examine the degree of admixture in the wave functions in the eighth zone along AH and in the ninth zone along $\Gamma K$ and to calculate the change in energy of these bands with change of volume. It is an interesting aside that these effects would not have occured in the absence of spin orbit coupling in rhenium.

*Note added in proof.* Since this paper was written, an article by Higgins and Kaehn has been published [Phys. Rev. **182**, 649 (1969)] in which the effect of impurity broadening on the singularities in the electron density of states and the superconducting transition temperature, associated with the passage of the Fermi energy through a critical point, was investigated. These authors report that the structure in $T_c$ as a function of Fermi energy is broadened by the order of $kT_c$ for pure metals ($\sim$4°K in the particular case of In which they consider), whereas for In with 2% Cd the impurity broadening is $\sim$50°K. However, since the effect of the electron-phonon interaction is to average the density of states over a region $\pm k\Theta_D$ about the Fermi energy, any structure in $T_c$ as a function of energy must be broadened over an energy of $2\Theta_D$, or $\sim$200°K in the case of In. This is clearly seen in Fig. 9.

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# Proximity Effect of Superconductors in High Magnetic Fields*

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The nucleation field $H_0$ for superconductivity at the boundary between a normal and a superconducting semi-infinite half-space is calculated. At this field, for temperatures smaller than the transition temperature $T_{cs}$ of the superconductor, a second-order phase transition occurs from the normal to the superconducting state as the magnetic field is decreased, and superconductivity is nucleated near the boundary between the superconducting and the normal metal. The calculation is general and is applied to clean and dirty superconductors. The normal metal also becomes a superconductor at a transition temperature $T_{cn}<T_{cs}$, and the above results apply to temperatures $T_{cn}\leq T\leq T_{cs}$ as well as $T<T_{cn}$, provided the Ginzburg-Landau equations apply. $H_0$ is temperature-dependent, and lies between the bulk nucleation field $H_{c2}$ and the surface nucleation field $H_{c3}$. The value of $H_0$ depends on the Bardeen-Cooper-Schrieffer coherence lengths $\xi_0$, the mean free paths $l$ in the normal states, the effective masses $m$, the electron densities $n$, and the transition temperatures $T_c$ of both metals. For example, one finds, in the limit when both metals are dirty ($l\ll\xi_0$), that $H_{c2}\leq H_0\leq H_{c3}$ for $0\leq\sigma_s/\sigma_n\leq\infty$, where the $\sigma$'s are the normal-state conductivities of the superconducting and the normal metal. This is not in agreement with previous calculations by Hurault, who concludes that when $\sigma_s/\sigma_n=1$, the value of $H_0$ is $H_{c2}$ for $T_{cn}\leq T\leq T_{cs}$. When $T<T_{cn}$, the value $H_0$ is strongly field- and temperature-dependent, particularly when $\sigma_s/\sigma_n\lesssim 1$. The above concept is applicable to internal boundary nucleation of superconductivity in the bulk of a superconductor.

## I. INTRODUCTION

WHEN a normal ($n$) and superconducting ($s$) metal are joined together, superconducting pairs exist near the $ns$ boundary in the $n$ metal while the number of superconducting pairs in the $s$ metal near the $ns$ boundary is reduced.[1] In a large magnetic field, superconductivity may be quenched in the bulk of the $s$ metal while it may still exist on the free surface of the $s$ metal up to the surface nucleation field[2] $H_{c3}$. When the surface is plated with a normal metal, $H_{c3}$ is reduced. This was investigated by Hurault[3] for two superconductors with different transition temperatures $T_{cs}$ and $T_{cn}$ for temperatures $T_{cn}\leq T\leq T_{cs}$ when both metals were "dirty," e.g., the mean free path $l$ was very small compared to the Bardeen-Cooper-Schrieffer (BCS)[4] coherence length $\xi_0$. He concluded that, when the conductivity of the $S$ metal in the normal state, $\sigma_s$, is larger than $\sigma_n$, the conductivity of the $N$ metal, the boundary nucleation field $H_0$ is larger than the bulk nucleation

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[1] See, for example, Orsay Group on Superconductivity, in *Quantum Fluids*, edited by D. F. Brewer (North-Holland Publishing Co., Amsterdam, 1966).
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field $H_{c2}$ and when $\sigma_s/\sigma_n \leq 1$, that $H_0 = H_{c2}$. This conclusion[3] has been generally accepted in the literature.[1,5]

Our experimental investigations[6,7] on Pb alloys plated with Cu lead us to suspect that $H_0$ might be larger than $H_{c2}$ even for $\sigma_s/\sigma_n < 1$, although one could always argue that the presence of oxide patches on the surface of the alloy does not allow for a perfect contact between the two metals. However, with sufficiently sensitive measuring apparatus we were always able to find superconductivity above $H_{c2}$ for all our specimens with nonmagnetic overlays. Other investigators found similar effects,[8–10] though all of these experiments[6–10] are open to criticism in one way or another as to the conclusion $H_0 > H_{c2}$ for $\sigma_s/\sigma_n < 1$. The above experiments prompted us to investigate this problem theoretically.

We present a general calculation of the proximity effect within the framework of the Ginzburg-Landau (GL) theory of superconductivity.[11] Our calculation is general, and is applicable to clean and dirty superconductors at temperatures $T_{cn} \leq T \leq T_{cs}$ as well as $T \leq T_{cn}$. In Sec. II we formulate the problem mathematecially; in Sec. III we discuss the boundary conditions. The general solution is outlined in Sec. IV and the numerical results are presented in Sec. V. Section VI is devoted to the conclusions in which we also discuss the difference between our approach and that of Ref. 3. We find that when both metals are dirty, for example, the conclusion[3] $H_0 = H_{c2}$ for $\sigma_s/\sigma_n \leq 1$ is not correct.

