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Calculation of the Superconducting Transition Temperature of Superimposed Films in the Diffusion Approximation*

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The de Gennes–Guyon–Werthamer theory of the proximity effect in the diffusion approximation has been extended by the use of coupled integral equations for the order parameters in the two metals. The two theories are in excellent agreement for Pb–Al superimposed films, but there are significant differences for Pb–Cu films. Several experiments have indicated that copper may be a superconductor ($T_c \approx 0.010°\mathrm{K}$); in view of various theoretical and experimental uncertainties, it is concluded that most of this evidence for superconductivity in copper must be considered doubtful. It is shown that different methods of cutting off divergent sums occurring in the theory can give significantly different results, introducing a further theoretical uncertainty.

I. INTRODUCTION

When a superconductor is placed in intimate contact with a normal metal, it is found that the combination displays the attributes of a superconductor; the resistance of the combination vanishes at a well-defined temperature, a nonzero energy gap exists in the normal metal, and a persistent current can be passed through the normal metal.[1]

The early literature of the proximity effect has been reviewed by Hilsch.[2] The basic theory of the calculation of the transition temperature was developed by de Gennes and Guyon,[3] Werthamer,[4] and de Gennes[5]; experiments using two known superconductors[6,7] have demonstrated that this theory is essentially correct. Several experiments[2,8–10] have been performed and the results analyzed in terms of this theory in an attempt to determine if various normal metals (e.g., Cu, Pt) are actually superconductors. The theory has been extended and used successfully[9,11] to deal with experiments in which the normal metal is magnetic (e.g., Fe, Ni, Gd, Cr).

In this paper, the de Gennes–Guyon–Werthamer calculation of the transition temperature for nonmagnetic normal metals is refined by the use of coupled integral equations for $\Delta_s(x)$ and $\Delta_n(x)$, the order parameters in the superconductor and the "normal" metal, respectively. The new theory is compared with other theories and with experiments on Pb–Al and Pb–Cu superimposed films; previous evidence for superconductivity in Cu is examined. The current status of the theory is reviewed, some questionable assumptions in the theory are listed and the difficulties encountered in generalizing the theory to remove these assumptions are pointed out.

II. THE TREATMENT OF THE CUTOFF

To avoid breaking the continuity of the presentation we discuss here the treatment of certain sums occurring in the theory.

In the theory of many problems in superconductivity there occur sums such as

$$S=\sum_{\nu=0}^{\infty}\frac{2}{2\nu+1+x},$$

which are formally divergent. The divergence is due to the neglect of the time dependence of the electron-phonon interaction,[12] and disappears when this is taken into account.

If we use the "usual" method of curing the divergence, the sum becomes

$$S=\ln(1.134\langle\Theta_{\mathrm{ph}}\rangle/T_c)-\chi(x), \qquad (1)$$

where $\langle\Theta_{\mathrm{ph}}\rangle$ is an average phonon frequency to be defined shortly,

$$\chi(x)=\sum_{\nu=0}^{\infty}\left(\frac{2}{2\nu+1}-\frac{2}{2\nu+1+x}\right)=\psi(\tfrac{1}{2}+\tfrac{1}{2}x)-\psi(\tfrac{1}{2}),$$

$$\psi(x)=d\ln\Gamma(x)/dx,$$

and we have made the usual identification

$$\sum_{\nu=0}^{\infty}\frac{2}{2\nu+1}=\ln\left(\frac{1.134\langle\Theta_{\mathrm{ph}}\rangle}{T_c}\right).$$

This treatment gives results in terms of tabulated functions but, as will be seen later, the results do not agree with the results obtained from other treatments of the cutoff.

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[1] P. H. Smith, S. Shapiro, J. L. Miles, and J. Nicol, Phys. Rev. Letters **6**, 686 (1961).

[2] P. Hilsch, Z. Physik **167**, 511 (1962).

[3] P. G. de Gennes and E. Guyon, Phys. Letters **3**, 168 (1963).

[4] N. R. Werthamer, Phys. Rev. **132**, 2440 (1963).

[5] P. G. de Gennes, Rev. Mod. Phys. **36**, 225 (1964).

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[7] G. Bergmann, Z. Physik **187**, 395 (1965).

[8] J. J. Hauser, H. C. Theuerer, and N. R. Werthamer, Phys. Rev. **136**, A637 (1964).

[9] J. J. Hauser, H. C. Theuerer, and N. R. Werthamer, Phys. Rev. **142**, 118 (1966).

[10] G. v. Minnigerode, Z. Physik **192**, 379 (1966).

[11] J. J. Hauser, H. C. Theuerer, and N. R. Werthamer, Phys. Letters **18**, 222 (1965).

[12] P. Morel and P. W. Anderson, Phys. Rev. **125**, 1263 (1962).

A more realistic treatment of the cutoff follows from the inclusion of the cutoff factor[13]

$$\langle \omega_{\text{ph}}^2/(\omega^2+\omega_{\text{ph}}^2)\rangle_{\text{phonons}}$$

in the summand, where $\omega=(2\nu+1)\pi T_c$.[14] If one replaces the true phonon spectrum by an Einstein spectrum centered at the average $\langle\omega_{\text{ph}}\rangle = \langle\Theta_{\text{ph}}\rangle = 3\Theta_D/4$ of a Debye spectrum, the sum becomes

$$S=\sum_{\nu=0}^{\infty}\frac{2}{2\nu+1+x}\,\frac{a^2}{(2\nu+1)^2+a^2}\,, \qquad (2)$$

where

$$a=3\Theta_D/(4\pi T_c).$$

We call this the "natural" cutoff. Since the phonon spectra of most metals are sharply peaked at a few frequencies, the use of a Debye spectrum would be no more realistic than the above model. The only way to improve the treatment, short of using the complete, true, phonon spectrum, is to use Einstein terms or Lorentzians centered at the peaks of the true phonon spectrum.

