Magnetic Susceptibility of a Thin Superconducting Film*

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The weak-field magnetic susceptibility of a thin superconducting film is calculated with a microscopic theory based on the work of Bardeen, Cooper, and Schrieffer. The finite sample size is taken into account by forming "Cooper pairs" from one-electron states whose wave functions vanish at the film boundary. Although the excitation spectrum of the superconductor remains essentially unchanged by this discrete quantization, the weak-field magnetic susceptibility is found to have a considerably lower value than previous theoretical estimates.

1. INTRODUCTION

IN this work the theory of Bardeen, Cooper, and Schrieffer[1] is applied to thin superconducting films. In particular the "Cooper pairs"[2] are formed from electronic wave functions which vanish at the surface of the film, and thus finite size effects are incorporated from the start. The main application considered here is the magnetic susceptibility in weak fields.[3] Previous calculations of this quantity, such as Schrieffer's,[4] made use of the nonlocal relation between current and vector potential appropriate to *bulk* superconductors. The present boundary conditions are, of course, rather unrealistic, as is the neglect of impurities distributed throughout the interior of the sample. On the other hand, the model chosen does permit a relatively complete study of the size effect by itself on the basis of a completely microscopic theory.

2. METHOD

The magnetic properties of the system will be derived using the standard perturbation treatment in which first-order changes in the wave function are used to calculate the current as a function of the applied field. The first step will be to derive an expression relating the current density to the total field. The expression for the current density may then be substituted into the appropriate Maxwell equation in order to derive, in a self-consistent manner, the magnetic vector potential. The calculation will be carried out in the London gauge: divergence of $\mathbf{A}$, $\mathbf{A}_\perp$ equal to zero. When one neglects the term of second order in the magnetic potential, the interaction Hamiltonian may be written

$$H_I=-i\frac{e}{mc}\int d\mathbf{r}\psi^\dagger(\mathbf{r})\mathbf{A}(\mathbf{r})\cdot\nabla\psi(\mathbf{r}). \quad (1)$$

The electron fields are expanded in creation and annihilation operators appropriate to a film of thickness a

$$\psi^\dagger(\mathbf{r})=\frac{1}{2\pi}\left(\frac{2}{a}\right)^{1/2}\sum_{\kappa,n,\sigma}C_{n\sigma}^\dagger(\kappa)u_\sigma \times\exp(-i\kappa\cdot\varrho)\sin n\pi\frac{z}{a}. \quad (2)$$

In this equation the position of an electron is specified by the polar vector ϱ in a plane containing one face of the film, and the distance z from that plane. The one-electron states are labeled by the spin-projection σ along some axis, the polar momentum $\hbar\kappa$, and the quantum number n characterizing the standing waves in the z direction; the $C_{n\sigma}^\dagger(\kappa)$ are the corresponding fermion creation operators. Perturbation theory, applied in the manner of BCS, then gives to lowest nonvanishing order, the following expression for the current density[1]

$$\mathbf{j}(\mathbf{r})=\langle\Phi^{(1)}|\mathbf{J}_P(\mathbf{r})|\Phi_0\rangle+\langle\Phi_0|\mathbf{J}_P(\mathbf{r})|\Phi^{(1)}\rangle +\langle\Phi_0|\mathbf{J}_D(\mathbf{r})|\Phi_0\rangle, \quad (3)$$

where the paramagnetic and diamagnetic portions of the current operator are defined by

$$\mathbf{J}_P(\mathbf{r})=-(e/2mi)(\psi^\dagger(\mathbf{r})\nabla\psi(\mathbf{r})-(\nabla\psi^\dagger(\mathbf{r}))\psi(\mathbf{r})), \quad (4)$$

$$\mathbf{J}_D(r)=-(e^2/mc)\psi^\dagger(\mathbf{r})\mathbf{A}(\mathbf{r})\psi(\mathbf{r}), \quad (5)$$