## II. FORMULATION OF PROBLEM

We consider two metals in intimate contact at $x = 0$. The semi-infinite half-space for $x > 0$ is filled with a superconductor $s$ whose transition temperature is denoted by $T_{cs}$. The semi-infinite half space for $x < 0$ is filled with a metal $n$ whose transition temperature is denoted by $T_{cn} < T_{cs}$. We assume that the applied magnetic field $H_0$ is parallel to the $z$ axis and is of such magnitude that superconductivity exists only near the boundary at $x \approx 0$. For $x \to \pm\infty$, we assume that both metals are in the normal state. Thus we think of $H_0$ as equivalent to the surface nucleation field $H_{c3}$ of the $s$ metal but modified by the properties of the $n$ metal because of the intimate contact with the latter at $x = 0$. The $n$ metal for $x \to -\infty$ is in the normal state when $T_{cn} < T \leq T_{cs}$ and also when $T \leq T_{cn}$, because $H_0$ is assumed to be larger than the corresponding $H_{c3}$ value of the free surface of the $n$ metal. In the latter case, we limit ourselves to the range of temperatures for which the $H_{c3}$ value of the equivalent free surface of the $n$ side is smaller or equal to the $H_{c3}$ value of the equivalent free surface of the $S$ side. In the present calculations we use the Ginzburg-Landau equations.[11] The use of these equations further restricts the exact temperature range to $T_{cs} - T \ll T_{cs}$ and $T_{cs} - T_{cn} \ll T_{cs}$. However, we know empirically that the temperature restrictions are not very stringent, and that our results will be at least qualitatively if not quantitatively correct when these restrictions are violated.

We neglect the cubic term in the Ginzburg-Landau (GL) equations, which are discussed in detail in Ref. 12, because near the interface nucleation field $H_0$ the amplitude of the order parameter $\Psi_s(x)$ of the $s$ side, and $\Psi_n(x)$ of the $n$ side, is small compared to the zero-field value of the order parameter on the $s$ side. We assume that $\Psi_n(x,y) = \Psi_n(x)e^{ik_n y}$ is a meaningful quantity on the $n$ side, and that $\Psi_n(x)$ is real and finite near the interface and zero in the bulk of $n$. On the $s$ side we assume that $\Psi_s(x,y) = \Psi_s(x)e^{ik_s y}$, where $\Psi_s(x)$ is finite at the interface and zero in the bulk of $s$. The GL equations on the $s$ side ($\zeta \geq 0^+$) and $n$ side ($\zeta \leq 0^-$) are [$i \equiv (s,n)$]

$$\{d^2/d\zeta^2 - [\zeta + a_i(\zeta) - \Gamma_i]^2 + \epsilon_i\}\Psi_i(\zeta) = 0, \tag{1}$$

$$j_i = -\frac{2eh}{m_i}\left(\frac{2\pi H_0}{\phi_0}\right)^{1/2}[\zeta + a_i(\zeta) - \Gamma_i]\Psi_i^2(\zeta). \tag{2}$$

We have used the following definitions:

$$\zeta = x(2\pi H_0/\phi_0)^{1/2}, \tag{3}$$

$$\phi_0 = hc/2e \equiv \text{fluxoid quantum}, \tag{4}$$

$$\epsilon_s = \phi_0/2\pi H_0 \xi_s^2 = H_{c2}/H_0, \tag{5}$$

$$\epsilon_n = \epsilon_s \xi_s^2/\xi_n^2, \tag{6}$$

where $H_{c2}$ refers to the bulk nucleation field on the $s$ side. The vector potential $\mathbf{A} \equiv (0,A_y,0)$ is

$$A_y = H_0 x + \Delta A_y(x) + A_y(0) = (\phi_0 H_0/2\pi)^{1/2} \times [\zeta + a(\zeta)] + H_0 x_0, \tag{7}$$

where $\Delta A_y(0) = a(0) = 0$ by definition and $A_y(0) = H_0 x_0$ is the value of the vector potential at $x = 0$. Furthermore,

$$\Gamma_n = (\phi_0/2\pi H_0)^{1/2} k_n - (2\pi H_0/\phi_0)^{1/2} x_0, \tag{8}$$

$$\Gamma_s = (\phi_0/2\pi H_0)^{1/2} k_s - (2\pi H_0/\phi_0)^{1/2} x_0. \tag{9}$$

It follows from Gor'kov[13] (after some manipulations)

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that $[i\equiv(s,n)]$

$$\xi_i^2=\frac{\hbar^2}{2m_i}\frac{7\zeta(3)\epsilon_F\chi(\rho_i)}{12\pi^2k^2T^2}\frac{T_{ci}}{T_{ci}-T}$$

$$\approx\frac{0.548\xi_{0i}^2}{0.754\xi_{0i}/l_i+1}\frac{T_{ci}}{T_{ci}-T}, \quad (10)$$

$$\chi(\rho_i)=\frac{8}{7\zeta(3)}\left(\frac{1}{\rho_i}\right)\left\{\frac{\pi^2}{8}+\frac{1}{2\rho_i}[\psi(\tfrac{1}{2})-\psi(\tfrac{1}{2}+\rho_i)]\right\}$$

$$\approx\frac{1}{1+7\zeta(3)\rho_i/\pi^2}, \quad (11)$$

$$\rho_i=\hbar v_{Fi}/2\pi kTl_i. \quad (12)$$

We have approximated $\chi(\rho_i)$ by the term given at the right-hand side of Eq. (11). The symbols are defined as: $k$ is Boltzmann's constant; $\xi_0=0.18\hbar v_F/kT_c$; $T_{ci}/T$ was assumed to be unity on the right-hand side of Eq. (10); $m_n$ and $m_s$ are the effective electron masses on the $n$ and $s$ sides, respectively; $\psi$ is the digamma function; $v_{Fn}$ and $v_{Fs}$ are the Fermi velocities; and $l_n$ and $l_s$ the mean free paths in the normal state on the $n$ and $s$ sides, respectively.[14] It should be noticed that $\xi_n^2<0$ for $T>T_{cn}$, and $\xi_n^2>0$ for $T<T_{cn}$, from which it follows that $\epsilon_n<0$ [Eq. (6)] for $T_{cn}<T<T_{cs}$, and $\epsilon_n>0$ for $T<T_{cn}$.

Furthermore, the GL order parameter $\Psi(\zeta)$ is defined by[13]

$$\Psi_i^2(\zeta)=\frac{7\zeta(3)n_i\chi(\rho_i)}{16\pi^2k^2T^2}\Delta_{Gi}^2(\zeta), \quad (13)$$

where $n$ is the number of electrons per unit volume, and $\Delta_G(\zeta)$ is the Gor'kov-Green's function. We shall discuss Eq. (13) in Sec. III in relation to the boundary conditions at $\zeta=0$.