A more "artificial," but nonetheless useful, method is to cut off the sum by writing

$$S=\sum_{\nu=0}^{L-1}\frac{2}{2\nu+1+x}+f\,\frac{2}{2L+1+x}\,, \qquad (3)$$

where $0<f\leq 1$, and L and f are determined from

$$\sum_{\nu=0}^{L-1}\frac{2}{2\nu+1}+f\,\frac{2}{2L+1}=\ln\left(\frac{1.134\langle\Theta_{\text{ph}}\rangle}{T_c}\right).$$

A similar cutoff has been used previously by Silvert and Cooper.[13]

All three cutoff methods clearly give the same results when Θ_D/T_c is very large; if this is not the case, the natural method [Eq. (2)] appears to be preferable since it is the most soundly based of the three.

In the following it will be assumed that all sums over ω contain an unwritten cutoff factor; these sums are to be taken as sums over ν, with $\nu = -\infty, \cdots, -1, 0, 1, \cdots, +\infty$. In all three methods, T_c is the transition temperature of the superimposed film.

Before developing the theory we define certain terms which describe the approximations made. An example of the "diffusion approximation" will be seen in the conversion of Eq. (26) into Eq. (27); the "dirty limit" requires that the mean free path l be very much less than ξ_ω, so that $l=\zeta_\omega$, where $\xi_\omega=\xi_0/|2\nu+1|$, $\xi_0=v_f/(2\pi T_c)$, and $1/\zeta_\omega=1/\xi_\omega+1/l$; the "very dirty limit" requires that l be very much less than ξ, where $\xi^2=v_f l/6\pi T_c$. The distinction between the diffusion approximation and the dirty limit is not quite as simple as indicated because the diffusion approximation, to some extent, does assume that $\zeta_\omega=l$.

We denote by S the metal with the higher transition temperature and by N the normal metal or the superconductor with the lower transition temperature; the N region extends from $x = -D_n$ to 0, and the S region from $x = 0$ to D_s. In the theory, there are many equations for the N region which, except for a few obvious changes such as the interchanging of subscripts, are identical with the equations for the S region. To avoid wasting space, we omit the equation for N and mark the equation for S with an asterisk; the first example of this procedure is Eq. (9*).

III. THE COUPLED INTEGRAL EQUATIONS THEORY

This theory, like all microscopic theories of the proximity effect, is based on the Gor'kov integral equation for the order parameter $\Delta(x)$. At a second-order superconducting transition, Δ vanishes continuously; hence, one can linearize the integral equation to obtain

$$\Delta(x) = V(x)T_c\sum_{\omega}\int K_\omega(x,x')\Delta(x')\,dx', \qquad (4)$$

where $V(x)$ is the BCS interaction constant at the point x and T_c is the transition temperature of the superimposed film sandwich.

The central problem in the theory of the proximity effect is the calculation of the kernel $K_\omega(x,x')$; once this task has been completed there still remains the problem of solving the integral equation (4) for $\Delta(x)$ and obtaining the transition temperature T_c as an eigenvalue.

In the diffusion approximation, the kernel can be easily calculated since in this case it obeys the simple differential equation[15]

$$\left(1-\frac{1}{\alpha^2(x)}\frac{\partial^2}{\partial x^2}\right)K_\omega(x,x')=\frac{\pi N(x)}{|\omega|}\,\delta(x-x'), \qquad (5)$$

where $\alpha=(\frac{1}{3}\xi_\omega\zeta_\omega)^{-1/2}$ and N is the density of states at the Fermi surface. De Gennes[5] has derived the following boundary conditions on K_ω:

$$K_\omega(x,x')/N(x)\,|_{x=0^-}=K_\omega(x,x')/N(x)\,|_{x=0^+}, \qquad (6)$$

$$[1/\alpha^2(x)]\partial K_\omega(x,x')/\partial x\,|_{x=0^-}=[1/\alpha^2(x)]\partial K_\omega(x,x')/\partial x\,|_{x=0^+}, \qquad (7)$$

$$\partial K_\omega(x,x')/\partial x=0 \quad\text{at}\quad x=D_s \quad\text{and}\quad x=-D_n. \qquad (8)$$

Equation (6) is valid in the very dirty limit $l\ll\xi$; Eq. (7), being derived from Eq. (5), is valid in the diffusion approximation and Eq. (8) is generally valid. We rewrite the integral equation (4) in the form

$$\Delta_s(x)=V_sT_c\sum_{\omega}\left(\int_0^{D_s}K_{\omega ss}(x,x')\Delta_s(x')\,dx' + \int_{-D_n}^{0}K_{\omega sn}(x,x')\Delta_n(x')\,dx'\right) \qquad (9^*)$$

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[13] W. Silvert and L. N. Cooper, Phys. Rev. **141**, 336 (1966).