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[3] A discussion of the effects of finite size on the excitation spectrum and on the pair-correlation function is given in the Ph.D. thesis of S. J. Krieger, University of California, Berkeley, California, 1963 (unpublished). For films of practical interest the excitation spectrum is essentially the same as for a bulk medium. [For a discussion of the possibility of resonances in the superconducting energy gap, see J. M. Blatt and C. J. Thompson, Phys. Rev. Letters **10**, 332 (1963); C. J. Thompson and J. M. Blatt, Phys. Letters **5**, 6 (1963); or David S. Falk, Phys. Rev. **129**, 2340 (1963). These resonances occur about the bulk energy gap and are almost certainly unobservable in any real superconductor.]

[4] J. R. Schrieffer, Phys. Rev. **106**, 47 (1957).

and $|\Phi^{(1)}\rangle$ is given, as usual, by

$$|\Phi^{(1)}\rangle=\sum_{i\neq 0}\frac{\langle\Phi_i|H_I|\Phi_0\rangle}{E_0-E_i}|\Phi_i\rangle. \tag{6}$$

Carrying out the calculation of the matrix elements in Eq. (3) we obtain for $\mathbf{j}(\mathbf{r})$ the two terms

$$\mathbf{j}_p(\mathbf{r})=\frac{e^2}{8m^2c}\frac{1}{(2\pi)^2}\left(\frac{2}{a}\right)\sum_{\kappa' n'}\sum_{\kappa n\sigma}L(\epsilon_n(\boldsymbol{\kappa}),\epsilon_{n'}(\boldsymbol{\kappa}'))(\boldsymbol{\kappa}+\boldsymbol{\kappa}')\boldsymbol{\kappa}'\cdot[\mathbf{a}_{n'-n}(\boldsymbol{\kappa}-\boldsymbol{\kappa}')-\mathbf{a}_{n'+n}(\boldsymbol{\kappa}-\boldsymbol{\kappa}')]$$
$$\times\exp[-i(\boldsymbol{\kappa}'-\boldsymbol{\kappa})\cdot\boldsymbol{\varrho}]\left[\cos(n-n')\pi\frac{z}{a}-\cos(n+n')\pi\frac{z}{a}\right]+\text{c.c.}, \tag{7}$$

$$\mathbf{j}_d(\mathbf{r})=-\frac{Ne^2}{mc}\mathbf{A}(\mathbf{r})\left[1-\sum_{\kappa n\sigma}\frac{N_{n\sigma}(\boldsymbol{\kappa})}{N}\cos n\pi\frac{z}{a}\right]. \tag{8}$$

The number of particles in the quantum state $(\boldsymbol{\kappa},n,\sigma)$ is specified by $N_{n\sigma}(\boldsymbol{\kappa})$; N represents the total number of particles. The temperature dependence is contained in the function $L(\epsilon_n(\boldsymbol{\kappa}),\epsilon_{n'}(\boldsymbol{\kappa}'))$ which is, in fact, just the function derived by Bardeen, Cooper, and Schrieffer [Eq. (4.22), Ref. 1]. In the zero-temperature limit to which we shall soon confine our attention it takes the form

$$L(\epsilon,\epsilon')=\frac{1}{2}\frac{E-E'}{\epsilon^2-\epsilon'^2}\left(1-\frac{\epsilon\epsilon'+\Delta^2}{EE'}\right). \tag{9}$$

We have adopted the short-hand notation $\epsilon=\epsilon_n(\boldsymbol{\kappa})$, $E=(\epsilon^2+\Delta^2)^{1/2}$ in the above; Δ represents the energy gap at zero temperature. Finally the function $\mathbf{a}_n(\boldsymbol{\kappa})$ is the Fourier transform of the vector potential over the volume of the sample

$$\mathbf{a}_n(\boldsymbol{\kappa})=\frac{1}{(2\pi)^2}\left(\frac{2}{a}\right)\int d\mathbf{r}e^{-i\boldsymbol{\kappa}\cdot\boldsymbol{\rho}}\cos n\pi\frac{z}{a}\mathbf{A}(\mathbf{r}). \tag{10}$$

