neglected those self-energy terms which are also present in the normal state, i.e., ζ_p and χ_p. Second, we have employed the normal state dielectric constant. Third, the energy gap, i.e., ϕ_p, has been approximated by the constant BCS value ϵ_0. The errors in the ratio $\Gamma_p^{\mathrm{ph},s}/\Gamma_p^{\mathrm{ph},n}$ which have been introduced by making the first two of these approximations are insignificant because they turn out to be of order $(\epsilon_0/\omega_D)^2$. However, a consideration of the dependence of the gap on the energy and the resulting modification in the density of states might give rise to a significant change in this ratio.

It also would be of great interest, especially with regard to the theory of thermal conductivity, to see how the ratio $\Gamma_p^{\mathrm{ph},s}/\Gamma_p^{\mathrm{ph},n}$ is altered when we go to finite temperatures. This calculation will be presented as part of a forthcoming investigation which is based on an extension of Nambu's self-consistency conditions to the case of finite temperatures.

ACKNOWLEDGMENTS

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Critical Fields of Thin Superconducting Films. I. Thickness Effects

A. M. Toxen
Thomas J. Watson Research Center, International Business Machines Corporation, Yorktown Heights, New York
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A theoretical model is presented with which the critical magnetic fields of thin superconducting films can be calculated from any theory of superconductivity for which the kernel of the current-vector potential relationship is known. The model is worked out in detail for the nonlocal theory of Pippard with specular boundary conditions, and the critical field is shown to be a function of film thickness and the nonlocal parameters ξ and $\xi_0\lambda_L^2$. The results are compared to critical-field data for pure indium films and are found to predict very well the observed thickness dependence of critical field. On the basis of reasonable assumptions, ξ_0 and $\lambda_L(0)$ are calculated from the indium critical field data to be 2600 ± 400 Å and 350 ± 30 Å, respectively.

INTRODUCTION

To interpret critical magnetic field measurements on superconducting films, a theory is needed which includes both strong-field effects and nonlocal effects—strong-field, to describe phenomena occurring at the critical field; nonlocal to adequately describe thickness and mean-free-path effects. Such a theory does not exist at present. It is the purpose of this paper to show how the critical fields of superconducting films can be related to the nonlocal microscopic parameters by the use of the Ginzburg-Landau theory[1] together with the nonlocal theories. The general scheme is as follows: Using the Ginzburg-Landau results, the critical field of a film is related to its susceptibility in a weak magnetic field. Using the nonlocal calculations of Schrieffer,[2] the weak-field susceptibility is related to the nonlocal parameters. Combining the theoretical expressions, the film critical field can be expressed directly in terms of the nonlocal parameters. The resulting model is compared to critical field data for pure indium films and is shown to be in good agreement. Because of the purity of these films, mean-free-path effects are unimportant and the detailed discussion of the theoretical model is limited to thickness effects. In a subsequent paper, mean-free-path effects will be discussed in detail and the results will be compared to critical-field data for alloy films.

[1] V. L. Ginzburg and L. D. Landau, Zhur. Eksp. i Teoret. Fiz. **20**, 1064 (1950).
[2] J. R. Schrieffer, Phys. Rev. **106**, 47 (1957).

THEORETICAL MODEL

For films thin enough so that the order parameter ψ_0 can be considered constant over the thickness of the film, Eqs. (61) and (62) of Ginzburg-Landau[1] give the following expressions for the film critical field:

$$(h_c/H_c)^2=\psi_0^2(2-\psi_0^2)/[1-(1/\eta)\tanh\eta], \tag{1}$$

and

$$(h_c/H_c)^2=[4\psi_0^2(\psi_0^2-1)\cosh^2\eta]/[1-(1/2\eta)\sinh 2\eta], \tag{2}$$

where

$$\eta\equiv\psi_0 a/\delta_0. \tag{3}$$

The quantity a is the film half-thickness, h_c is the film critical field, H_c is the bulk critical field, and δ_0 is the weak-field penetration parameter. For $h_c/H_c>1$, Eqs. (1) and (2) can be solved numerically to obtain a

relationship between h_c/H_c and δ_0/a, which is of the form

$$h_c/H_c = F(\delta_0/a). \tag{4}$$

The function $F(\delta_0/a)$ is plotted in Fig. 1. For $h_c/H_c > \sqrt{(24/5)}$, Eq. (4) simplifies to

