured for $\theta\approx0$, and evidence of surface superconductivity was found in the thickest film studied, but not in thinner films. This is consistent with the numerical calculations of St. James and de Gennes.

I. INTRODUCTION

WHEN a *thick* superconducting film is placed in a perpendicular magnetic field, the field penetrates the film and the intermediate state is formed.[1–5] The film is driven completely into the normal state at a critical field H_{ci} given by

$$H_{ci}\approx H_{cb}[1-(\Delta/d)^{1/2}], \tag{1}$$

where d is the thickness of the film, H_{cb} is the thermodynamic critical field, and Δ is a length giving a measure of the energy contained in the interface between the normal and the superconducting regions which make up the intermediate state.

For a sufficiently *thin* film the behavior is quite different. Using Ginzburg-Landau[6] (GL) theory, Tinkham[7] showed that when a magnetic field H is applied perpendicular to the surface of a sufficiently thin superconducting film, the field penetrates the film and the mixed state discovered by Abrikosov[8] forms, as opposed to the intermediate state. The film makes a second-order phase transition into the normal state at a critical field $H_{c\perp}$ given in GL theory by

$$H_{c\perp}=4\pi\lambda^2H_{cb}^2/\varphi_0, \tag{2}$$

where λ is a suitable penetration depth, and $\varphi_0=hc/2e=2.07\times10^{-7}$ G cm^2 is the flux quantum. Using the GL relation $\varphi_0=2\sqrt{2}\pi\lambda\xi_TH_{cb}$, the expression for $H_{c\perp}$ may be written as

$$H_{c\perp}=\sqrt{2}(\lambda/\xi_T)H_{cb}=\sqrt{2}\kappa H_{cb} \tag{3}$$

or

$$H_{c\perp}=\varphi_0/2\pi\xi_T^2, \tag{4}$$

where κ is the GL parameter and ξ_T is the temperature-dependent coherence length discussed by de Gennes.[9] Physically, ξ_T is the distance over which the superconducting order parameter changes. This result for $H_{c\perp}$ is identical with the critical field H_{c2} for a bulk type-II superconductor ($\kappa>1/\sqrt{2}$). Surprisingly, for a sufficiently thin film the result is valid for type-I ($\kappa<1/\sqrt{2}$) as well as type-II superconductors.

In the original work Tinkham reasoned that a film is sufficiently thin to enter the mixed state if $d<\xi_T$. Maki,[10] Lasher,[11] and Fetter and Hohenberg[12] have found more exact expressions for the critical thickness. Their results show that the critical thickness is of the order of λ^2/ξ_T, but since λ and ξ_T are typically quite similar in type-I superconductors, these two criteria do not differ greatly in practice.

For a field applied at an arbitrary angle θ to the surface of the film, Tinkham[7,13] showed that the critical field is found by solving

$$(H_c\cos\theta/H_{c||})^2+H_c\sin\theta/H_{c\perp}=1 \tag{5}$$

for H_c. The parallel critical field $H_{c||}$ was found earlier by GL[6] to be

$$H_{c||}=(24)^{1/2}(\lambda H_{cb}/\mathrm{d}). \tag{6}$$

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† Present address: Bell Telephone Laboratories, Inc., Murray Hill, N.J.
‡ Present address: Physics Department, Harvard University, Cambridge, Mass.
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II. THEORY

The results stated above for $H_{c\parallel}$ and $H_{c\perp}$ are now rather well-known consequences of GL theory. The angular-dependence formula (5) was first obtained by rather physical arguments,[7,13] but subsequently shown[14] to be also a straightforward consequence of GL theory. Because the account in Ref. 14 is rather brief and inaccessible, we feel it is desirable to present the argument here in somewhat more detail.

All of the above results, including the angular-dependence formula, may be obtained by solving the linearized GL equation

$$\alpha\Psi+(1/2m)(i\hbar\nabla+2e\mathbf{A}/c)^2\Psi=0, \qquad (7)$$

subject to a suitable boundary condition at the surfaces of the film and suitable assumptions of thinness. Within the general limitations of GL theory, this linearized equation is appropriate for determining the critical field, provided the phase transition is of second order, since then the term in $|\Psi|^2\Psi$ in the full GL equation is negligible compared to the linear terms. Moreover, as $\Psi\to 0$, we may take $\mathbf{A}=\mathbf{A}_{\text{ext}}$, since the screening currents become negligible as $|\Psi|^2$. Thus the second GL equation, which determines the supercurrent density in terms of $\mathbf{A}$ and Ψ, plays no role in the determination of H_c in this case.

We choose a coordinate system in which x is measured normal to the film from the midplane. The magnetic field H is chosen to lie in the xz plane at an angle θ from the plane of the film. For convenience, the vector potential is chosen to have only a y component, which is given by

$$A_y=H(x\cos\theta-z\sin\theta). \qquad (8)$$

Inserting this vector potential into (7), the equation to be solved is

$$-\nabla^2\Psi+(2\pi A_y/\varphi_0)^2\Psi-(4\pi i/\varphi_0)A_y\partial\Psi/\partial y=\Psi/\xi_T^2, \qquad (9)$$

where we have replaced the parameter α by ξ_T according to the defining relation $\xi_T=(\hbar^2/2m|\alpha|)^{1/2}$. This partial differential equation is to be solved subject to the GL boundary conditions

$$\partial\Psi/\partial x-(2\pi iA_x/\varphi_0)\Psi|_{x=\pm d/2}=\partial\Psi/dx|_{x=\pm d/2}=0, \qquad (10)$$

since both surfaces face insulating materials. In general, no simple analytic solution exists. We resort instead to a variational calculation, noting that the linearized GL equation may be derived by minimizing the expression

$$F=\int\{|(\nabla-2\pi i\mathbf{A}/\varphi_0)\Psi|^2-|\Psi|^2/\xi_T^2\}dV \qquad (11)$$

and that at a second-order transition to the normal state this expression, being proportional to the free-energy difference, vanishes. Thus, we can find a *rigorous lower bound* to the critical field by choosing a trial function for Ψ and computing the value of H (in A) for which F becomes zero by cancellation of the two terms in the volume integral.