Equations (1) and (2) can be integrated once, and if one integrates over all space from $\zeta=-\infty$ to $\zeta=+\infty$ with the boundary conditions: $\Psi_n(-\infty)=0$; $(d\Psi_n/d\zeta)_{-\infty}=0$; $\Psi_s(\infty)=0$; $(d\Psi_s/d\zeta)_{\infty}=0$; $a_n(0^-)=a_n(0^+)=0$ (by definition), and assumes that the magnetic field $H(\zeta)$ is continuous everywhere, one gets

$$\frac{1}{m_n}\left[\left(\frac{d\Psi_n}{d\zeta}\right)_{0^-}^2+(\epsilon_n-\Gamma_n^2)\Psi_n^2(0^-)\right]-\frac{1}{m_s}\left[\left(\frac{d\Psi_s}{d\zeta}\right)_{0^+}^2+(\epsilon_s-\Gamma_s^2)\Psi_s^2(0^+)\right]+\frac{c}{4eh}H_0\left[\left(\frac{H(\zeta)}{H_0}\right)^2+1\right]_{-\infty}^{+\infty}=0. \quad (14)$$

For the lowest-energy state the total current must be zero, and therefore $H(+\infty)=H(-\infty)=H_0$. Hence it follows from Eq. (14) that

$$\epsilon_n+S_n^2-\Gamma_n^2=\gamma(\epsilon_s+S_s^2-\Gamma_s^2), \quad (15)$$

where

$$S_n=\left(\frac{d\Psi_n(\zeta)/\Psi_n(0^-)}{d\zeta}\right)_{0^-}, \quad (16)$$

$$S_s=\left(\frac{d\Psi_s(\zeta)/\Psi_s(0^+)}{d\zeta}\right)_{0^+}, \quad (17)$$

$$\gamma=\frac{m_n}{m_s}\frac{\Psi_s^2(0^+)}{\Psi_n^2(0^-)}. \quad (18)$$

At the boundary nucleation field $H_0$ the internal magnetic field is uniform in space for the lowest-energy state, which means that $a(\zeta)=0$ and therefore Eq. (1) reduces to

$$-\frac{d^2\Psi_s}{d\zeta^2}+(\zeta-\Gamma_s)^2\Psi_s=\epsilon_s\Psi_s, \quad \text{for} \quad \zeta\geq 0^+ \quad (19)$$

$$-\frac{d^2\Psi_n}{d\zeta^2}+(\zeta-\Gamma_n)^2\Psi_n=\epsilon_n\Psi_n, \quad \text{for} \quad \zeta\leq 0^-. \quad (20)$$

It is the aim of the present investigation to solve Eqs. (19) and (20) with condition (15), the appropriate boundary conditions, and the definition of $\epsilon_n$ [Eqs. (6) and (10)].

## III. BOUNDARY CONDITIONS

Boundary conditions have been investigated by de Gennes[15] and Zaitsev.[16] It follows from the second general GL equation that when one makes the actual (not the mean) current continuous across a boundary at $r=0$, that the following condition must be satisfied:

$$\frac{1}{m_n}\Psi_n(0^-)\left[\nabla-i\frac{2\pi}{\phi_0}\mathbf{A}\right]_{\perp 0^-}\Psi_n(\mathbf{r})=\frac{1}{m_s}\Psi_s(0^+)\left[\nabla-i\frac{2\pi}{\phi_0}\mathbf{A}\right]_{\perp 0^+}\Psi_s(\mathbf{r}). \quad (21)$$

Equation (21) is the same as the product of the two continuous quantities of the two different cases considered by Zaitsev[16] (see his note added in proof). Therefore, when the boundary exhibits diffuse or specular electron scattering $(n_i\chi(\rho_i)/m_i)\Delta_{Gi}[\nabla-i(2\pi/\phi_0)\mathbf{A}]_\perp\Delta_{Gi}$ must be continuous. When one substitutes the value for $\Delta_{Gi}$ from Eq. (13) into this expression, one obtains Eq. (21). For our particular case $A_x=0$ and $\nabla_\perp=d/dx$, so that

[14] Similarly, the GL penetration depth $\lambda$ is $\lambda^2=\lambda_L^2(0)T_c/2\chi(\rho)\times(T_c-T)$, where $\lambda_L^2(0)=mc^2/4\pi e^2n$, and the $\kappa$ value is $\kappa=\lambda/\xi=0.955\lambda_L(0)\times(0.754/l+1/\xi_0)$. In the dirty limit, $\lambda$ becomes $\lambda=0.614\lambda_L(0)\times[(\xi_0T_c)/l(T_c-T)]^{1/2}$.

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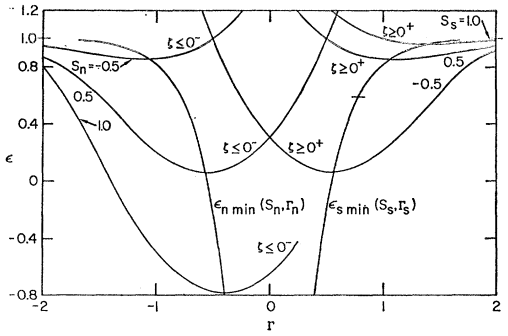


FIG. 1. Shown are the eigenvalues $\epsilon_s$ and $\epsilon_n$ of Eqs. (19) and (20) as a function of the nucleation centers $\Gamma_s$ and $\Gamma_n$ for constant values of the boundary conditions $S_s$ and $S_n$ at $\zeta=0$ as defined by Eqs. (16) and (17). The $n$ side is defined for $\zeta\leq 0^-$ and the $s$ side for $\zeta\geq 0^+$. The horizontal bar on the $\epsilon_{s\,min}(S_s,\Gamma_s)$ curve corresponds to the eigenvalue of the surface nucleation field $H_{c3}$. [$\epsilon_s=0.5901=H_{c2}/H_{c3}$]. To the right-hand side of $\epsilon_{s\,min}$ the value of $\epsilon_s+S_s^2-\Gamma_s^2=Z_s<0$ [see Eq. (27)] and to the left-hand side of $\epsilon_{s\,min}$ the value of $Z_s>0$. Similarly, to the left-hand side of $\epsilon_{n\,min}$ the value of $\epsilon_n+S_n^2-\Gamma_n^2=Z_n<0$ [see Eq. (28)] and to the right-hand side of $\epsilon_{n\,min}$ the value of $Z_n>0$.