[14] We use the system of units obtained by formally setting $\hbar$ and k_B equal to unity.

[15] This is the diffusion equation as first used by de Gennes (Ref. 5) but altered by Silvert and Cooper (Ref. 13) to avoid making the dirty limit assumption.

and solve the differential equation (5), using the boundary condition (8) and the symmetry[5] $K_\omega(x, x') = K_\omega(x', x)$, obtaining

$$K_{\omega ss}(x, x') = (N_s\pi\alpha_s/2\,|\,\omega\,|)\{\exp(-\alpha_s\,|\,x-x'\,|) + \exp[-\alpha_s(2D_s-x-x')]\} + A_s \cosh\alpha_s(D_s-x)\cosh\alpha_s(D_s-x'),$$

$$K_{\omega sn}(x, x') = A_{sn}\cosh\alpha_s(D_s-x)\cosh\alpha_n(D_n+x'). \qquad (10^*)$$

It is easily verified that the sum rule of de Gennes[5],

$$\int K_\omega(x, x')\,dx' = \pi N(x)/|\,\omega\,|, \qquad (11)$$

gives the same conditions on the coefficients as the boundary condition (7); this is reasonable since K_ω is a simple sum of exponentials, and in one case it is integrated and in the other differentiated. Applying the boundary conditions (6) and (7) and solving the resulting equations for A_s, A_n, and A_{sn} yields

$$A_s = \frac{N_s\pi\alpha_s}{|\,\omega\,|}\,\frac{\alpha_n N_s \cosh\alpha_n D_n - \alpha_s N_n \sinh\alpha_n D_n}{d} \times \exp(-\alpha_s D_s),$$

$$A_{sn} = \frac{N_s N_n \alpha_s \alpha_n \pi}{|\,\omega\,|\,d}, \qquad (12^*)$$

where

$$d = \alpha_n N_s \sinh\alpha_s D_s \cosh\alpha_n D_n + \alpha_s N_n \cosh\alpha_s D_s \sinh\alpha_n D_n.$$

The first term in $K_{\omega ss}$ is just the diffusion kernel for a superconductor occupying all space; this term plus the second term give the diffusion kernel for a superconductor extending from $-\infty$ to D_s. The third term is required to satisfy the boundary conditions at $x=0$.

The two coupled, linear, homogeneous, integral equations must, except in very special cases,[5] be solved numerically on a high-speed digital computer; the method we have chosen is to expand $\Delta_s(x)$ and $\Delta_n(x)$ in series of simple functions

$$\Delta_s(x) = \sum_{i=1}^{m_s} a_{si} f_{si}(x). \qquad (13^*)$$

We choose m_s and m_n to be sufficiently large so that no change in T_c is found on using several more terms. These expressions are inserted in (9); the integrals are performed and one obtains

$$\sum_{i=1}^{m_s} a_{si} C_{ssi}(x) + \sum_{i=1}^{m_n} a_{ni} C_{sni}(x) = 0. \qquad (14^*)$$

We use m_s values of x in the S region in the first equation and m_n in N in the second. The transition temperature T_c is obtained by demanding that the determinant vanish. With this value of the transition temperature, it is a simple matter to solve for the a_s's and a_n's and, hence, determine $\Delta_s(x)$ and $\Delta_n(x)$. We have used polynomials of even degree in (D_s-x) and (D_n+x) in the expansions; it is possible that other expansions would result in faster computation.

The calculation of the coefficients C in (14) is straightforward except for one difficulty associated with the cutoff. When x and x' are in the same metal, as in the calculation of $C_{ssi}(x)$, there is no difficulty concerning the Debye temperature to be used in the cutoff; when x and x' are in different metals, however, as in the calculation of $C_{sni}(x)$, it is not clear how the cutoff should be handled if the Debye temperatures in the two metals are different. We have chosen $\Theta_D = \Theta_D(x)$, but this question deserves further study. Because all the ω sums in Eq. (14) converge except when $x=0$, one cannot use the usual cutoff method [Eq. (1)] and still treat all the sums consistently.

The significance of this theory of the proximity effect is that coupled integral equations for $\Delta_s(x)$ and $\Delta_n(x)$ are used for all values of the film thicknesses; the only previous use of coupled integral equations for the prediction of T_c has been by de Gennes[5] in the thin film, or Cooper,[16] limit $D_s \ll \xi_s$ and $D_n \ll \xi_n$. De Gennes[5] also derived the kernels for the case $D_s = D_n = \infty$; the theory presented here is a generalization of his results to finite film thicknesses.

Having completed the development of the theory, we now compare it with previous theories.