In choosing a trial function, we can be certain that $|\Psi|$ is not a function of y because there is no explicit y dependence of any term in (11) to favor such a dependence of Ψ, and any variation of Ψ would add a positive term $\sim|\partial\Psi/\partial y|^2$. A variation only in the phase of Ψ, of the form e^{iky}, can be cancelled by a gauge transformation which adds the constant $k\varphi_0/2\pi$ to A_y, so there can be no effect on the minimum energy due to such a variation in phase. Thus we can take $\Psi(x,z)$ with no loss of accuracy, and (11) becomes

$$F=\int\{|\partial\Psi/\partial x|^2+|\partial\Psi/\partial z|^2+(2\pi H/\varphi_0)^2 \times(x\cos\theta-z\sin\theta)^2|\Psi|^2-|\Psi|^2/\xi_T^2\}dV. \qquad (12)$$

Next we note that the optimum x variation is determined by the balance between the term $\sim x^2H^2\cos^2\theta|\Psi|^2$, which favors a smaller $|\Psi|^2$ at larger x^2 (i.e., nearer the surfaces), and the term $|\partial\Psi/\partial x|^2$, which favors Ψ independent of x. Evidently, as the sample gets thinner, so that x^2 is restricted to smaller values, the first term gets less important, and in the limit of very thin film, we expect $\partial\Psi/\partial x=0$. This automatically satisfies the boundary condition

$$\partial\Psi/\partial x|_{x=\pm d/2}=0.$$

Since the only characteristic length in (12) is ξ_T, we expect that this approximation will be good if $d\ll\xi_T$. We shall show this more precisely later.

With the approximation that Ψ is a function only of z, (12) may be integrated over x in a trivial way, noting that $\langle x^2\rangle=\frac{1}{12}d^2$ and $\langle x\rangle=0$. Thus (12) reduces to

$$F=Yd\int\left\{\left|\frac{d\Psi}{dz}\right|^2+\left(\frac{2\pi H\sin\theta}{\varphi_0}\right)^2z^2|\Psi|^2+\left[\left(\frac{2\pi H\cos\theta}{\varphi_0}\right)^2\frac{d^2}{12}-\frac{1}{\xi_T^2}\right]|\Psi|^2\right\}dz, \qquad (13)$$

where d is the film thickness and Y is its width in the y direction. Since we have reduced Ψ to a function of a single variable, the rest of the minimization can be carried out exactly. Applying the calculus of variations to (13), we obtain the ordinary differential equation

$$-\frac{d^2\Psi}{dz^2}+\left(\frac{2\pi H\sin\theta}{\varphi_0}\right)^2z^2\Psi=\left[\frac{1}{\xi_T^2}-\left(\frac{\pi Hd\cos\theta}{\sqrt{3}\varphi_0}\right)^2\right]\Psi, \qquad (14)$$

which is the same as (9) with $\partial\Psi/\partial x=\partial\Psi/\partial y=0$ and x^n replaced by an average value, namely, $\langle x\rangle=0$ and $\langle x^2\rangle=\frac{1}{12}d^2$. This eigenvalue problem has the familiar form of the harmonic-oscillator Schrödinger equation from quantum mechanics. The solution for the ground

[14] M. Tinkham, in Conference on the Physics of Type-II Superconductivity, Cleveland, Ohio, 1964 (unpublished).

state is

$$\Psi = c\exp(-\pi H\sin\theta z^2/\varphi_0), \tag{15}$$

with eigenvalue $(2\pi H\sin\theta/\varphi_0)$. Equating this eigenvalue to the coefficient in the right side of (14) and simplifying, we find

$$(H_c\cos\theta/H_{c\|})^2 + H_c\sin\theta/H_{c\perp} = 1, \tag{16}$$

where

$$H_{c\|} = \sqrt{3}\varphi_0/\pi d\xi_T \tag{17a}$$

and

$$H_{c\perp} = \varphi_0/2\pi\xi_T^2. \tag{17b}$$

If $H_{c\|}$ given by (17a) is set equal to the original GL expression for $H_{c\|}$, Eq. (6), the relationship $\varphi_0 = 2\sqrt{2}\pi\lambda\xi_T H_{cb}$ is recovered. If we use this relationship to eliminate ξ_T in (17b), the expression for $H_{c\perp}$ given by (2) is obtained. Note that the significance of (16) is that the value of H satisfying it provides a lower bound to the true critical field as a function of θ, a bound which becomes exact as $(d/\xi_T)\to 0$.

The particular eigenfunction found above describes a superconducting strip running in the y direction and of width $\sim(\varphi_0/\pi H\sin\theta)^{1/2}$. This width reduces to $(\varphi_0/\pi H_{c\perp}) = \sqrt{2}\xi_T$ when $\theta = \frac{1}{2}\pi$, and diverges as $\theta\to 0$. There exist infinitely many degenerate eigenfunctions of this sort which, for a fixed gauge choice, have variations in phase $\sim\exp(ik_n y)$ and whose centers are displaced to positions z_n, where $z_n = k_n\varphi_0/2\pi H\sin\theta$. As discussed by Abrikosov,[8] these degenerate solutions may be superposed to form a periodic array of vortices, with a single quantum of flux passing through the area associated with each vortex. However, the single Gaussian strip solution will have exactly as high a critical field $H_c(\theta)$ as the vortex solution formed by superposition, and hence critical-field measurements are unable to distinguish among the possible solutions. The determination of which solution is enegetically favored *below* $H_c(\theta)$ depends on nonlinear terms which we have neglected. For $\theta = \frac{1}{2}\pi$, the triangular Abrikosov array is expected[11,12] to be most favorable.

Now let us consider the case for a thicker film where the restriction that Ψ does not depend on x is relaxed while still retaining the boundary condition that $\partial\Psi/\partial x = 0$ at the surface. This will give us an indication of the accuracy of the simple solutions found above. In the parallel orientation, the only position-dependent term in the free-energy expression is proportional to $H^2x^2|\Psi|^2$. As noted above, this term favors having $|\Psi|^2$ decrease away from the midplane of the film $x=0$, but it will not cause any variation in the z direction. A simple variational trial function having the desired properties and satisfying the boundary condition is

$$\Psi = [1 + c\cos(2\pi x/d)]\exp(-\beta z^2), \tag{18}$$

where the variational parameter c is expected to be negative to reduce $|\Psi|^2$ away from the center. Inserting (18) into (12) and minimizing, we find

$$c = a - (a^2+2)^{1/2} \approx -(h/\pi)^2, \tag{19}$$

where $a = (\pi/h)^2 - \frac{1}{8}$ and $h = Hd^2/\varphi_0$. Inserting $H = H_{c\|} \approx \sqrt{3}\varphi_0/\pi d\xi_T$, we find $c \approx -3d^2/\pi^4\xi_T^2$. Using the optimized value of c, the improved value of $H_{c\|}$ is found (by setting $F=0$) to be

$$H_{c\|} = (\sqrt{3}\varphi_0/\pi d\xi_T)(1 + 9d^2/\pi^6\xi_T^2 + \cdots). \tag{20}$$

From the smallness of the coefficient of d^2/ξ_T^2, we see that the approximate solution found earlier is good to 1% if $d \lesssim \xi_T$. In fact, if $d > d_c \approx 1.8\xi_T$, the optimum parallel field solution is the surface nucleation configuration discussed by St. James and de Gennes,[15,16] which leads to vortices threading the film when the two degenerate solutions for the two surfaces are superposed, and the symmetric one-dimensional $\Psi(x)$ treated here is inappropriate. For thicknesses small enough to have the simple vortex-free solution, the maximum departure from the simple result (17a) is only 3%.