Eq. (21) reduces to

$$S_n=\gamma S_s, \tag{22}$$

where $S_n$, $S_s$, and $\gamma$ are defined by Eqs. (16)–(18). It follows, as Zaitsev[16] shows, that $\Delta_{Gi}$ is continuous for a plane boundary and $(m_i)^{1/2}\Delta_{Gi}$ (the Fermi energy $\epsilon_F$ is the same at $\zeta=0^+$ and $\zeta=0^-$) for a rough boundary. Therefore, one obtains from Eq. (13) for a plane boundary $\Psi_s^2(0^+)/\Psi_n^2(0^-)=n_s\chi(\rho_s)/n_n\chi(\rho_n)$ and for a rough boundary $\Psi_s^2(0^+)/\Psi_n^2(0^-)=m_n n_s\chi(\rho_s)/m_s n_n\chi(\rho_n)$. Hence the $\gamma$ value for a plane boundary becomes

$$\gamma_p=\frac{m_n}{m_s}\frac{n_s}{n_n}\frac{\chi(\rho_s)}{\chi(\rho_n)}\approx\frac{m_n}{m_s}\frac{n_s}{n_n}\frac{1+0.754(\xi_{0n}/l_n)}{1+0.754(\xi_{0s}/l_s)}, \tag{23}$$

where $T_{cn}/T$ and $T_{cs}/T$ were assumed to be unity in the last expression of Eq. (23). For a rough boundary plane the $\gamma$ value becomes

$$\gamma_r=(m_n/m_s)\gamma_p. \tag{24}$$

The reader should note that the ratio of the square of order parameters $\Psi_n^2(0^-)$ and $\Psi_s^2(0^+)$ at the $ns$ boundary is determined by the normal-state microscopic properties of the two metals and that $\gamma$ is a measure of this ratio [Eq. (18)]. $\Psi(\zeta)$ is, in general, discontinuous at $\zeta=0$. When the effective electron masses on both sides are the same, one determines from Eqs. (18), and (22)–(24) that the scattering mechanism at the $ns$ boundary is of no concern, and that

$$\gamma=\gamma_p=\gamma_r=\Psi_s^2(0^+)/\Psi_n^2(0^-)=n_s\chi(\rho_s)/n_n\chi(\rho_n)=S_n/S_s.$$

## IV. GENERAL SOLUTION

In order to find the nucleation field $H_0$, which is the largest field at which superconductivity exists at the $ns$ boundary, one has to find the lowest unique eigenvalue $\epsilon_s$ of Eq. (19). $H_0$ will depend on $\gamma$, which is a material parameter and is a measure of the discontinuity of the absolute value of the order parameter and its slope at the $ns$ boundary, and also on a parameter $\alpha(T)$, which is a measure of the temperature with respect to $T_{cn}$ and $T_{cs}$, and which is defined by Eq. (25). It follows from Eqs. (6) and (10) that

$$\frac{\epsilon_n}{\epsilon_s}=\frac{m_n}{m_s}\frac{\chi(\rho_s)}{\chi(\rho_n)}\frac{T_{cs}}{T_{cn}}\frac{T_{cn}-T}{T_{cs}-T}=\alpha(T), \quad (T_{cn}\neq T_{cs}). \tag{25}$$

In terms of $\gamma_p$, Eq. (25) reduces to

$$\alpha(T)\approx\gamma_p\frac{n_n}{n_s}\frac{T_{cn}-T}{T_{cs}-T}, \quad (T_{cn}\neq T_{cs}). \tag{26}$$

Equations (15), (19), (20), (22), and (25) are five equations with six unknown quantities: $\epsilon_n$, $\epsilon_s$, $S_n^2$, $S_s^2$, $\Gamma_n^2$, and $\Gamma_s^2$. These equations contain also the material parameters $\gamma$, $m_n/m_s$, $n_s/n_n$, $T_{cn}$, $T_{cs}$ and the temperature $T$. In order to solve these equations uniquely, we demand that for a constant value of the slope $S_s$ of the normalized order parameter on the $s$ side at $\zeta=0^+$ the eigenvalue $\epsilon_s(=H_{c2}/H_0)$ in Eq. (19) must have its lowest value and must be unique. This means that we interpret the largest value of $H_0$ to be the boundary nucleation field. When one integrates Eq. (1) once, substitutes the appropriate boundary conditions, and makes the total current zero on the $s$ side, one obtains

$$\epsilon_s+S_s^2-\Gamma_s^2=0. \tag{27}$$

It follows therefore from Eq. (15) that

$$\epsilon_n+S_n^2-\Gamma_n^2=0. \tag{28}$$

Hence Eq. (15) is replaced by Eqs. (27) and (28) and the problem can be solved uniquely.

In order to find $H_0/H_{c2}$ as a function of $\gamma$ and $\alpha(T)$ we proceeded as follows. We selected a value for $S_s$, solved the normalized Eq. (19) for $\zeta\geq 0^+$ with the boundary condition $[\Psi_s(\zeta)/\Psi(0^+)]_{0^+}=1$, $S_s$ fixed, $\Psi_s(\infty)/\Psi_s(0^+)=0$, and found the lowest eigenvalue $\epsilon_s$ which indeed satisfied Eq. (27), thus $\epsilon_s$ $(=H_{c2}/H_0)$ and $\Gamma_s$ were determined for this value of $S_s$. We selected some $\gamma$ value which then determined $S_n$ from Eq. (22). With this $S_n$ value we solved the normalized Eq. (20) with $[\Psi_n(\zeta)/\Psi_n(0^-)]_{0^-}=1$ and $\Psi_n(-\infty)/\Psi_n(0^-)=0$ for $\zeta\leq 0^-$. The smallest value of $\epsilon_n$ and the corresponding value of $\Gamma_n$ was found from Eq. (20) and it did indeed satisfy Eq. (28). Then from the ratio $\epsilon_n/\epsilon_s$ [Eq. (25)] we were able to determine the corresponding $\alpha(T)$-value which is a material and temperature parameter. Thus for a given value of $S_s$ we could determine $H_0/H_{c2}$ as a function of $\gamma$ and $\alpha(T)$. This was repeated for many values of $S_s$ and the boundary nucleation field $H_0/H_{c2}$ was then obtained as a function of $\gamma$ and $\alpha(T)$. Thus the microscopic parameter of the two metals