IV. COMPARISON OF THE VARIOUS THEORIES

A. The de Gennes–Guyon–Werthamer Theory in the Dirty Limit

The most commonly used theory of the proximity effect is that due to de Gennes and Guyon,[3] Werthamer,[4] and de Gennes,[5] as modified by Hauser, Theuerer, and Werthamer.[8] To obtain the equations used in this theory from the new theory, we set $K_{\omega sn} = K_{\omega ns} = 0$ in (9), and keep only the term $\exp(-\alpha\,|\,x-x'\,|)$ in $K_{\omega ss}$ and $K_{\omega nn}$. The integral equations (9) for $\Delta_s(x)$ and $\Delta_n(x)$ then become

$$\Delta_s(x) = N_s V_s T_c \times \sum_\omega \frac{\pi\alpha_s}{2\,|\,\omega\,|}\int_0^{D_s} \exp(-\alpha_s\,|\,x-x'\,|)\,\Delta_s(x')\,dx'. \qquad (15^*)$$

The function $\cos q_s(D_s-x)$ satisfies the boundary condition $d\Delta(x)/dx = 0$ at a free surface[17] and the above approximate integral equation for $\Delta_s(x)$ if one extends the limits of the integral to $-\infty$ and $+\infty$ and if q_s satisfies

$$\sum_{\nu=0}^{\infty} \frac{2}{2\nu+1+q_s^2\xi_s^2} = \frac{1}{N_s V_s}, \qquad (16)$$

where $\xi_s^2 = v_{fs} l_s/(6\pi T_c)$; we have made the dirty-limit assumption $\zeta_\omega = l$.

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[16] L. N. Cooper, Phys. Rev. Letters **6**, 689 (1961); IBM J. Res. Develop. **6**, 75 (1962).

[17] C. Caroli, P. G. de Gennes, and J. Matricon, J. Phys. Radium **23**, 707 (1962).

Since we expect $\Delta_n(x)$ to fall off exponentially in the normal metal, we choose $\Delta_n(x) \propto \cosh q_n(D_n+x)$; disregarding difficulties with the limits of the integral we find, by analogy with the equation for q_s,

$$\sum_{\nu=0}^{\infty} \frac{2}{2\nu+1-q_n^2\xi_n^2} = \frac{1}{N_n V_n}. \qquad (17)$$

All information regarding the boundary conditions satisfied by Δ_s and Δ_n at the interface has, of course, been lost by decoupling the integral equations. Assuming equal cutoffs in the two metals, de Gennes[5] has derived from Eqs. (6), (7), and (9) the boundary conditions

$$\Delta_s(0)/N_s V_s = \Delta_n(0)/N_n V_n, \qquad (18)$$

$$\left.\frac{\xi_s^2}{V_s}\frac{d\Delta_s(x)}{dx}\right|_{x=0} = \left.\frac{\xi_n^2}{V_n}\frac{d\Delta_n(x)}{dx}\right|_{x=0}. \qquad (19)$$

Combining Eqs. (16), (17), (18), and (19) with

$$\Delta_s(x) \propto \cos q_s(D_s - x),$$
$$\Delta_n(x) \propto \cosh q_n(D_n + x), \qquad (20)$$

and using the usual cutoff method [Eq. (1)] gives the three equations used in the dirty-limit form of this theory:

$$\chi(q_s^2\xi_s^2) = \ln(T_{cs}/T_c), \qquad (21)$$

$$N_s\xi_s^2 q_s \tan q_s D_s = N_n \xi_n^2 q_n \tanh q_n D_n, \qquad (22)$$

$$\chi(-q_n^2\xi_n^2) = \ln(T_{cn}/T_c). \qquad (23)$$

It is clear from the derivation of this theory from the new theory that it should only be valid for large film thicknesses; it has, however, given results which agree surprisingly well with experiment for all values of the film thicknesses.[6,7] This agreement will be investigated later. In the Cooper limit, however, this theory does not reduce to the correct result; instead it predicts that $T_c=0$ only when $D_s=0$, even for the case $V_n<0$, where T_c must obviously be zero for sufficiently small, but nonzero, D_s.

B. The Theory of Moormann in the Dirty Limit

The theory of Moormann[18] can be obtained from the coupled integral equations theory in much the same manner as that of de Gennes, Guyon, and Werthamer; the only difference is that Moormann keeps the boundary condition (18) but replaces the boundary condition (19) on the derivatives of $\Delta(x)$ at $x=0$ by a condition on the integrals of $\Delta_s(x)$ and $\Delta_n(x)$. This condition was derived from the sum rule (11) and is

$$\int dx\, N(x)\Delta(x) \ln(T_c(x)/T_c) = 0, \qquad (24)$$

where $T_c(x) = T_{cn}$ for $x<0$ and T_{cs} for $x>0$. Using Eqs. (18), (20), and (24), he derives the relation

$$N_s N_s V_s \ln\left(\frac{T_{cs}}{T_c}\right)\frac{\tan q_s D_s}{q_s} + N_n N_n V_n \ln\left(\frac{T_{cn}}{T_c}\right)\frac{\tanh q_n D_n}{q_n} = 0, \qquad (25)$$

which, with Eqs. (21) and (23), forms the fundamental set of equations in this theory; Eq. (22) is discarded.

The condition (25) guarantees that the correct results are obtained in the Cooper limit, so it would seem that (25) is preferable to (22). We have found, however, that Moormann's theory can give unphysical results; T_c is not a single-valued function of D_s for large D_n and small T_{cn}. It is far from obvious on theoretical grounds which condition is preferable; both appear to us to be equally valid within the framework of a noncoupled integral equations theory. We believe that the difficulty lies in the fact that the coupled integral equations solutions for $\Delta_s(x)$ and $\Delta_n(x)$ do not satisfy Eq. (20). No such difficulty arises in the new theory since $\Delta(x)$, apart from a constant multiplicative factor, is uniquely determined by solving the integral equations, and there is no need for boundary conditions on $\Delta(x)$.