$$h_c/H_c = (\sqrt{6})\delta_0/a. \tag{5}$$

From Eq. (66) of Ginzburg-Landau, which relates the magnetic moment of a thin film to the penetration parameter of the film, we can obtain an expression relating the film susceptibility in a weak magnetic field to the weak-field penetration parameter:

$$\kappa/\kappa_0 = 1 - (\delta_0/a)\tanh(a/\delta_0), \tag{6}$$

where κ is the film susceptibility in weak field, and κ_0 is the bulk susceptibility in weak magnetic field. For very thin films, i.e., $\delta_0/a \gg 1$, we obtain from Eq. (6)

$$\kappa/\kappa_0 \simeq (1/3)(a/\delta_0)^2. \tag{7}$$

By the simultaneous solution of Eqs. (4) and (6), a relation can be obtained between the film critical field and the weak-field susceptibility. This is of the form

$$h_c/H_c = G(\kappa/\kappa_0), \tag{8}$$

and is plotted in Fig. 2. From Eqs. (5) and (7), the thin-film limit of Eq. (8) is obtained.

$$h_c/H_c = (\kappa/2\kappa_0)^{-\frac{1}{2}}. \tag{9}$$

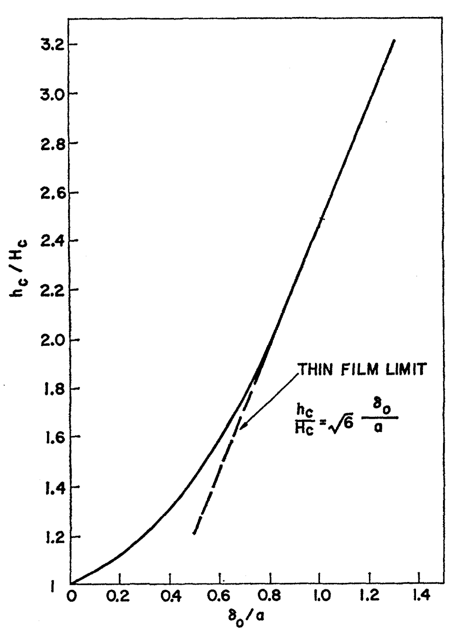

FIG. 1. Relationship between film critical field and weak-field penetration parameter as predicted by the Ginzburg-Landau theory. The quantity h_c/H_c is the ratio of the film critical field to the bulk critical field; the quantity δ_0/a is the ratio of the weak-field penetration parameter to the film half-thickness.

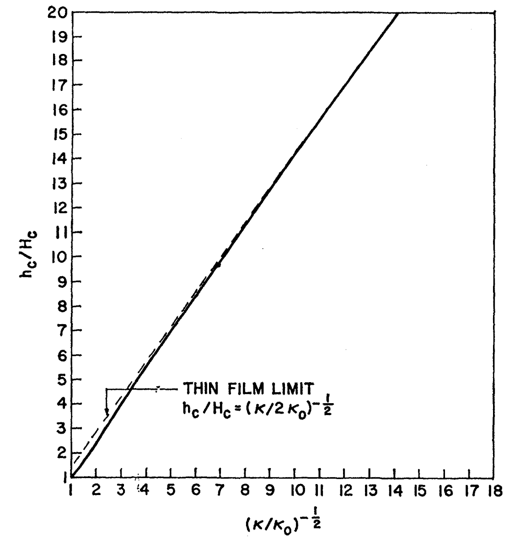

FIG. 2. Relationship between film critical field and film susceptibility as predicted by the Ginzburg-Landau theory. The quantity h_c/H_c is the ratio of the film critical field to the bulk critical field; the quantity κ/κ_0 is the ratio of the film susceptibility in a weak magnetic field to the bulk susceptibility in a weak magnetic field.

Schrieffer,[2] assuming specular reflection at film surfaces, obtained for the weak field susceptibility of a thin superconducting film

$$(\kappa/\kappa_0)_{\text{spec}} = 1 - \frac{2}{a^2}\sum_{n=0}^{\infty}[k_n^2 + K(k_n)]^{-1}, \tag{10}$$

where $k_n = (2n+1)\pi/2a$ and $K(k_n)$ is the kernel obtained from the relationship between current density and vector potential.