If the field is perpendicular to the film $(\theta = \frac{1}{2}\pi)$, the only position-dependent term in (12) is $\sim H^2z^2|\Psi|^2$. In this case, we expect Ψ to be rigorously independent of x and the simple solution above leading to $H_{c\perp} = H_{c2} = \varphi_0/2\pi\xi_{T2}$ to be exact regardless of the thickness of the film, provided the film is of type-II material so that $H_{c2} > H_{c\perp}$. However, if $H_{c2} < H_{ci}$, then there will be a transition to the intermediate state and the critical field is given by (1). This has been studied in some detail by Guyon *et al.*,[17] and by Lasher.[11] We confine our attention to films thin enough to avoid this complication.

If the field is at an intermediate angle θ, there are terms in (12) proportional to xz as well as x^2 and z^2. The simple variational approximation that Ψ is independent of x completely eliminates any contribution from the xz term in (12), whereas it gives an accurate account of the z^2 term and at least an average account of the x^2. To respond to the xz term, we try a variational function of the form

$$\Psi = [1 + cz\sin(\pi x/d)]\exp(-\beta z^2), \tag{21}$$

which satisfies the boundary condition of $\partial\Psi/\partial x = 0$ at the surface, while having an xz term for small x. This form for Ψ is especially chosen to respond to the xz term; it does not reduce to the form given by (18). The true solution for Ψ is a combination of these solutions, but since we wish to find the contribution due to xz while maintaining only an average account of the x^2 term, it is permissable to consider only that part of the correction to Ψ which responds to the xz term. When this solution for Ψ is optimized, one finds that β is still given by $\pi H\sin\theta/\varphi_0$, as in the simple solution. Minimizing F with respect to c, we find an improved $H_c(\theta)$,

[15] D. Saint James and P. G. de Gennes, Phys. Letters **7**, 306 (1963).

[16] D. Saint James, Phys. Letters **16**, 218 (1965).

[17] E. Guyon, C. Caroli, and A. Martinet, J. Phys. (Paris) **25**, 683 (1964).

lying above the one given by (16) although having the same end points at $\theta=0, \frac{1}{2}\pi$. By restricting attention to $\theta\approx 0$, a more tractable analysis results, and one finds the logarithmic slope

$$H_{c\|}^{-1}\left|\frac{dH_c(\theta)}{d\theta}\right|_{\theta=0}\approx\frac{\sqrt{3}\xi_T}{d}\left(1-\frac{1}{5}\frac{d^2}{\xi_T^2}+\cdots\right), \quad (22a)$$

which may be written as

$$H_{c\|}^{-1}\left|\frac{dH_c(\theta)}{d\theta}\right|_{\theta=0}\approx\frac{H_{c\|}}{2H_{c\perp}}\left(1-\frac{12}{5}\frac{H_{c\perp}^2}{H_{c\|}^2}+\cdots\right). \quad (22b)$$

Subsequent to the original report of this work, St. James[16] has carried out exact computer solutions for this intial slope. His exact results follow our simple analytic approximation quite well for $d\lesssim\xi_T$, but show an interesting singular change in behavior at the critical thickness d_c, mentioned above, at which vortices enter the film even in parallel field. St. James's result is shown in Figs. 9 and 10. Yamafuji *et al.*[18] have given an improved solution for the entire angular dependence for d/ξ not too small.

The above discussion is based upon the GL theory which, in its original form, does not account for the nonlocal relationship between the superconducting current density and the magnetic vector potential. Bardeen[19] has outlined the necessary modifications to account for this nonlocal nature of superconductivity. Later Gor'kov[20] formulated a microscopic GL theory which has been used to calculate $H_{c\|}(t)$ in certain limits. Maki[21] has used this method to calculate $H_{c\|}(t)$ for a dirty film, $l_0\ll\xi_T(0)$, where l_0 is mean free path for scattering within the volume of the film at 4.2°K. Thompson and Baratoff[22] have calculated $H_{c\|}(t)$ in the anomalous limit; $d\ll l_0$, $d\ll\xi_T(0)$, $l_0\gg\xi_T(0)$. As yet calculations have not been made for the perpendicular critical field of a thin film.

Since a complete set of calculations based on the microscopic theory are not available, we shall proceed along the lines of the phenomenological theory of Pippard.[23] Pippard found that the above-mentioned nonlocal nature of superconductivity could be accounted for by using a nonlocal relationship between the superconducting current density and the magnetic vector potential analogous to Chambers's[24] result for normal conductivity. For an infinite half-space in the limit where $\xi^3<\xi_0\lambda_L^2$, the Pippard relationship between the superconducting current density and the magnetic vector potential reduces to the London relationship if the penetration depth is defined as

$$\lambda(t)=\lambda_L(t)(\xi_0/\xi)^{1/2}. \quad (23)$$

Here $\lambda_L(t)$ is the London penetration depth, ξ_0 is the Pippard coherence length which is a measure of the length over which the magnetic vector potential must be averaged to determine the superconducting current density in pure material, and ξ is a reduced coherence length which is assumed to be of the form[23,24]

$$1/\xi=1/\xi_0+1/l_0. \quad (24)$$

Following this result, we will assume that the nonlocal nature of superconducting may be accounted for in the local GL theory by using a suitable penetration depth.

The above penetration depth is only suitable for an infinite half-space. In the study of thin films it has been found useful[25] to define an effective mean free path which will accont for the film geometry as well as for scattering within the volume of the film. According to the size-effect theory of normal conductivity, in a thin film the effective mean free path is given by

$$1/l_{\text{eff}}=1/l_0+3/8d. \quad (25)$$

As discussed by Millstein and Tinkham,[26] we theoretically expect l_{eff} to be somewhat smaller for the superconducting case and to depend on the orientation of the field. For parallel fields, the vector potential $A_y=Hx$ changes sign in going through the thickness of the film, whereas the electric field driving the current in a normal film is uniform through the film cross section. Thus we might expect to replace d by $\sim\frac{1}{2}d$ in (25) for $(l_{\text{eff}})_{\|}$. For perpendicular fields, the vector potential is uniform in x over the film thickness, but varies periodically in the yz plane because of the vortex structure. Millstein and Tinkham accounted for this by using

$$(1/l_{\text{eff}})_{\perp}=1/l_0+[(3/8d)^2+1/2\xi_T^2]^{1/2}. \quad (26)$$

For the films to be discussed here, either $l_0<\xi_T$ or $d<\xi_T$, or both, so (26) effectively reduces to (25). In fact, we will use (25) for *all* orientations because the structure of the thin films for which $1/d$ corrections are most important is believed to be so irregular that refinements based on ideal film geometry would not be justified.