The two angular integrations in momentum space along with one integration over magnitude κ may be carried out in Eq. (7) so that we obtain

$$\mathbf{j}(\mathbf{r})=-\frac{3}{4\pi}\frac{1}{\Lambda_T c}\frac{\pi\Delta(0)}{v_0}\int d\mathbf{r}'\frac{J(\boldsymbol{\varrho}-\boldsymbol{\varrho}';z,z';T)\mathbf{PP}\cdot\mathbf{A}(\mathbf{r}')}{R^4}, \tag{11}$$

$$J(\boldsymbol{\varrho}-\boldsymbol{\varrho}';z,z';T)=\frac{2\Lambda_T\Delta^2(T)}{\pi\Delta(0)\Lambda}\int_0^\infty\frac{d\epsilon}{\epsilon}\left\{\frac{1-2f(\Delta)}{\Delta}-\frac{1-2f(E)}{E}\right\}\left\{\sin\frac{2R\epsilon}{v_0}+\sin\left[\frac{2[P^2+(z+z')^2]^{1/2}}{v_0}\epsilon\right]\Big/\left[\frac{P^2+(z+z')^2}{R^2}\right]^2\right.$$
$$-2\cos[k_F([P^2+(z+z')^2]^{1/2}-[P^2+(z-z')^2]^{1/2})]\sin\left[\frac{[P^2+(z+z')^2]^{1/2}}{v_0}\epsilon\right]\Big/$$
$$\left.\frac{[P^2+(z+z')^2][P^2+(z-z')^2]}{R^4}\right\}. \tag{12}$$

The notation is the same as that of BCS[1] except for the obvious changes to polar coordinates. Thus

$$\Lambda=\frac{m}{Ne^2},\quad 1-\frac{\Lambda}{\Lambda_T}=\frac{2\epsilon_F}{\kappa_F{}^5}\int_0^\infty d\kappa\kappa^4L(\epsilon,\epsilon),$$

and f represents the Fermi function. Finally v_0 is the velocity at the Fermi surface and the quantity $\mathbf{P}$ is defined as $\mathbf{P}=\boldsymbol{\varrho}-\boldsymbol{\varrho}'$. In deriving Eq. (12) it has been assumed that in the limit $\Delta\rightarrow 0$ the contribution of the paramagnetic current cancels the diamagnetic current. In effect this amounts to the neglect of the small Landau diamagnetism.

3. THIN FILM LIMIT AT ZERO TEMPERATURE

At zero temperature the expression (12) simplifies somewhat. In addition to the elimination of the Fermi functions the final integration over energy may be performed. The details of the calculation are given in Ref. 3, and involve the introduction of the Fourier transform of the current,

$$\mathbf{j}_m(\mathbf{q})=\frac{1}{(2\pi)^2}\left(\frac{2}{a}\right)\int d\mathbf{r}\exp(-i\mathbf{q}\cdot\boldsymbol{\varrho})\cos m\pi\frac{z}{a}\mathbf{j}(\mathbf{r}). \tag{13}$$

The results of a somewhat tedious calculation, valid for

$q\xi_0$, $a/\xi_0 \ll 1$ are

$$\mathbf{j}_m(\mathbf{q}) = -\frac{c}{4\pi}\sum_n K_{mn}(\mathbf{q})\,\mathbf{a}_n(\mathbf{q})\,, \tag{14}$$

$$\begin{aligned} K_{mn}(\mathbf{q}) = \frac{4\pi}{\Lambda c^2}\frac{3}{2}\frac{a}{\xi_0}\int_0^1 dx\int_0^1 dx' \cos m\pi x \cos n\pi x' \\ \times\{\ln(\xi_0/a)^2 - (2C+1) - \ln|x-x'|^2 \\ -2[K_0(\eta e^{i\pi/\Delta}(xx')^{1/2}) + K_0(\eta e^{-i\pi/\Delta}(xx')^{1/2})] \\ +2(a/\xi_0)(x+x'+|x-x'|)\}\,. \end{aligned} \tag{15}$$