It is clear that if Eq. (10) is substituted into Eq. (8), one obtains a quite general relationship between film critical field and what ever parameters determine the kernel K. In particular, for the nonlocal theory of Pippard,[3]

$$(\kappa/\kappa_0)_{\text{spec}} = 1 - 2\sum_{n=0}^{\infty}\left[\frac{\pi^2}{4}(2n+1)^2 + \frac{1}{\beta\alpha^2(2n+1)^3}\{[1+\alpha^2(2n+1)^2] \times \arctan\alpha(2n+1) - \alpha(2n+1)\}\right]^{-1}, \tag{11}$$

where

$$\beta = \tfrac{1}{3}\pi\xi_0\lambda_L^2/a^3 \quad \text{and} \quad \alpha = \tfrac{1}{2}\pi\xi/a. \tag{12}$$

In the Pippard model, ξ is an effective coherence distance, ξ_0 is the coherence distance in pure material, and λ_L is the London penetration depth. If now Eq. (11) is substituted into Eq. (8), the desired expression relating film critical field to the nonlocal parameters

[3] A. B. Pippard, Proc. Roy. Soc. (London) **A216**, 547 (1953).

$\xi_0\lambda_L^2$ and ξ is obtained.

$$h_c/H_c=g(\xi_0\lambda_L^2/a^3,\xi/a), \tag{13}$$

where g is a function which can be numerically evaluated. For very thin films, i.e., $\beta\gg1$, $\alpha\gg1$, Eq. (11) can be expanded into a power series in β^{-1} and α^{-1}, and the resulting expression for the susceptibility is

$$(\kappa/\kappa_0)_{\text{spec}}\simeq0.518\beta^{-1}-0.658\beta^{-1}\alpha^{-1}+\cdots. \tag{14}$$

The substitution of Eq. (14) into Eq. (9) yields an expression for the critical field in the thin-film limit.

$$(h_c/H_c)_{\text{spec}}\simeq2.01(\xi_0\lambda_L^2/a^3)^{\frac{1}{2}}. \tag{15}$$

Thus, in the thin-film limit, the critical field should vary with thickness as $a^{-\frac{3}{2}}$.

For the case of random scattering, Schrieffer's expression for the susceptibility is more difficult to calculate and involves the solution of an integral equation. A result, valid only in the thin-film limit, is given by Rogers[4] as

$$(\kappa/\kappa_0)_{\text{rand}}\simeq(3/8)(a^3/\xi_0\lambda_L^2). \tag{16}$$

Substitution of Eq. (16) into Eq. (9) gives the critical field in the thin-film limit to be

$$(h_c/H_c)_{\text{rand}}\simeq2.31(\xi_0\lambda_L^2/a^3)^{\frac{1}{2}}. \tag{17}$$

Comparison of Eq. (17) to Eq. (15) indicates that the nonlocal calculation is not too sensitive to the type of surface scattering assumed. Except for the numerical coefficient, Eq. (17) is similar to limiting expressions obtained by Douglass[5] and Ferrell and Glick.[6]

DISCUSSION OF RESULTS

In Figs. 3 and 4, are shown plots of critical field vs film thickness calculated from Eq. (13) on the IBM 7090 computer for various values of the nonlocal parameters $\xi_0\lambda_L^2$ and ξ. In Fig. 3, curves A, B, and C were calculated for different values of $\xi_0\lambda_L^2$, holding ξ fixed. In the limit $a\rightarrow\infty$, the curves converge, for in this limit $h_c/H_c\rightarrow1$. In the limit $a\rightarrow0$, the curves are parallel to one another and have a slope of $-\frac{3}{2}$, as one would expect from the limiting law of Eq. (15). In Fig. 4, curves A, B, and C were calculated for various values of ξ, holding $\xi_0\lambda_L^2$ fixed. Here the curves must converge, not only in the limit $a\rightarrow\infty$, but also in the limit $a\rightarrow0$ [as Eq. (15) predicts]. Consequently, the calculated value of critical field is, in general, more sensitive to changes in $\xi_0\lambda_L^2$ than to changes in ξ.