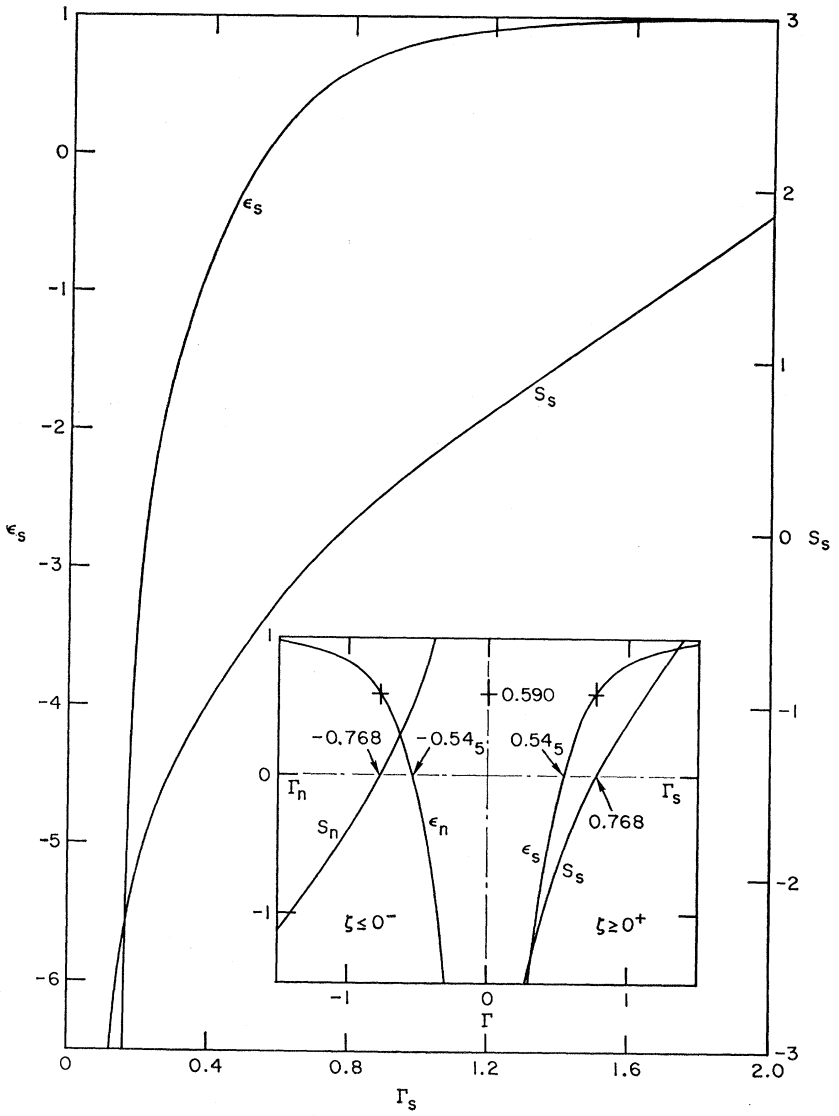


FIG. 2. Shown is $\epsilon_s$, corresponding to the minima of Fig. 1, as a function of $\Gamma_s$. At this value of $\epsilon_s$ Eqs. (19) and (27) are satisfied. This figure shows also $S_s$, the boundary condition at $\zeta=0^+$ [Eq. (17)] as a function of $\Gamma_s$. The insert shows schematically $\epsilon_n$ and $S_n$ as a function of $\Gamma_n$ and their relation to $\epsilon_s$, $S_s$, and $\Gamma_s$ (notice the symmetry).

and the temperature $T$ determine the value of the boundary nucleation field $H_0$. In Sec. V we shall show more of the pertinent numerical results relating to Eqs. (19), (20), (22), (25), (27), and (28).

## V. NUMERICAL RESULTS

Figure 1 shows the solutions of Eq. (19) which are those marked by $\zeta \geq 0^+$ and of Eq. (20), which are those marked by $\zeta \leq 0^-$, for various values of the slope $S_s$ at $\zeta=0^+$ and $S_n$ at $\zeta=0^-$ when in each instant the boundary conditions $[\Psi_n(\zeta)/\Psi(0^-)]_{0^-}=1$; $[\Psi_s(\zeta)/\Psi_s(0^+)]_{0^+}=1$; $\Psi_n(-\infty)/\Psi(0^-)=0$; and $\Psi_s(\infty)/\Psi(0^+)=0$ were satisfied. Equations (27) and (28) are satisfied only at the minimum of each curve, and the value of $\epsilon_s$ at this minimum is plotted separately as a function of the corresponding value of $\Gamma_s$ in Fig. 2. There exists a high degree of symmetry between the solutions of Eqs. (19) and (20). When $S \rightarrow -S$, $\Gamma \rightarrow -\Gamma$ and $\zeta \rightarrow -\zeta$ the values of $\epsilon$ are the same. The values of $\Gamma_s$ which correspond to the minima of $\epsilon_s$ stay always on the $s$ side, and similarly $\Gamma_n$ for the minima of $\epsilon_n$ stay always on the $n$ side.

As $\Gamma_s \rightarrow \infty$ the value of $\epsilon_s \rightarrow 1$, and as $\Gamma_s \rightarrow 0$ the value of the minimum of $\epsilon_s \rightarrow -\infty$. Similarly, as $\Gamma_n \rightarrow -\infty$ the value of $\epsilon_n \rightarrow 1$, and as $\Gamma_n \rightarrow 0$ the value of the minimum of $\epsilon_n \rightarrow -\infty$. Because of this symmetric behavior it is sufficient to consider only the solutions of $\epsilon_s$ which are shown in Fig. 2 together with the values of $S_s$ as a function of $\Gamma_s$. The insert shows schematically $\epsilon_n$ and $S_n$ as a function of $\Gamma_n$ on the $n$ side and compares these values with $\epsilon_s$, $S_s$, and $\Gamma_s$ on the $s$ side. All the results in Fig. 2 satisfy also Eq. (27) on the $s$ side and Eq. (28) on the $n$ side. When $S_s=0$, one finds $\epsilon_s=0.5901=1/1.695$. This determines $H_{c3}/H_{c2}$ for a superconductor-vacuum interface at $\zeta=0$. The value of $\epsilon_n=0$