Moormann points out that there is little difference between the predictions of his theory and those of the de Gennes–Guyon–Werthamer theory as long as $T_{cn} \approx T_{cs}$; substantial differences are found if $T_{cn} \ll T_{cs}$. The predictions of these two theories and those of the coupled integral equations theory will be compared later.

C. The Theory of Silvert and Cooper

Silvert and Cooper[13,19] have derived, by a variational method, a condition for T_c[20]; this condition and a very simple trial function are used to derive an expression for T_c. Unfortunately, the simplicity of the trial function and the use of several simplifying mathematical assumptions make it difficult to estimate the accuracy of the theory; we have therefore not compared this theory with experiment in Sec. VI.

V. DIFFICULTIES WITH THE THEORY

Caroli and Hurault have pointed out to the author that the differential equation (5) is not valid when x or x' is within l of the interface; in this case $K_\omega(x, x')$ is sensitive to the reflecting properties of the interface. Since a proper consideration of this problem would require a detailed microscopic calculation of the effects of the interface, it is assumed in the present theory, as it has been in all theories (except those in which an adjustable parameter is inserted to take care of such

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[18] W. Moormann, Z. Physik **197**, 136 (1966).

[19] W. Silvert, Phys. Letters **16**, 238 (1965).

[20] This condition may be of use in solving the coupled integral equations (9); this possibility has been examined by R. Yeh and L. P. Kadanoff (to be published).

effects) that the interface is perfectly transmitting. This assumption may be sufficiently accurate for very dirty films, but it is not clear how dirty the films must be.

Probably the most severe restriction on the theory is the requirement $l \ll \xi$ for the validity of the boundary condition (6). According to de Gennes,[5] the most general form of this boundary condition is

$$K_\omega(x,x')\,|_{x=0^+} = a[K_\omega(x,x') + b\,\partial K_\omega(x,x')/\partial x]_{x=0^-}.$$

He argues that $b \approx l$ and hence that the derivative term, being $\approx \alpha K_\omega(x,x')$ if $K_\omega \propto \exp(-\alpha\,|\,x-x'\,|)$, is negligible in the very dirty limit. Since $l/\xi \gtrsim 0.3$ when the films are deposited at 4°K, the use of (6) is questionable even in this case; again it appears that a microscopic calculation of the effects of the interface is required for a more accurate treatment.

The differential equation (5) is not valid when x or x' is within ζ_ω of the interface for another reason[21]; the objection arises from the fact that the diffusion kernel is not correct when $|\,x-x'\,| \lesssim \zeta_\omega$. This objection is most easily understood by examining the kernel, valid for all values of l/ξ, which was derived by Werthamer[4] for a superconductor occupying all space:

$$K_\omega(x,x') = \frac{N}{2\,|\,\omega\,|}\int_{-\infty}^{\infty} dq\, \exp[iq(x-x')] \times \left(\frac{\xi_\omega q}{\tan^{-1}\zeta_\omega q} - \frac{\xi_\omega}{l}\right)^{-1}. \quad (26)$$

The diffusion kernel for a superconductor occupying all space is derived from this by setting $\tan^{-1}x = x - \frac{1}{3}x^3$, simplifying, and performing a contour integration; the result is

$$K_\omega(x,x') = (N\pi\alpha/2\,|\,\omega\,|)\exp(-\alpha\,|\,x-x'\,|). \quad (27)$$

The important point is that (26) diverges at $x=x'$ whereas (27) does not; the range of the singularity is given by $|\,x-x'\,| \lesssim \zeta_\omega$. Since both (26) and (27) satisfy the sum rule (11), the diffusion kernel should be adequate as long as $\Delta(x)$ varies slowly in space; this is not the case near the interface, for Silvert and Cooper[13] have shown that the discontinuity in $V(x)$ results in $\Delta(x)$ having infinite slope at the interface. The magnitude of this singularity is approximately $(\alpha\xi_\omega)^{-1}$ and the range is approximately ζ_ω, so the diffusion kernel may be sufficiently accurate for dirty films.

Moormann[18] has attempted to generalize the theory to remove this last objection. He retains the boundary condition (25) but uses the kernel (26) instead of the diffusion kernel (27) in the noncoupled integral equations (15). The expressions (20) for $\Delta_s(x)$ and $\Delta_n(x)$ are used to solve the integral equations in the manner described previously; he derives relations analogous to Eqs. (21) and (23) except that the χ function is replaced by a more complicated function. A major difficulty with this theory is that it was developed to apply to clean films ($l \gtrsim \xi$), and in this case the singularity at $x=0$ is expected to be important; the expressions (20) do not, however, display the proper behavior.

It would be desirable to extend the coupled integral equations treatment to satisfy the objection of Silvert and Cooper to the use of the diffusion approximation. Because the sum rule (11) and the boundary condition (7) gave the same relations for the coefficients A_s, A_n, and A_{sn} in the diffusion approximation, it is probably unnecessary to attempt to generalize (7); this would be difficult because the generalization by Moormann[18] of the differential equation (5) for $K_\omega(x,x')$ is of infinite order. In any case, (11) must be satisfied. The forms of the kernels (10) can probably be generalized without using this differential equation.