In their classic paper, Bardeen, Cooper, and Schrieffer[27] (BCS) found that Pippard's intuitive ideas were substantially correct. According to BCS, if $l\ll\xi_0$, the dirty limit applies and λ is given by

$$\lambda(t)=\lambda_L(t)[\xi_0/\xi J(0,t)]^{1/2}, \quad (27)$$

where $J(R,t)$ is a function comparable to the e^{-R/ξ_0}

[18] K. Yamafuji, T. Kawashima, and F. Irie, Phys. Letters **20**, 123 (1966).
[19] J. Bardeen, in *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 15, p. 326.
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[22] R. S. Thompson and A. Baratoff, Phys. Rev. Letters **15**, 971 (1965).
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[25] M. Tinkham, Phys. Rev. **110**, 26 (1958).
[26] J. Millstein and M. Tinkham, Phys. Rev. **158**, 325 (1967). See Appendix.
[27] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

which appears in Pippard's relationship between $\mathbf{j}_s$ and $\mathbf{A}$, and falls off in a similar distance. However, whereas the Pippard exponential is always unity for $R=0$, the BCS $J(0,t)$ varies from 1.0 at $t=0$ to 1.33 at $t=1.0$. The temperature dependence of $J(0,t)$ may be calculated from the BCS result

$$|\lambda_\infty(0)/\lambda_\infty(t)|^3=J(0,t)[\lambda_L^2(0)/\lambda_L^2(t)]. \quad (28)$$

The temperature dependence of $\lambda_\infty(t)$ is taken from Fig. 6 or (5.56) of BCS; the temperature dependence of $\lambda_L(t)$ has been calculated by Mühlschlegel.[28] The resulting temperature dependence of $J(0,t)$ is shown in Fig. 1.

Finally, with our approximations, (2) and (6) for the critical fields become

$$H_{c\perp}=\frac{4\pi\lambda_L^2(t)H_{cb}^2(t)}{\varphi_0 J(0,t)}\left[1+\xi_0\left(\frac{1}{l_0}+\frac{3}{8d}\right)\right], \quad (29)$$

$$H_{c\parallel}=\frac{(24)^{1/2}\lambda_L(t)H_{cb}(t)}{d[J(0,t)]^{1/2}}\left[1+\xi_0\left(\frac{1}{l_0}+\frac{3}{8d}\right)\right]^{1/2}. \quad (30)$$

The above discussion has been based on the GL equations which are rigorously valid only near T_c, even though they seem to give a good qualitative account of the phenomena all the way down to $T\approx 0$. However, de Gennes[29] and Maki[21] have shown that in the limit of a very dirty material ($l/\xi_0\to 0$) an equation of the form of (7) rigorously determines H_c at all temperatures. According to these treatments, the temperature dependence of the critical fields is found from

$$-\ln t=-\Psi(\tfrac{1}{2})+\Psi[\tfrac{1}{2}+\mathrm{Un}(t)/4\pi t], \quad (31)$$

where $\Psi(x)=\Gamma'(x)/\Gamma(x)$ is the digamma function and $\mathrm{Un}(t)$, defined by this equation, is called the universal function by de Gennes. Limiting values are $\mathrm{Un}(0)=1.76=\Delta(0)/kT_c$ and $\mathrm{Un}(t)\approx(8/\pi)(1-t)$ for $t\approx 1$. (There is a misprint in this connection in Ref. 9.) One can view $\mathrm{Un}(t)$ as giving the temperature dependence of $1/\xi_T^2$ in (9) for dirty materials over the complete temperature range as $1/\xi_T^2=(0.54/l\xi_0)\,\mathrm{Un}(t)$. de Gennes[9] has outlined the use of $\mathrm{Un}(t)$ for a number of specific cases. In terms of the universal function, the critical fields for a thin dirty film normalized to their values at $t=0$ are given by

$$H_{c\parallel}(t)/H_{c\parallel}(0)=[\mathrm{Un}(t)/\mathrm{Un}(0)]^{1/2} \quad (32a)$$

and

$$H_{c\perp}(t)/H_{c\perp}(0)=\mathrm{Un}(t)/\mathrm{Un}(0). \quad (32b)$$

The temperature dependence of the critical fields is calculated according to the above expressions and (31); the result is given in Figs. 3 and 5.

If the extreme dirty limit does not obtain, it is not possible to reduce the critical-field problem to the solution of a differential equation of the GL form, and more elaborate integral equation techniques are required. Helfand and Werthamer[30] have solved for $H_{c2}(t)$ for bulk samples of arbitrary mean free path, and find that the curve is very insensitive to l/ξ_0, the extremes being only ~4% apart. Thus we expect only rather small errors even if we use the GL-type theory outside its true range of validity.

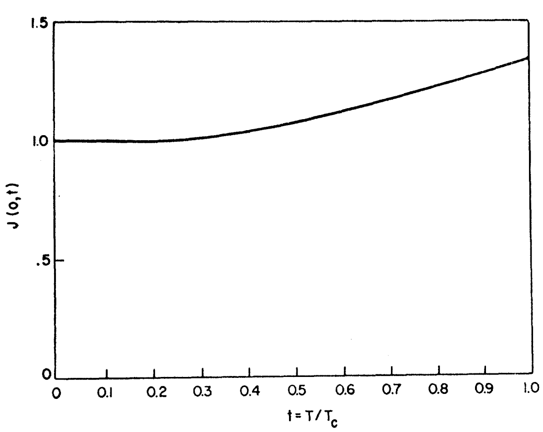

FIG. 1. Temperature dependence of $J(0,t)$.

III. SAMPLE PREPARATION

Sixteen tin films were prepared by electron beam evaporation of 99.9999% pure tin onto glass substrates cooled to 77°K in a vacuum of less than 5×10^{-8} Torr during evaporation. The thinnest film was 100 Å thick and the thickest was 2500 Å. Film strips 10 mm long and 1 mm wide were trimmed with a razor blade and copper leads were soldered to the film with indium solder. Eleven films were deposited at a slow rate of 10 Å/sec. The resistivity ratio of these films was nearly independent of film thickness, indicating that volume scattering dominated surface scattering ($l_0<d$). Since $l_0<d$, these films are dirty. Table I lists the thickness and resistivity ratio for these films; the films are designated as TD1 through TD11.

Five films, listed as TC1 through TC5, were deposited at a relatively fast rate of 300 Å/sec. The resistivity ratio for these films generally increased with thickness, indicating that surface scattering was comparable to volume scattering; hence these films are considered to be relatively clean. Here the films are classified as clean or dirty only with respect to their normal resistance. A film is clean with respect to the superconducting properties when $l_0>\xi_0$ and is dirty if $l_0<\xi_0$. For all of the films to be discussed here $l_0<\xi_0$; hence they are dirty superconductors.

The mean free path for volume scattering at 4.2°K is found in a later section and is given in Table I. For the

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TABLE I. Film properties.