In Fig. 5, the theoretical model is compared to experimental data obtained for indium films.[7] The critical-field data shown were obtained at $T=0.9T_c$ and $0.95T_c$. The best fit to the data is estimated to be $\xi_0\lambda_L^2(0.9T_c)=(1.62\pm0.08)\times10^9$ (Å)^3, $\xi_0\lambda_L^2(0.95T_c)=(3.23\pm0.16)\times10^9$ (Å)^3, and $\xi=2600\pm400$ Å at both temperatures. In practice, the values for $\xi_0\lambda_L^2$ are largely determined from the thin-film critical-field data; the value for ξ is largely determined by the thick-film data. Hence, the values for $\xi_0\lambda_L^2$ and ξ are very nearly independently determined. Residual resistivity measurements made upon these films[7] indicate that the intrinsic electronic mean free path in the normal state at low temperatures is greater than 10^4 Å. Hence, it can be assumed that $\xi\simeq\xi_0$ with an error of no more than about 2%. It then follows that for $\xi_0=2600\pm400$ Å, one can calculate from the above values of $\xi_0\lambda_L^2$ the following values for λ_L: $\lambda_L(0.9T_c)=790\mp60$ Å and $\lambda_L(0.95T_c)=1115\mp90$ Å.

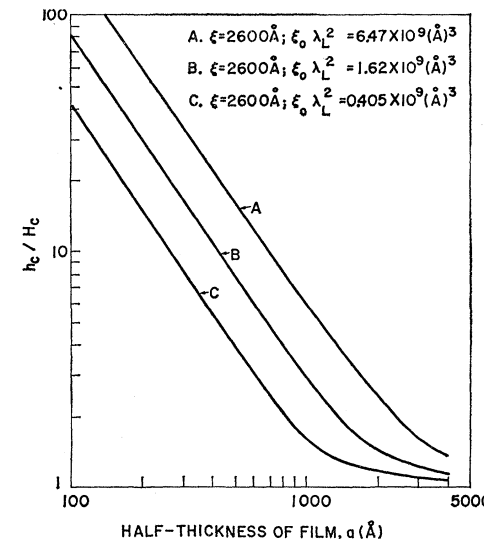

FIG. 3. The variation with film thickness of the ratio of film critical field to bulk critical field. The curves are calculated from Eq. (13) of the text for various values of $\xi_0\lambda_L^2$, holding ξ fixed.

There are several criteria by which we can check this model.

(1) The observed thickness dependence of critical field is in very good agreement with that predicted by the model.

(2) The fact that ξ is temperature independent (at the two temperatures shown) is consistent with the prediction of the BCS[8] theory.

(3) The temperature dependence of λ_L obtained from the data of Fig. 5, $[\xi_0\lambda_L^2(0.95T_c)/\xi_0\lambda_L^2(0.9T_c)]^{\frac{1}{2}}=1.41$ is in good agreement with the theoretical calculation of Mühlschlegel,[9] who also obtained

$$\lambda_L(0.95T_c)/\lambda_L(0.9T_c)=1.41.$$

(4) Using Mühlschlegel's results, $\lambda_L(0)$ can be calculated from $\lambda_L(0.95T_c)$ or $\lambda_L(0.9T_c)$ and is $\lambda_L(0)$

[4] K. T. Rogers, Ph.D. thesis, University of Illinois, 1960 (unpublished).
[5] D. H. Douglass, Jr., Phys. Rev. **124**, 735 (1961).
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[7] A. M. Toxen, Phys. Rev. **123**, 442 (1961).
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[9] B. Mühlschlegel, Z. Physik **155**, 313 (1959).

$=350\pm30$ Å. From $\lambda_L(0)$ and ξ_0, the bulk penetration depth at $T=0°$K, $\lambda(0)$, can be calculated from either the Pippard theory or the BCS theory, and the result can be checked against experiment.

From the Pippard theory,

$$\lambda/\lambda_\infty \simeq 1+1.1007(\lambda_\infty/\xi_0)^{0.830}, \tag{18}$$

where

$$\lambda_\infty = \frac{8}{9}\frac{3^{1/6}}{(2\pi)^{1/3}}(\xi_0\lambda_L{}^2)^{1/3} \tag{19}$$

for specular reflection. From Eqs. (18) and (19), $\lambda(0)$ is 486 Å. From BCS, for $\xi_0/\lambda_L(0)=7.4$, $\lambda(0)/\lambda_L(0)\simeq1.4$, giving for $\lambda(0)$ the value 490 Å. These values for $\lambda(0)$ lie within about 10% of the experimental value reported by Dheer,[10] 430 ± 20 Å, which is good agreement.