The author feels that the theoretical and experimental difficulties with clean films (the importance of the reflecting properties of the interface, the difficulties in finding the proper boundary conditions on K_ω at the interface, the danger of interdiffusion, etc.) outweigh the experimental uncertainties with dirty films (inhomogeneous films and uncertainties in the material constants). Also, in the clean limit, the mean free path l must be independently and rather accurately known; in the dirty limit, l occurs only in the product $v_f l$ for which accurate estimates can be made. For these reasons, we agree with other authors (e.g., de Gennes[5]) that experiments using clean films are not as informative as those using dirty films.

VI. COMPARISON OF THE VARIOUS THEORIES WITH EXPERIMENT

To avoid repetition, we make here two criticisms which apply to nearly all the experiments to be considered. The first is that lead has been used for the superconductor in all the experiments, despite the fact that the theories are weak-coupling theories; the effects due to the strong-coupling nature of this metal have not been estimated. The second is that only Hilsch[2] and Minnigerode[10] give data on the variation of the film resistivities with the film thicknesses; if there are such variations and if they are due to changes in the structure of the films and not to surface scattering, then the true resistivities must be used in the calculations, not the resistivities for very thick films. Only the artificial cutoff [Eq. (3)] has been used in the calculations for the coupled integral equations theory; the natural cutoff [Eq. (2)] is considerably more difficult to apply, and the extra effort has been deemed unjustified in view of these criticisms.

We consider first those experiments which have used the proximity effect in an attempt to find the BCS interaction constant in metals which are not known to be superconductors. We restrict ourselves to those experiments in which the films were deposited at low

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[21] The discussion in this paragraph is based on the work of Silvert and Cooper (Ref. 13) and J. P. Hurault (private communication).

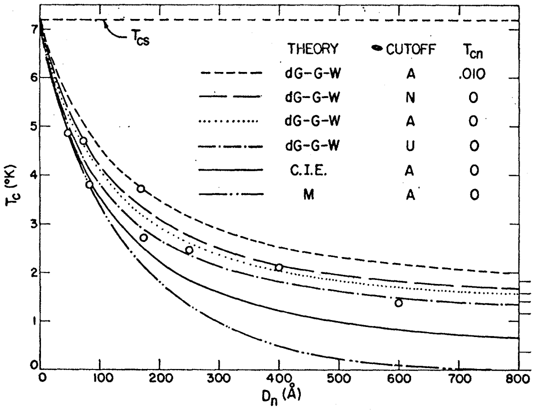

FIG. 1. Comparison of the various theories with the experiments of Hauser, Theuerer, and Werthamer on Pb-Cu films with $D_s = 150$ Å. The abbreviations used are: dG-G-W, de Gennes-Guyon-Werthamer; C.I.E., coupled integral equations; M, Moormann; N, natural [Eq. (2)]; A, artificial [Eq. (3)]; U, usual [Eq. (1)]. The values of θ, where $\theta = T_c$ ($D_n = \infty$), for the theoretical curves are marked at the lower right-hand corner of the graph; θ is taken to be 1.36°K for the experimental results.

temperatures to avoid various objectionable effects such as interdiffusion, etc.[9]; in addition, such experiments are suited for the use of dirty-limit theories because of the short electron mean free paths.

Hauser, Theuerer, and Werthamer[8] have measured the transition temperatures of Pb-Cu superimposed films deposited at 77°K; the results of their measurements, together with the predictions of the various theories, are given in Fig. 1. We have used the dirty-limit form ($\zeta_\omega = l$) of all the theories. The coherence lengths were calculated from $\xi^2 = \hbar v_f l/(6\pi k_B T_c)$; the quantity $v_f l$ is determined from[8] $v_f l = (\pi k_B/e)^2/(\rho\gamma)$, where ρ is the resistivity and γ is the electronic specific-heat coefficient. The density of states N is proportional to γ. The material constants[22] used were $T_{cs} = 7.2$°K, $\rho_s = 18$ $\mu\Omega$ cm, $\rho_n = 10$ $\mu\Omega$ cm, $\Theta_{Ds} = 90$°K, $\Theta_{Dn} = 343$°K, $\gamma_s = 1.72 \times 10^3$ ergs/cm^3 °K^2, and $\gamma_n = 0.977 \times 10^3$ ergs/cm^3 °K^2. We draw the following conclusions from Fig. 1:

(1) The three theories give markedly different results.

(2) The theoretical results are quite sensitive to the cutoff method used; this is a direct result of the small Θ_D/T_c value for lead.

(3) The experimental results, in conjunction with the de Gennes-Guyon-Werthamer theory, provide no evidence for superconductivity in copper.

(4) Since the experimental points lie above the theoretical curves, the coupled integral equations theory and Moormann's theory both indicate that copper might be a superconductor.

Since there might have been an intermediate layer of oxide between the two films, we have replotted the experimental and theoretical results in Fig. 2, using $t = (T_c - \theta)/(T_{cs} - \theta)$ and $\theta = T_c(D_n = \infty)$; as de Gennes[5] first pointed out, such an intermediate layer should not, in a first approximation, affect the results when the data are plotted in this manner. We have replotteg only the curves from Fig. 1 in which the artificial cutoff was used; this was done for clarity because the de Gennes-Guyon-Werthamer theory is relatively insensitive to the cutoff method used (in this kind of plot). This method of plotting the results has not, however, removed the disagreements between the various theories. Except for the point at $D_n = 600$ Å, the data are fitted best by the coupled integral equations theory using $T_{cn} = 0$, in contradiction to the conclusion reached from the examination of Fig. 1. We conclude that the data give no evidence for superconductivity in copper.