Film	$H_{c\parallel}(0.8)$ (Oe)	$H_{c\perp}(0.8)$ (Oe)	d_s (Å)	d_r (Å)	RRR	l_{os} (Å)	l_{or} (Å)
TD1	9000	205	100	120	4.8	525	...
TD2	8540	178	110	130	3.9	830	1350
TD3	6430	197	135	145	3.8	850	855
TD4	3780	186	215	250	3.6	510	430
TD5	3324	169	240	240	4.4	565	640
TC1	2162	192	420	395	3.8	340	330
TD6	1782	128	425	430	4.9	650	540
TD7	1515	139	570	580	5.1	500	515
TC2	675	78	760	720	12.5	1250	2630
TD8	1080	153	785	815	5.0	400	455
TC3	486	72	1115	1165	10.3	1370	1240
TD9	625	144	1125	1230	4.7	415	390
TD10	540	154	1445	1300	5.7	370	505
TC4	378	78	1790	1700	12.5	920	1390
TD11	378	125	2360	2240	4.8	460	380
TC5	324	61	2500	2240	15.6	1315	1730

rapidly deposited films l_0 is consistently longer than for the slowly deposited films but there are exceptions; film TD3 is quite clean and film TC1 is quite dirty. A more noticeable fact is that the mean free path for our films is much smaller than for clean bulk material where mean free paths of 10 000 Å are easily obtained for tin at 4.2°K. It is likely that l_0 is controlled by structural impurities which are introduced into the film when they are warmed to room temperature after evaporation and subsequently cooled to 4.2°K; structural impurities result from the stress introduced by the difference in thermal contraction between the tin film and the glass substrate.

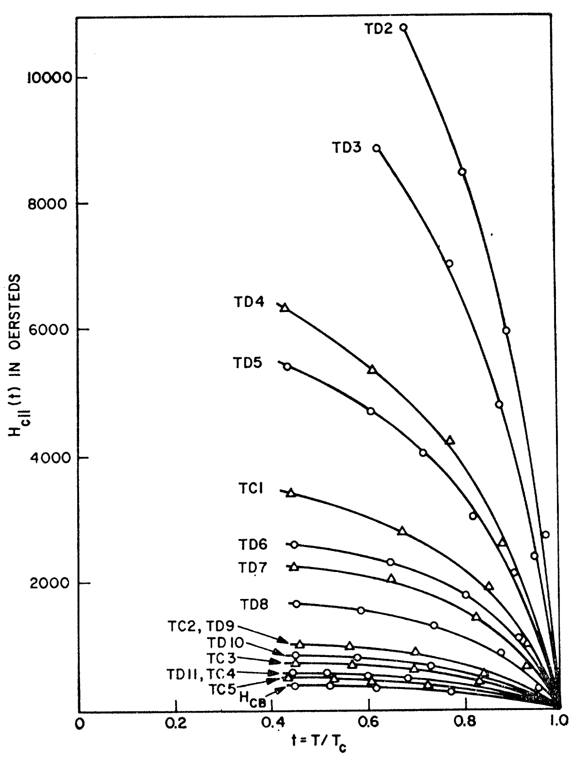

FIG. 2. $H_{c\parallel}$ versus t for several tin films.

IV. EXPERIMENTS

A number of experiments may be done to investigate the presence of the mixed state in a thin superconducting film. Chang, Kinsel, and Serin[31] measured the magneti-

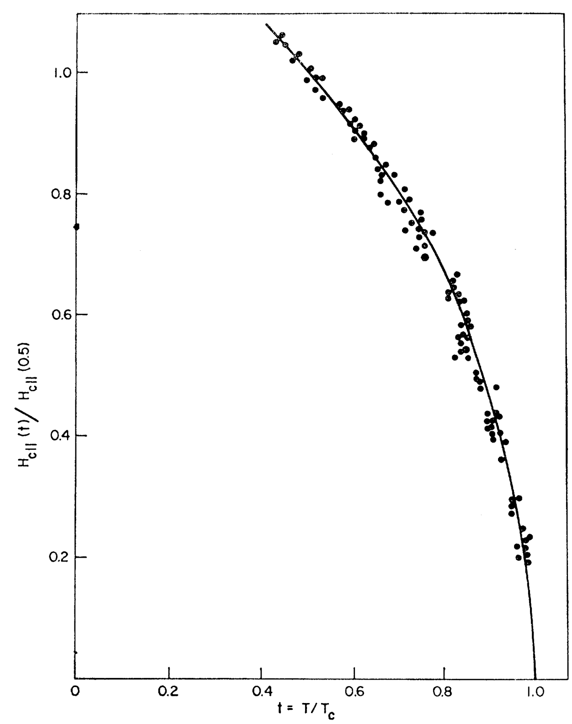

FIG. 3. $H_{c\parallel}(t)/H_{c\parallel}(0.5)$ versus t for several tin films. The scatter in the data at $t=0.5$ results from choosing $H_{c\parallel}(0.5)$ from a smooth curve drawn through the data for each individual film. The solid curve is based on (32a) but would not be distinguishably different if (30) were used.

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zation curve in a perpendicular field for two pure tin films of thickness 850 and 2600 Å as a function of temperature. Miller, Kingston, and Quinn[32] made similar magnetization measurements for several indium-tin alloy films. In both of these works the critical field was well fitted to a $(1-t^2)/(1+t^2)$ dependence predicted from using the Gorter-Casimer two-fluid model for the temperature dependence of $\lambda(t)$ and $H_{cb}(t)$ in (2). The dependence of $H_{c\perp}$ upon film thickness and purity was not studied. $H_{c\parallel}$ and $H_{c\perp}$ have been measured in tunneling experiments by Burger, Deutscher, Guyon, and Martinet[33] as a function of temperature for Sn–In, In–Pb, and Pb–Bi alloy films of various thicknesses. Since these alloys are type-II superconductors in bulk form, it is not surprising that evidence for the mixed state was found. The dependence of $H_{c\perp}$ on film thickness for pure Pb films at 4.2°K was studied by Cody and Miller.[34] They found that for films thinner than 8000 Å, $H_{c\perp}$ was a decreasing function of film thickness in accordance with the prediction of the mixed state; on the other hand, $H_{c\perp}$ was found to be an increasing function of film thickness for films thicker than 8000 Å in accordance with the theory of the intermediate state.

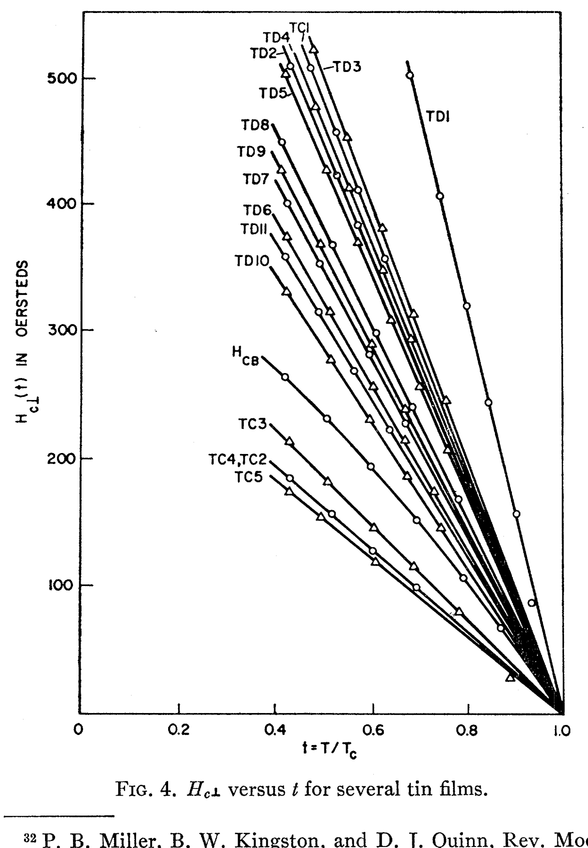

FIG. 4. $H_{c\perp}$ versus t for several tin films.