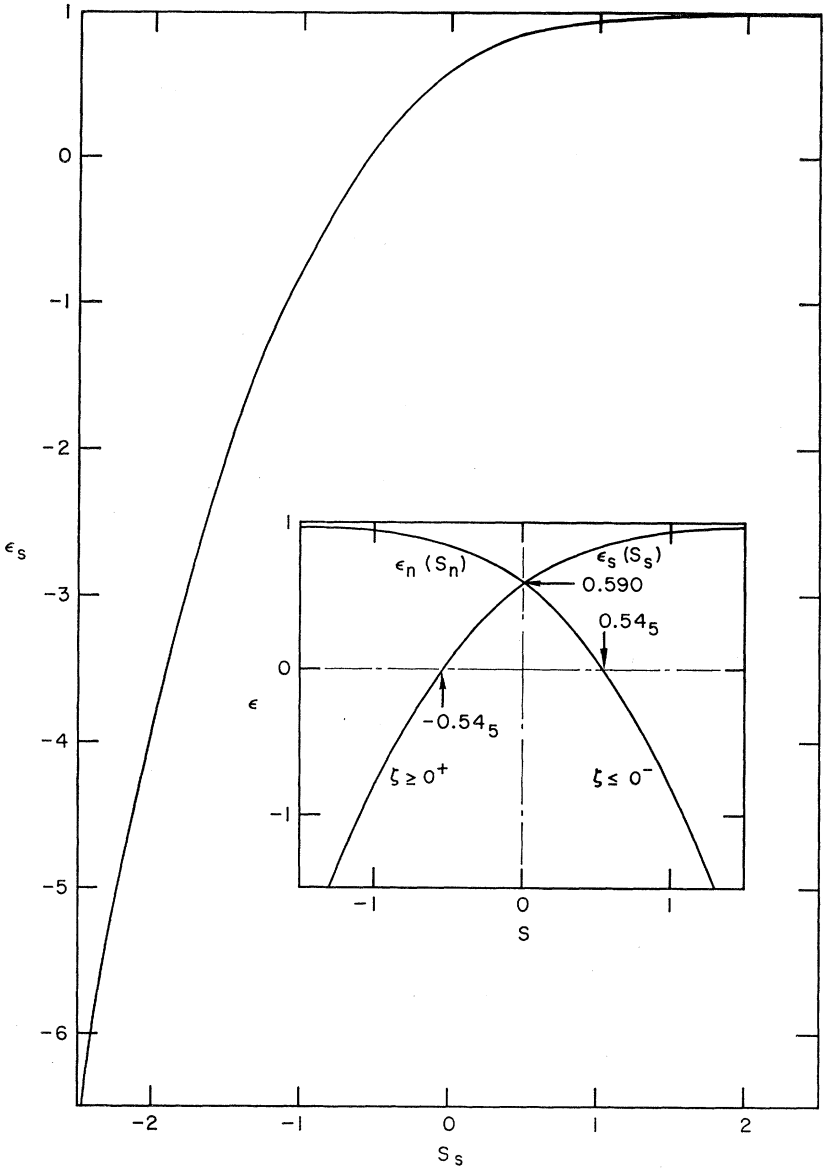


FIG. 3. Shown are the lowest eigenvalues $\epsilon_s$ of Eq. (19) as a function of the boundary condition $S_s$ when Eq. (27) is satisfied. The $\epsilon_s$ values correspond to those of the minima in Fig. 1. The insert shows schematically $\epsilon_n$ and $\epsilon_s$. Figures 4 and 5 were constructed from this plot. For details see text.

when $\Gamma_n \approx -0.54_5$ and $S_n \approx 0.54_5$. From Eq. (25) it can be seen that $\epsilon_n = 0$ when $T = T_{cn}$.

Figure 3 shows $\epsilon_s$ as a function of $s_s$ when Eq. (27) is satisfied. The insert shows schematically $\epsilon_n$ as a function of $s_n$ and its relation to $\epsilon_s$ and $s_s$. From the information contained in Fig. 3 we were able to calculate the boundary nucleation field $H_0(H_0/H_{c2} = 1/\epsilon_s)$ as a function of the parameters $\gamma$ [Eqs. (23) or (24)] and $\alpha(T)$ [Eqs. (25) or (26)] by the methods outlined in Sec. IV.

Figure 4 shows $H_0/H_{c2}$ as a function of $1/\gamma$ with $\alpha(T)$ as a parameter, and Fig. 5 shows $H_0/H_{c2}$ as a function of $\alpha(T)$ with $\gamma$ as a parameter. It is emphasized that solutions for $H_0/H_{c2}$ exist for $0 < \gamma < 1$, and that for $\gamma = 1$ the value of $H_0/H_{c2} \neq 1$ except when $\alpha(T) \to -\infty$, which is the case when $T \to T_{cs}$. When $\alpha(T) \gtrsim 0 (T \lesssim T_{cn})$ the values of $H_0/H_{c2}$ are appreciably different from unity and in this temperature range it might be easy to test the above theory for values of $\gamma \lesssim 1$. It was assumed in Fig. 5 that the value of $s_n \to 0$ when $\gamma \to 0$. That limit is rather fictitious. It requires that $n_n/n_s \to \infty$ while $\gamma \to 0$ such that $\alpha(T)$ is finite [see Eq. (26)].

It follows from Eq. (23) that when both metals are dirty ($l_s \ll \xi_{0s}$; $l_n \ll \xi_{0n}$),

$$\gamma_p = \sigma_s/\sigma_n, \tag{29}$$

where the conductivities $\sigma[= l_n(e^2/v_F m)]$ are those of the metals in the normal state. Thus, in this particular instance, $\gamma_p$ can be readily measured and $\alpha(T)$ determined from Eq. (26).