Although the bulk penetration depth calculated from ξ_0 and $\lambda_L(0)$ is in good agreement with the measured value reported by Dheer, the values of ξ_0 and $\lambda_L(0)$ taken individually are not in very good agreement with values calculated by Dheer from his normal-state high-frequency surface impedance measurements. Dheer obtained for these quantities, $\lambda_L(0)=205$ Å, and $\xi_0=4400$ Å, compared to $\lambda_L(0)=350\pm30$ Å and $\xi_0=2600\pm400$ Å. From a free-electron model calculation, it can be shown that the values of $\lambda_L(0)$ and ξ_0 obtained from the data of Fig. 5 are self-consistent but imply a value of surface impedance different from that measured by Dheer. The London penetration depth can be related to the normal-state free-electron parameters in the following way[11]:

$$\lambda_L{}^2(0)=m^*c^2/4\pi ne^2, \tag{20}$$

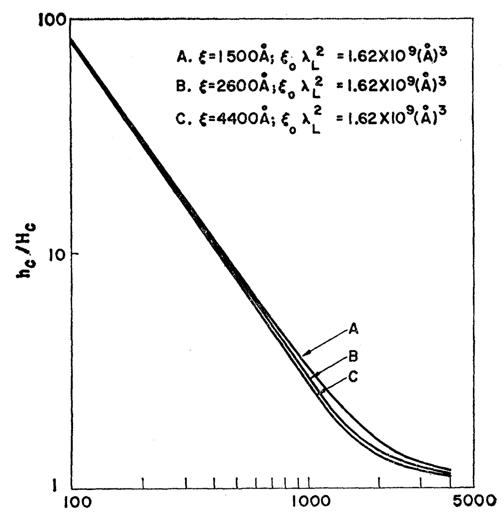

FIG. 4. The variation with film thickness of the ratio of film critical field to bulk critical field. The curves are calculated from Eq. (13) of the text for various values of ξ, holding $\xi_0\lambda_L{}^2$ fixed.

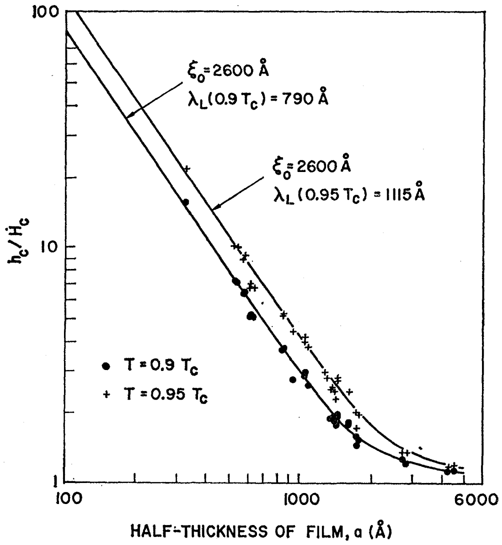

FIG. 5. Comparison of the theoretical model to experimental data. The solid curves are calculated from Eq. (13) of the text for the values of the nonlocal parameters indicated. The dots and pluses represent critical-field data for indium films.

where m^* is the electronic effective mass, e is the electronic charge, and n is the density of electrons. The dc resistivity is given by[12]

$$\rho=m^*v_F/ne^2l, \tag{21}$$

where v_F is the Fermi velocity, and l is the electron mean free path. From Eqs. (20) and (21), one easily obtains the relation

$$\lambda_L{}^2(0)=c^2\rho l/4\pi v_F. \tag{22}$$

The expression for the coherence length, ξ_0, is given by BCS to be

$$\xi_0=\hbar v_F/\pi\epsilon_0(0), \tag{23}$$

where $\epsilon_0(0)$ is the energy gap at $T=0°$K. Combining Eqs. (22) and (23), we obtain

$$\xi_0\lambda_L{}^2(0)=\hbar c^2\rho l/4\pi^2\epsilon_0(0), \tag{24}$$

which relates $\xi_0\lambda_L{}^2(0)$ to two measurable quantities: $\epsilon_0(0)$, which has been measured in several ways for indium;[13,14] and ρl, which can be obtained by high-frequency surface impedance measurements, such as those made on indium by Dheer and Roberts.[15] From Eqs. (2, 11, 3), (2, 11, 8), and (11, 7, 18) of Ziman,[16] we can relate v_F to ρl and to γ, the coefficient of electronic specific heat in the normal state.

$$v_F=(\pi^2k^2/e^2)(1/\gamma\rho l). \tag{25}$$

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[14] I. Giaever and K. Megerle, Phys. Rev. **122**, 1101 (1961).
[15] D. C. Roberts (unpublished). See T. E. Faber, Proc. Roy. Soc. (London) **A241**, 531 (1957).
[16] J. M. Ziman, *Electrons and Phonons* (Oxford University Press, New York, 1960).