[32] P. B. Miller, B. W. Kingston, and D. J. Quinn, Rev. Mod. Phys. **36**, 70 (1964).
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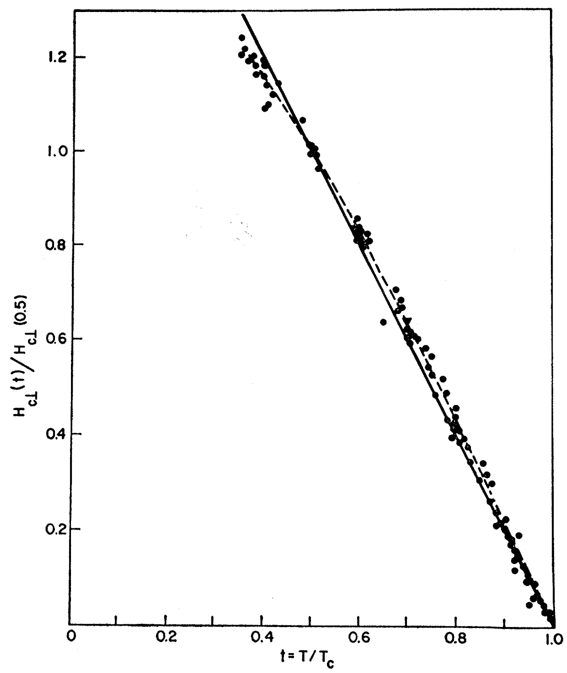

FIG. 5. $H_{c\perp}(t)/H_{c\perp}(0.5)$ versus t for several tin films. The scatter in the data at $t=0.5$ results from choosing $H_{c\perp}(0.5)$ from a smooth curve drawn through the data for each individual film. The solid line gives $H_{c\perp}(t)/H_{c\perp}(0.5)$ according to (29) and the dashed line according to (32b).

We have measured the dependence of $H_{c\parallel}$ and $H_{c\perp}$ on film thickness, mean free path for volume scattering, and temperature for tin films. These measurements present, on one set of samples, a complete study of the dependence of the critical fields upon film thickness, purity, and temperature. $H_c(\theta)$ has also been measured for various films at several temperatures. The critical fields were determined by measuring the resistive transition in a magnetic field. The range of the magnetic field over which the resistive transition occurred was generally less than 5% of the mean value of the field at which the transition occurred. The critical field is defined by extrapolating the transition back to zero resistance. The current density in the films was less than 200 A/cm². In all cases the current could be increased by a factor of 10 without changing the value of the critical field.

Temperature Dependence of $H_{c\parallel}$

The observed values of $H_{c\parallel}(t)$ for a number of tin films are shown in Fig. 2. For temperatures near T_c the theoretical temperature dependence of $H_{c\parallel}$ is contained in $\lambda_L(t)$, $H_{cb}(t)$, and $J(0,t)$, according to (30). For temperatures much less than T_c the results obtained by solving (31) and (32a) for $H_{c\parallel}(t)/H_{c\parallel}(0)$ are believed to be more accurate. The experimental results are in substantial agreement with either formulation of the temperature dependence as shown in Fig. 3; for the scale of Fig. 3 it is not possible to distinguish between the two solutions.

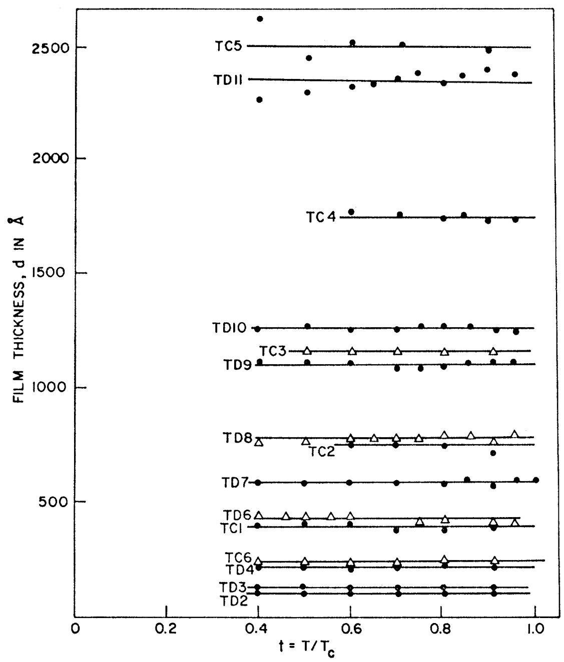

FIG. 6. Apparent film thickness from the superconducting critical fields d_s versus t.

Temperature Dependence of $H_{c\perp}$

$H_{c\perp}(t)$ is shown in Fig. 4 for each film and $H_{c\perp}(t)/H_{c\perp}(0.5)$ is shown in Fig. 5 for all films. The theoretical results according to (29) and (32b) are also shown. For $t\simeq 1$ the experimental points are in agreement with either formulation but for lower temperatures the agreement is significantly better with (32b). If the intermediate state were present, the temperature dependence would be given essentially by $H_{cb}(t)$. Since this was not found, these films are all sufficiently thin that the intermediate state is not formed.

Thickness Dependence of $H_{c\parallel}$ and $H_{c\perp}$

The film thickness may be determined in terms of $H_{c\parallel}$ and $H_{c\perp}$ by eliminating λH_{cb} between (2) and (6). The result is

$$d=(6\varphi_0 H_{c\perp}/\pi H_{c\parallel}^2)^{1/2}. \tag{33}$$

The thickness of each film calculated in this way from the critical fields at several temperatures is shown in Fig. 6, where it is seen that the calculated film thickness is independent of temperature as it must be. In Table I the average thickness calculated from the critical fields (i.e., a superconductive property) is given as d_s.

The film thickness may also be estimated from the normal-state resistance at room temperature, $R(300)$, and at 4.2°K, $R(4.2)$. Assuming that Matthiessen's rule is valid, and that $R(4.2)$ is the residual resistance, the thickness is given by

$$d=\rho_b(300)L/W[R(300)-R(4.2)], \tag{34}$$

where L is the length of the film, W is the width, and $\rho_b(300)$ is the resistivity of bulk tin at 300°K taken to be 11.1×10^{-6} Ω cm. The "resistive" film thickness according to this expression is given in Table I as d_r.