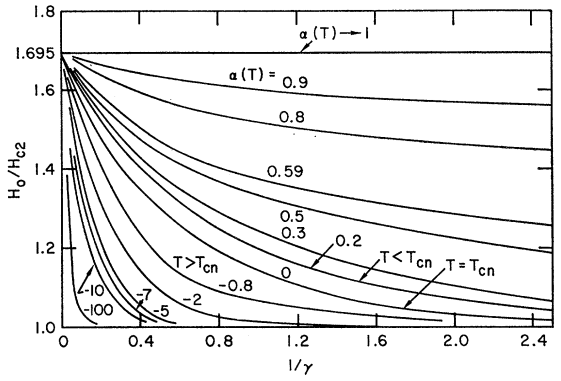


FIG. 4. Boundary nucleation field $H_0$, normalized with respect to the bulk nucleation field $H_{c2}$, is plotted as a function of $1/\gamma$. The material parameter $\gamma$ is defined by Eqs. (23) and/or (24). The parameter $\alpha(T)$ is dependent on the temperature $T$. $\alpha(T)>0$ $T<T_{cn}$, and $\alpha(T)<0$ for $T>T_{cn}$. When $T\to T_{cs}$ the value of $H_0/H_{c2}\to 1.695$ for all temperatures in the GL domain, and when $\gamma\to 0$ the values of $H_0/H_{c2}\to 1$ for all $T>T_{cn}$. For $T<T_{cn}$ see text.

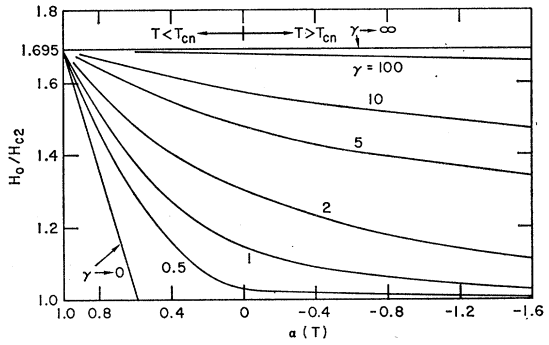


FIG. 5. Shown is the boundary nucleation field $H_0$, normalized with respect to the bulk nucleation field $H_{c2}$, as a function of the temperature parameter $\alpha(T)$ which is defined by Eq. (25) or (26). $\gamma$ is a material parameter defined by Eqs. (23) and/or (24). $\alpha(T)=0$ when $T=T_{cn}$, and $\alpha(T)\to-\infty$ when $T\to T_{cs}$. $\alpha(T)>0$ for $T<T_{cn}$. For details see text.

When both metals are clear ($l_s\gg\xi_{0s}$; $l_n\gg\xi_{0n}$) $\gamma_p$ is

$$\gamma_p=(m_n/m_s)n_s/n_n. \tag{30}$$

When $N$ is clean ($l_n\gg\xi_{0n}$) and $s$ dirty ($l_s\ll\xi_{0s}$) the value of $\gamma_p$ is small compared to the latter case (both metals clean) and $\gamma_p$ and $\alpha(T)$ is

$$\gamma_p\approx 1.33\frac{m_n}{m_s}\frac{n_s}{n_n}\frac{l_s}{\xi_{0s}}=7.38\sigma_s\frac{m_n}{n_n}\frac{kT_{cs}}{e^2\hbar}, \tag{31}$$

$$\alpha(T)\approx 1.33\frac{m_n}{m_s}\frac{l_s}{\xi_{0s}}\frac{T_{cn}-T}{T_{cs}-T}. \tag{32}$$

This particular situation might be suited for testing the above theory. When $n$ is dirty and $s$ is clean the value of $\gamma_p$ is large compared to the case when both metals are clean.

When the value of $T$ is such that $\alpha(T)$ becomes larger than unity, the $n$ and $s$ sides interchange their functions [at $\alpha(T)=1$, $\xi_s=\xi_n$], and the corresponding appropriate value of $\alpha(T)$ is again smaller than unity.

In order that the reader gets a better feeling for the shape of the functions $\Psi_n(\zeta)$ and $\Psi_s(\zeta)$ we show these in Fig. 6 for three different cases ($\gamma=0.5$, 1, 2) when $T=T_{cn}$ and the effective electron masses on the $n$ and $s$ side are the same. For each case considered $\Psi_n(0^-)$ is normalized to unity and $\Psi_n(\zeta)$ is the same for all three cases.

## VI. CONCLUSIONS

The boundary nucleation field $H_0$ is, in general, smaller than $H_{c3}(=1.695H_{c2})$ and its value is governed by the temperature $T$ and 10 independent parameters: $T_{cn}$, $T_{cs}$, $m_n$, $m_s$, $n_n$, $n_s$, $\xi_{0s}^2$, $\xi_{0s}^2$, $l_n$, and $l_s$ via the expressions given by Eqs. (23) [or (24)] and (26). The final results are tabulated in Figs. 4 and 5. In the dirty limit, Eq. (29) applies for $\gamma_p$ whose value can be between zero and infinity. We find quite generally when $\gamma>0$ that $H_0>H_{c2}$, although near $T_{cs}[\alpha(T)\to-\infty]$ the value of the nucleation field $H_0$ approaches $H_{c2}$ for $\gamma$ values of the order of unity and smaller. When $T<T_{cn}$, the values of $H_0$ pull away from $H_{c2}$toward $H_{c3}$ for all $\gamma$ values. Near and below $T_{cn}$, the above theory could be readily tested when $n$ is clean and $s$ is dirty. The $\gamma$ and $\alpha(T)$ values of the latter case are given by Eqs. (31) and (32). Experiments by Burger *et al.*[17] are not of such a nature as to be able to distinguish between the results of Ref. 3 and our results. Controlled experiments would be highly desirable.

At this point it is appropriate to point out the difference between Ref. 3 and our approach. Reference 3 is limited to $n$ and $s$ metals which are dirty [Eq. (29)] and to temperatures between $T_{cn}$ and $T_{cs}$. In Ref. 3 it is also assumed that the order parameters are real functions on the $n$ and $s$ sides, respectively. We have introduced complex order parameters; we find that we can

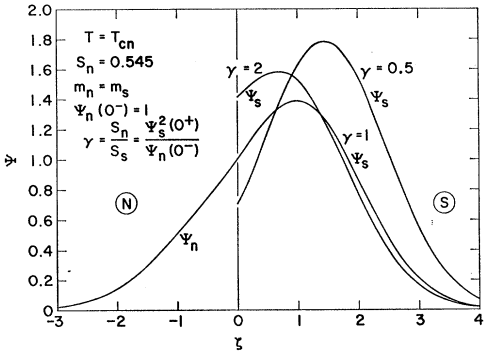


FIG. 6. Shown are $\Psi_n(\zeta)$ and $\Psi_s(\zeta)$ for $\gamma=0.5$, 1 and 2 and $T=T_{cn}$. $\Psi_n(0^-)$ is assumed to be unity and $\Psi_n(\zeta)$ is the same in this instance for all the three cases considered. The effective electron masses are assumed to be the same in the $n$ and the $s$ metal.