The above analysis of these experimental results in an attempt to derive information about the BCS interaction constant in copper must be considered somewhat meaningless in view of the experiments of Bassewitz and Minnigerode,[23] which showed that copper films produced at 77°K are only $\frac{2}{3}$ as dense as bulk copper; the porous nature of such films means that the material constants and the film thicknesses may be seriously in error.

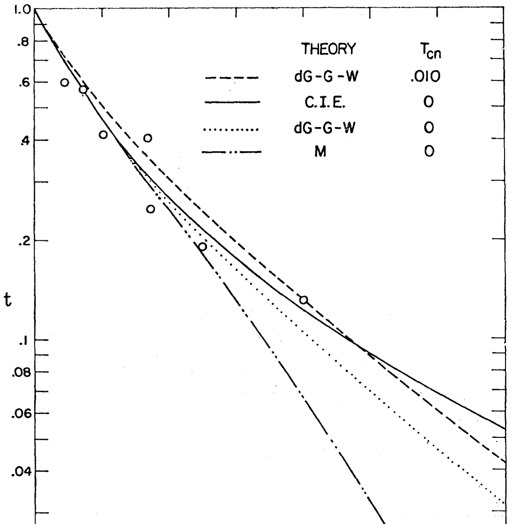

FIG. 2. The theoretical curves and experimental data of Fig. 1 replotted using the reduced temperature $t = (T_c - \theta)/(T_{cs} - \theta)$. Only the artificial cutoff forms of the various theories are plotted. The abbreviations used are defined in the caption for Fig. 1. The experimental value of t is less than 0.01 for $D_n = 600$ Å.

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[22] The resistivities are taken from the experimental paper; the Debye temperatures and the electronic specific-heat coefficients are taken from K. A. Gschneidner, Jr., in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York), Vol. **16**, p. 275.

[23] A. v. Bassewitz and G. v. Minnigerode, Z. Physik **181**, 368 (1964).

Hauser, Theuerer, and Werthamer[8,9] have also measured the transition temperatures of Pb–Pt superimposed films. Since the data do not indicate that Pt may be a superconductor, we shall not discuss these experiments.

Hilsch[2] has measured the transition temperatures of Pb–Cu films. We have not analyzed the data because the films were deposited at 10°K, resulting in even more porous copper films than those of Hauser, Theuerer, and Werthamer. In addition, the published data are the average of the two different orders of condensation whereas one requires the data for the condensation order giving the larger depression in T_c for a proper analysis.[9]

Minnigerode[10] has also performed experiments on Pb–Cu films but the films were deposited at 200°K in order to avoid the above-mentioned porosity. Unfortunately, the mean free paths in the lead films are sufficiently large, as a result of this high condensation temperature, so that dirty-limit theories do not apply; hence, the present form of the coupled integral equations theory cannot be used to analyze the data. Minnigerode has analyzed his data using the generalized form of Moormann's theory and finds that they are best fitted by assuming that copper is a superconductor with $T_c \sim 0.07$°K. Because of the large discrepancies between Moormann's theory and the coupled integral equations theory shown in Figs. 1 and 2, and the fact that the results of the latter lie *above* those of the former, it must be concluded that a prediction of superconductivity in Cu is unwarranted. The Cooper limit formula may, however, be valid for some of the film thickness combinations used by Minnigerode; using this formula, these data are again well fitted by assuming a T_c of approximately 0.07°K for Cu. These very-thin film data of Minnigerode must be considered to be the only positive evidence for superconductivity in Cu.

We now turn to analyze those experiments which use two known superconductors. We consider first the experiments of Hauser and Theuerer[6] on Pb–Al films. The data are plotted in Fig. 3 along with the results of some of the theories; again the dirty-limit forms were used. The same material constants as before were used for lead; the material constants[22] used for aluminum were: $T_{cn}=1.2$°K, $\rho_n=0.18\ \mu\Omega$ cm, $\Theta_{Dn}=423$°K, and $\gamma_n=1.36\times10^3$ ergs/cm^3 °K^2. For the sake of clarity, only two theoretical curves are plotted in Fig. 3, the coupled integral equations theory using the artificial cutoff [Eq. (3)] and the de Gennes–Guyon–Werthamer theory using the usual cutoff [Eq. (1)]. The difference in the theoretical curves is almost entirely due to the use of different cutoffs; using the artificial cutoff for all three theories, the results of the de Gennes–Guyon–Werthamer theory lie a maximum of 0.025°K higher, and the results of Moormann's theory lie a maximum of 0.13°K higher, than those of the coupled integral equations theory. The experimental points lie midway between the two plotted curves. We note that the calculations of Hauser and Theuerer for the de Gennes–Guyon–Werthamer theory differ slightly from our calculations for this theory, probably because we have used a different (and more recent) value of γ_n. It appears from Fig. 1 that using the coupled integral equations theory with the natural cutoff [Eq. (2)] would increase the transition temperature above that obtained using the artificial cutoff and thus further increase the disagreement between theory and experiment.