In Fig. 7, $H_{c\perp}(0.8)$ versus d is plotted. The solid line gives the result for the clean-film limit, where $l_0\gg\xi_0$, in which case (29) becomes

$$H_{c\perp}=19.5(1+863/d), \tag{35}$$

where we have taken $H_{cb}(0.8)=109$ Oe, $\lambda_L(0.8)=575$ Å, $J(0,0.8)=1.22$, and $\xi_0=2300$ Å,[35,36] and where d is measured in Å. The dirty-film results lie well above this line, indicating that there is considerable volume scattering in these films. The data for the clean (i.e., rapidly deposited) films generally lie closer to the result for the clean-film limit than the data for the dirty (i.e., slowly deposited) films. From (29) in the limit of $l\gg d$ the perpendicular critical field is independent of d; this behavior is found for films thicker than 500 Å. For films thinner than 500 Å, $H_{c\perp}$ is a decreasing function of film thickness in accordance with the dependence of λ on d when $d\lesssim l_0$. For four of the clean films $H_{c\perp}<H_{cb}$; therefore, $\kappa<1/\sqrt{2}$, and these films are composed of intrinsically type-I superconducting material. Even so, the critical field is determined by the relation appropriate to type-II superconductors which indicates that the mixed state is present.

Mean Free Path for Volume Scattering

The mean free path for volume scattering may be obtained from the critical fields by eliminating the film

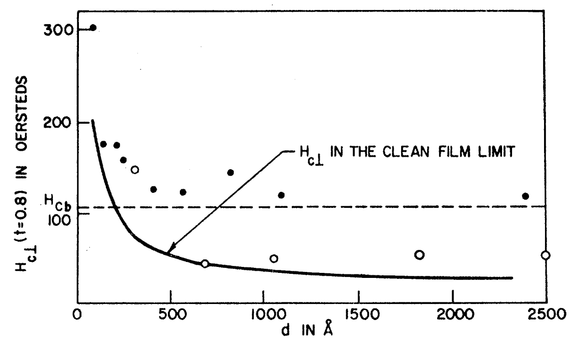

FIG. 7. $H_{c\perp}$ versus d at $t=0.80$ for several films. The data points for the slowly deposited films are closed circles and the data points for the rapidly deposited films are open circles. The solid line is for the clean-film limit, $l_0\gg\xi_0$, according to (35).

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[36] J. Bardeen and J. R. Schreiffer, Progr. Low Temp. Phys. **3**, 170 (1961).

thickness between the expression for $H_{c||}$ and $H_{c\perp}$. Neglecting any small difference between l_{eff} for parallel and perpendicular magnetic fields, the result is

$$l_0=\xi_0 \Big/ \left[\frac{J(0,t)\varphi_0 H_{c\perp}}{4\pi\lambda_L^2 H_{cb}^2} - 1 - \tfrac{1}{8}(3\xi_0 H_{c||})\left(\frac{\pi}{6\varphi_0 H_{c\perp}}\right)^{1/2}\right]. \tag{36}$$

l_0 is given in Table I as l_{os}; the critical fields at $t=0.8$ as given in Table I have been used. As expected, the slowly deposited films generally have a shorter mean free path than the rapidly deposited films.

The mean free path may be determined independently from the resistance at room temperature and at 4.2°K. Assuming that Matthiessen's rule is valid, l_0 is given by

$$1/l_0=[(\mathrm{RRR}-1)l(300°\mathrm{K})]^{-1}-3/8d, \tag{37}$$

where RRR is the residual resistance ratio $R(300)/R(4.2)$. This mean free path is given in Table I as l_{or}, where a mean free path for tin at $T=300$°K of 95 Å has been used. Once again, the slowly deposited films generally have a shorter mean free path than the rapidly deposited films. The agreement between the two mean free paths for each film is generally satisfactory, considering the approximate and indirect manner in which l_{os} and l_{or} were obtained.

Angular Dependence of the Critical Field

Figure 8 shows $H_c(\theta)/H_{c||}$ versus θ at various temperatures for several films. The solid line results from

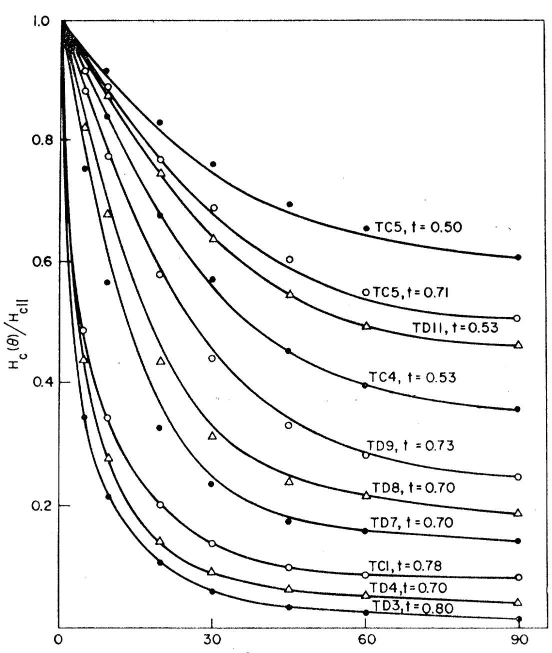

FIG. 8. $H_c(\theta)/H_{c||}$ versus θ for various films at various temperatures. The solid line is calculated from (5).

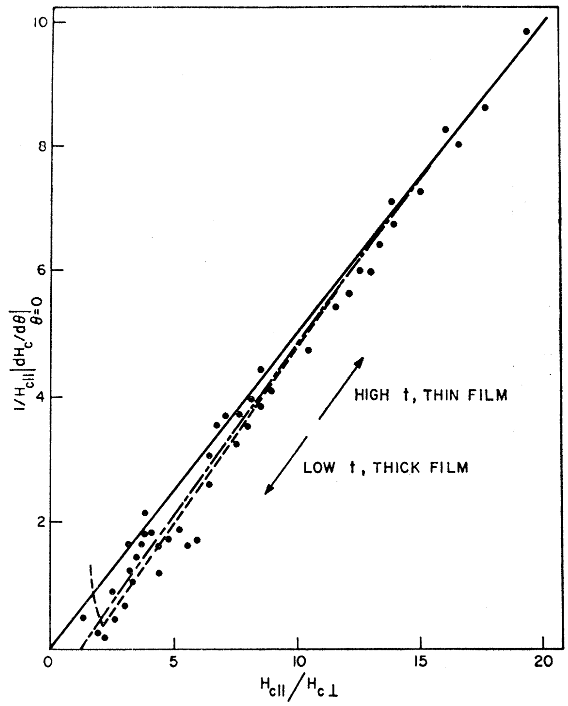

FIG. 9. $1/H_{c||}\,|dH_c/d\theta|_{\theta=0}$ versus $H_{c||}/H_{c\perp}$ for several films at various temperatures. The solid line is a plot of the thin-film limit $1/H_{c||}\,|dH_c/d\theta|_{\theta=0}=\frac{1}{2}H_{c||}/H_{c\perp}$. The chain line is a plot of the more exact calculation (22b). The dashed line is the result of an exact numerical calculation made by St. James (Ref. 16).