[17] J. P. Burger, G. Deutscher, J. P. Hurault, and A. Martinet, Ref. 10, Vol. 2A, p. 186.

select lower eigenvalues than Hurault did, and hence larger boundary nucleation fields. This can be seen readily when one compares Eq. (5) of Ref. 3 to our Eq. (15). They are similar, when written in the same notation, except that $\Gamma_n=\Gamma_s$ in Ref. 3, because it was assumed that $k_n=k_s=0$ [see Eqs. (8) and (9)]. Also our $\gamma$ value in Eq. (15) has to be replaced by $\gamma/\alpha^2$, where $\alpha^2$ is some material and temperature parameter and is not to be confused with $\alpha(T)$ defined by Eq. (25). Although the approach in Ref. 3 with $\Gamma_n=\Gamma_s$ reduces essentially to five equations with five unknowns, one does not have the freedom to adjust the $k$ values to select the lowest eigenvalue $\epsilon_s$ in Eq. (19). For example, one can assume that $k_n=0$ in our problem such that $x_0$ is defined by $\Gamma_n=-x_0(2\pi H_0/\Phi_0)^{1/2}$. We then have the freedom to select a $k_s$ value which adjusts $\Gamma_s$ such that one obtains the lowest eigenvalue for $\epsilon_s$ from Eq. (19) for a fixed value of $S_s$. It should be noticed that this value of $\epsilon_s$ is unique. Furthermore, Hurault's $\alpha^2$ value becomes irrevelant in our approach, because Eq. (15) splits up into Eqs. (27) and (28). However, one would expect that the final results in Ref. 3 should also depend on $\alpha^2$, which does not seem to be the case. It should be noticed that the actual values of $k_s$, $k_n$, and $x_0$ are irrelevant. What is of importance is their differences as can be seen readily from Eqs. (8) and (9), because only $\Gamma_n$ and $\Gamma_s$ appear in our equations.

It might be noticed that all the quantities which are shown in Figs. 4 and 5 are measurable. All theoretical quantities such as $S_s$, $S_n$, $\Gamma_s$, and $\Gamma_n$, which cannot be measured directly, have been eliminated from the final results. The above calculations were performed for two semi-infinite half-spaces. To realize this configuration experimentally one should use a solid superconducting cylinder whose radius is large compared to $\xi_s$ and $l_s$, and evaporate on its surface a $n$ metal whose thickness is large compared to $|\xi_n|$ and $l_n$. An alternative configuration would be to use a superconducting film, thick compared to $\xi_s$ and $l_s$, which is plated on one side with a ferro- or antiferromagnetic material such as Ni or Cr to eliminate the sheath on one side. On the other side, one could evaporate a thick nonmagnetic $n$ film and measure $H_0$.

$\xi_n^2$ as given by Eqs. (10)–(12) applies when the $n$ metal is nonmagnetic, because $v_{Fn}/l_n=1/\tau_{nt}$ in Eq. (12), where $\tau_{nt}$ is the transport relaxation time due to electron scattering in the nonmagnetic material. When the $n$ metal is ferro- or antiferromagnetic, we have to replace in Eq. (12) $1/\tau_{nt}$ by $1/\tau_{nt}+1/\tau_{ns}$, where $\tau_{ns}$ is the electron-spin-scattering relaxation time in the $n$ metal. At low temperature $\tau_{ns}$ is usually much smaller than $\tau_{nt}$ and therefore the modified value of $\rho_n$ [Eq. (12)] is controlled by $\tau_{ns}$. This tends to make $\rho_n\gg1$ and therefore $\xi_n^2\propto\tau_{ns}$. Hence $\xi_n^2$ becomes very small and negative such that $\epsilon_n$ [Eq. (6)] becomes very large and negative. Therefore $\alpha(T)$ [Eq. (25)] becomes very large and negative, and it can be seen readily from Fig. 4 that for all values of $\gamma<\infty$ the value of $H_0$ is close to $H_{c2}$ provided $\alpha(T)$ is sufficiently large and negative. This is in agreement with experiments of Refs. 5–7 and 18 and the conclusions[5,18] that $|\xi_n|$ is small for a magnetic material.

The above calculations can also be applied to internal surfaces in the bulk of a superconductor. If, for example, a superconducting metal is cold-worked, one may expect that regions of slightly varying transition temperatures are created in the metal. If this should be so, an "internal proximity" effect could appear. Let us assume that $\alpha(T)$ is, in this case, a meaningful quantity. Then one would expect that at these internal boundaries the value of $\gamma\sim1$. Therefore $S_s\sim S_n$, and it can be seen readily from the insert of Fig. 3 that $\epsilon_s$ could be anywhere between $\epsilon_s=1(H_0=H_{c2})$ and $\epsilon_s=0.590(H_0=H_{c3})$ depending on the value of $S$. If there is no barrier, then, by our definition, superconductivity nucleates far from the boundary surface at $\zeta=0(\Gamma_s\gg1)$ where $\epsilon_s=1$, and therefore $H_0=H_{c2}$. If there is a barrier present, and $S_s\to0$, then $H_0\to H_{c3}$. So in the limiting case the matrix of the bulk of a superconductor could nucleate at $H_{c3}$ provided suitable internal surfaces are available for such a nucleation process. Experiments seem to support qualitatively this conclusion.[19–21]

Boyd[22] has suggested nucleation of superconductivity at internal tunneling barriers and has calculated $H_0/H_{c2}$ as a function of a theoretical parameter which is experimentally inaccessible. The case he has considered, however, is quite different from the present one. Tilley[23] has extended Boyd's calculation to two-planar defects, but his solutions for $d/\xi>1.84$ are faulty because one of the independent solutions of Weber's differential equation was neglected.[24]

## ACKNOWLEDGMENT

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