From Eqs. (23), (24), and (25), we obtain the desired relationship between ξ_0 and $\xi_0\lambda_L^2(0)$ [or ξ_0 and $\lambda_L(0)$]:

$$\xi_0=\hbar^2c^2k^2/4\pi e^2\epsilon_0^2(0)\gamma\xi_0\lambda_L^2(0). \quad (26)$$

If we substitute into Eq. (26), $\xi_0\lambda_L^2(0)=0.319\times10^9$ (Å)^3, obtained by extrapolating to $T=0$°K, the measured values for $\xi_0\lambda_L^2$; $\epsilon_0(0)=1.75kT_c$, where $T_c=3.41$°K; and $\gamma=1.7$ mJ/mole-deg^2, which is the average of calorimetric values obtained by Clement and Quinnell,[17] and Bryant and Keeson,[18] we obtain $\xi_0=2800$ Å, in remarkable agreement with 2600±400 Å obtained by curve-fitting. From Eq. (24), we obtain $\rho l=0.98\times10^{-11}$ Ω-cm^2 for the above values of $\xi_0\lambda_L^2(0)$ and $\epsilon_0(0)$. This value for ρl is quite a bit larger than the value of 0.57×10^{-11} Ω-cm^2 reported by Dheer, but agrees reasonably well with the value of 0.89×10^{-11} Ω-cm^2 obtained by Roberts.

Although thickness effects have been emphasized in this paper, impurity effects can also be calculated through their effect upon ξ and this will be the subject of a subsequent paper. For according to the Pippard theory,

$$1/\xi=1/\xi_0+1/l. \quad (27)$$

In addition, this model can be extended to properties of films other than the critical fields. For through Eqs. (6) and (10), nonlocal equations for δ_0 may easily be obtained. From these, nonlocal relations for surface energy, critical current, etc., might be obtained and compared with experiment. Finally, it is clear that although only the Pippard kernel has been discussed in this paper, calculations could be carried out for other kernels.

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Critical Field of Thin Superconducting Shapes

J. J. Hauser and E. Helfand
Bell Telephone Laboratories, Murray Hill, New Jersey

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Considerations of the thermodynamics pertaining to the critical field of small superconducting samples of various shapes results in an explicit relation for the ratio of the critical field of small samples to that of bulk in terms of the magnetic moment. The magnetic moment has been calculated using Miller's modification of the Bardeen-Cooper-Schrieffer kernel which includes mean free path. The critical-field ratios of various shapes in decreasing order are sphere, cylinder in parallel field, cylinder in transverse field, and plate in parallel field. The findings are compatible with the fact that dislocations (cylinder like) may be the filaments responsible for hard superconductivity. Under certain conditions the filaments could be numerous and large enough for an appreciable fraction of the sample to appear superconducting in a specific heat measurement. The size of the filaments would also account for the lack of latent heat observed in hard superconductors. Because of the relative orientation of dislocations with respect to the applied field, not all dislocations will serve equally as filaments, thus explaining the current density vs critical-field curve and accounting for an anisotropic critical field when there is a preferred orientation of dislocations.

I. INTRODUCTION

The problem under consideration is the calculation of the stabilization, with respect to transition to normal state in a magnetic field, of a superconducting sample of small size. The transition of a material in a magnetic field is the result of the competition of two effects; the lower Gibbs free energy of electrons in the superconducting state, and the increase in free energy caused by the Meissner effect. When the sample is small, however, a nonvanishing fraction of the sample is penetrated by the magnetic field so that field exclusion is not as strong a destabilization factor.

In this paper, some of the thermodynamics involved in the problem will be reviewed. The relations for the critical fields will be derived in terms of the London and Bardeen-Cooper-Schrieffer (BCS) theories. Finally, explicit results will be obtained for several specimen shapes, and examined with reference to filaments as the possible explanation of hard superconductivity.

II. THERMODYNAMICS

The Gibbs free energy for a superconductor may be expressed as

$$dG=-\mathfrak{M}\cdot d\mathbf{H}_0, \quad (1)$$

where $\mathfrak{M}$ is the total magnetic moment of the sample, and $\mathbf{H}_0$ is the externally applied field.

In order to find the difference between a super-