solving (5) at numerous values of θ using the experimental values for $H_{c||}$ and $H_{c\perp}$.[37] The agreement is excellent for the thinnest films. For thicker films, the measured values of $H_c(\theta)/H_{c||}$ lie below the theoretical prediction. For still thicker films, films TC4 and TD11, the measurements and the theory agree. For the thickest film, TC5, the measurements lie above the theory at both temperatures. According to Yamafuji, Kawashima, and Irie,[18] $H_c(\theta)/H_{c||}$ is larger than the thin-film limit (5) for thick films, where the order parameter varies across the film. This is in agreement with the data for film TC5 at two temperatures. There is no known reason for the data for films TD9, TD8, and TD7 to fall below the thin-film limit; however, an error of 2.5% in the determination $H_{c||}$ could account for this discrepancy.

$dH_c/d\theta$ in the Limit $\theta=0$

The behavior of the critical field, or, more specifically, $dH_c/d\theta$, near $\theta=0$ is dependent upon the variation of the order parameter across the film. The effect of a variation in Ψ across the film is most easily seen in a graph of $1/H_{c||}\,|dH_c/d\theta|$ at $\theta=0$ versus $H_{c||}/H_{c\perp}$, as shown in

[37] We thank J. Millstein for writing a FORTRAN program to solve (5) for $H_c(\theta)$.

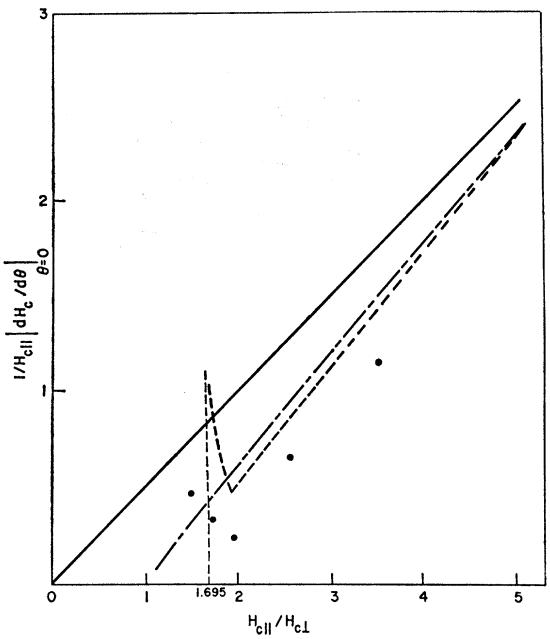

FIG. 10. $1/H_{c\|} \mid dH_c/d\theta \mid_{\theta=0}$ versus $H_{c\|}/H_{c\perp}$ for the thick film TD11 at various temperatures. The three curves are the same as in Fig. 9.

Fig. 9. In this figure, the experimental points are compared with three theoretical curves representing successive approximations. The first is the thin-film limit of (22b), namely,

$$1/H_{c\|} \mid dH_c/d\theta \mid_{\theta=0} = H_{c\|}/2H_{c\perp}.$$

Next is the second approximation represented by both terms of (22b). Finally, we show the St. James curve[16] resulting from an exact numerical solution which nearly agrees with (22b) for $H_{c\|}/H_{c\perp}>2$. The cusp at $H_{c\|}/H_{c\perp}=2$ in the St. James calculation is due to the onset of surface superconductivity. The experimental data are for all films at several temperatures. The thicker the film and the lower the temperature, the smaller will be the value of $H_{c\|}/H_{c\perp}$ as $H_{c\|}/H_{c\perp}=2\sqrt{2}\xi_T/d$.

In Fig. 10, the data are shown for film TD11 at five different temperatures; at the lowest temperatures evidence for surface superconductivity is seen. The data all lie below the theoretical result, which if true is not understood. It is possible that the discrepancy is due to underestimating $dH_c/d\theta$ at $\theta=0$, which was determined by plotting H_c for $0\leq\theta\leq2°$ and graphically estimating $dH_c/d\theta$ at $\theta=0$. Since $dH_c/d\theta$ is rapidly increasing as θ approaches zero, this method is likely to underestimate $dH_c/d\theta$ at $\theta=0$. It is also not understood why one point should occur for $H_{c\|}/H_{c\perp}<1.695$, the limiting value for bulk samples.

V. CONCLUSIONS

The agreement between these measurements and theory indicates that when a thin film is placed in a magnetic field with a perpendicular component, the mixed state is formed in a type-I film as well as in a type-II film. This behavior is in contrast with the intermediate state which is known to be present in thicker type-I films. The experimental data have included $H_c(\theta, t)$ for $0\leq\theta\leq\frac{1}{2}\pi$ and $0.4\leq t\leq1$ for a large number of films of varying thickness and purity.

The theory which we have used to find $H_c(\theta, t)$ for comparison with the data is basically the GL theory generalized in two directions: (1) We have used Pippard's phenomenological theory as supported by the BCS microscopic theory to develop an effective penetration depth parameter taking account of nonlocal, impurity, and sample-size effects; and (2) we have used the Maki–de Gennes theory of magnetic effects in dirty superconductors to extend the temperature dependence beyond $t\lesssim1$. This composite approach was used, despite its evident approximate nature, because no detailed results for the full complexity of the problem are available from a consistent completely microscopic treatment.

The temperature dependence of our results near $t=1$ is well described either by simple GL theory with parameters taken from Mühlschlegel's calculations according to BCS or by the Maki–de Gennes theory. For lower temperature, however, better agreement with experiment was obtained using the Maki–de Gennes results. This is as expected, since the Mühlschlegel-BCS calculation gives the temperature dependence of λ^2H_{cb} or $\kappa_3(t)$, whereas the de Gennes universal function is related to $\kappa_1(t)$, which is appropriate for the determination of the upper critical field.[38] Near T_c, $\kappa_1(t)=\kappa_3(t)=\kappa$, but differences develop at lower temperatures.

ACKNOWLEDGMENTS

Much of the experimental apparatus used here was expertly constructed by Al Langden and Silverio Montalvo under the supervision of Cliff Grandt at the University of California.

[38] A. L. Fetter and P. C. Hohenberg, "Theory of Type-II Superconductors," in *Treatise on Superconductivity*, edited by R. D. Parks (Marcel Dekker, Inc., to be published); N. R. Werthamer, "The Ginzburg-Landau Equations," in *Treatise on Superconductivity*, edited by R. D. Parks (Marcel Dekker, Inc., to be published).