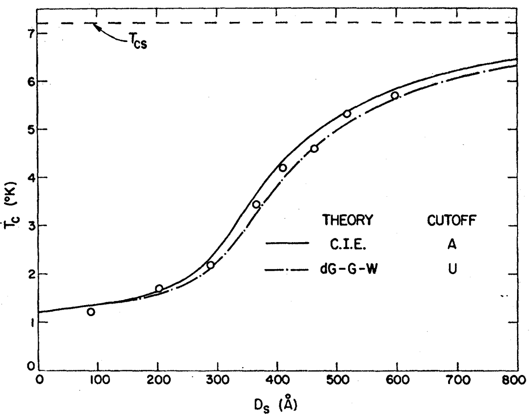

FIG. 3. Comparison of the various theories with the experiments of Hauser and Theuerer on Pb–Al films with $D_n=4400$ Å. The abbreviations used are defined in the caption for Fig. 1. Four experimental points with $D_s>800$ Å have not been plotted.

The agreement with experiment is good, but it should be better. In addition to the comments at the beginning of this section, we note that the aluminum films were condensed at 400°C and hence, are well annealed. Using Chambers's value[24] of $\rho l=490\ \mu\Omega$ cm Å for Al we find $l_n=2700$ Å; since ξ_n, the coherence length in aluminum, is 1300 Å at 7.2°K and 3200 Å at 1.2°K, the films may not be sufficiently dirty for the theory to apply.

Bergmann[7] has measured the transition temperatures of Pb–In superimposed films; the data are fitted equally well by the de Gennes–Guyon–Werthamer theory,[7] by Moormann's theory,[18] and by the coupled integral equations theory.

VII. CONCLUSIONS

It has been shown that different methods of treating the cutoff of sums lead to significantly different results when Θ_D/T_c is not very large; this sensitivity of the results to the cutoff method employed can be greatly reduced by replotting the results.

It has been shown that the three theories of the proximity effect discussed here, the de Gennes–Guyon–Werthamer theory, the theory of Moormann, and the coupled integral equations theory, give much the

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[24] R. G. Chambers, Proc. Roy. Soc. (London) **A215**, 481 (1952).

same results for Pb–Al films and probably for all film combinations in which $T_{cn} \approx T_{cs}$; large differences between the predictions of these theories are found for Pb–Cu films and probably for all film combinations in which $T_{cn} \approx 0°K$. In addition, it has been found that Moormann's theory gives unphysical results in the case $D_n \gg \xi_n$ and $T_{cn} \approx 0°K$.

Except for the very thin film data of Minnigerode,[10] evidence for superconductivity in Cu obtained from experiments using Pb–Cu superimposed films[2,8,10] must be considered doubtful due to experimental and theoretical uncertainties.

Additional experiments using two known superconductors are required in order to compare theory and experiment more critically; such experiments are in progress.

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Piezomagnetism of α-Fe_2O_3 and the Magnetoelastic Tensor of Fe^{3+} in Al_2O_3†

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A theory is developed for the piezomagnetism of insulating antiferromagnets based on a single-ion Hamiltonian and a molecular-field model of exchange. The piezomagnetic constants are found in terms of the single-ion magnetoelastic tensors of the magnetic ions. In contrast to magnetostriction, where the macroscopic magnetoelastic tensors are obtained by summing microscopic magnetoelastic tensors, the piezomagnetic tensor involves the difference of the microscopic magnetoelastic tensors of the ions on the two antiferromagnetic sublattices. The theory is then applied to the piezomagnetism of α-Fe_2O_3. The single-ion magnetoelastic tensor is measured for Fe^{3+} in Al_2O_3 using electron paramagnetic resonance under uniaxial strain. The piezomagnetic constants of α-Fe_2O_3 in the low-temperature ($\bar{3}m$) phase are predicted on the single-ion model to be

$$P_{11} = 4.5 \times 10^{-12} \text{ emu/cc per dyn/cm}^2,$$

$$P_{14} = 8.5 \times 10^{-12} \text{ emu/cc per dyn/cm}^2.$$

The single-ion contribution to the piezomagnetic constants of α-Fe_2O_3 in the high-temperature ($2/m$) phase are predicted to be

$$P_{14} = P_{36} = 7.9 \times 10^{-12} \text{ emu/cc per dyn/cm}^2,$$

$$P_{15} = -2P_{31} = 2P_{33} = -1.8 \times 10^{-12} \text{ emu/cc per dyn/cm}^2,$$

$$P_{24} = 8.5 \times 10^{-12} \text{ emu/cc per dyn/cm}^2,$$

$$P_{24} = 9.0 \times 10^{-12} \text{ emu/cc per dyn/cm}^2,$$

$$P_{32} \approx 0.$$

Appropriate experimental values of the piezomagnetic constants of α-Fe_2O_3 are not yet available for comparison with the theory.

I. INTRODUCTION

HEMATITE or α-Fe_2O_3 is a magnetic crystal which has engendered considerable interest due to its complicated magnetic properties. The most striking feature is the phase transition[1] which occurs at about −16°C. Above this temperature α-Fe_2O_3 is a weak ferromagnet,[2] and below it a pure antiferromagnet. The symmetry of the crystal is $D_{3d}{}^6$ and the magnetic symmetry above the transition point is $2/m$, the spins lying in the basal plane with a small canting angle to give a net moment. Below the transition point the symmetry is $\bar{3}m$ and the spins are aligned along the c

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[1] F. J. Morin, Phys. Rev. **78**, 819 (1950).

[2] I. Dzialoshinski, J. Phys. Chem. Solids **4**, 241 (1959).