Here C is Euler's constant and η is defined as $\eta = 2(2k_F aa/\xi_0)^{1/2}$. By substituting Eq. (14) into the Maxwell equation

$$\left[q^2 + \left(\frac{m\pi}{a}\right)^2\right]\mathbf{a}_m(\mathbf{q}) = \frac{4\pi}{c}\mathbf{j}_m(\mathbf{q}) + \left[q^2 + \left(\frac{m\pi}{a}\right)^2\right]\mathbf{a}_m^{(0)}(\mathbf{q})\,, \tag{16}$$

a set of linear equations for the functions $\mathbf{a}_m(\mathbf{q})$ is obtained:

$$\left[q^2 + \left(\frac{m\pi}{a}\right)^2\right]\mathbf{a}_m(\mathbf{q}) + \sum_n K_{mn}(\mathbf{q})\,\mathbf{a}_n(\mathbf{q}) = \left[q^2 + \left(\frac{m\pi}{a}\right)^2\right]\mathbf{a}_m^{(0)}(\mathbf{q})\,. \tag{17}$$

This set of equations takes the simplest form when $\mathbf{a}_m^{(0)}(\mathbf{q})$, the externally applied potential, represents a constant field $\mathbf{B}_0$ parallel to the film. We then have

$$\begin{aligned} \mathbf{a}_m^{(0)}(\mathbf{q}) &= aB_0\hat{x}\delta(\mathbf{q})\,, && m=0\,,\\ &= 0\,, && m = \text{even integer}\,,\\ &= -[4aB_0/(m\pi)^2]\hat{x}\delta(\mathbf{q})\,, && m = \text{odd integer}\,. \end{aligned} \tag{18}$$

It follows that $\mathbf{a}_m(\mathbf{q}) \propto \delta(\mathbf{q})$ so that by defining $\delta(\mathbf{q})a_m = \hat{x}\cdot\mathbf{a}_m(\mathbf{q})$ we have only to solve the reduced equations

$$\left(\frac{m\pi}{a}\right)^2 a_m + \sum_n K_{mn}a_n = \left(\frac{m\pi}{a}\right)^2 a_m^{(0)}\,. \tag{19}$$

These equations split naturally into the equation for a_0

$$K_{0,0}a_0 + \sum_n K_{0,2n+1}a_{2n+1} = 0 \tag{20}$$

and the equation for the odd a_m

$$(2m+1)^2\left(\frac{\pi}{a}\right)^2 a_{2m+1} + K_{2m+1,0}a_0 + \sum_n K_{2m+1,2n+1}a_{2n+1} = -\frac{4B_0}{a}\,. \tag{21}$$

Substituting Eq. (20) for a_0 into Eq. (21), we obtain a set of equations for the coefficients a_{2m+1}. Introducing the notation

$$|a\rangle = \begin{bmatrix} a_1 \\ a_2 \\ \vdots \\ a_{2m+1} \end{bmatrix}, \quad |a_0\rangle = -\frac{4B_0 a}{\pi^2}\begin{bmatrix} 1^{-2} \\ 3^{-2} \\ \vdots \\ (2m+1)^{-2} \end{bmatrix},$$

$$\hat{K}_{mn} = \left(\frac{a}{\pi}\right)^2 (2m+1)^{-2} \times[K_{2m+1,2n+1} - K_{00}^{-1}(K_{2m+1,0}K_{0,2n+1})]\,,$$

the solution to this set of equations may be written

$$|a\rangle = (1+\hat{K})^{-1}|a_0\rangle\,. \tag{22}$$

Now

$$|\hat{K}| \approx \frac{4\pi}{\Lambda c^2}\frac{a}{\xi_0}\left(\frac{a}{\pi}\right)^2 \approx 10^{-9}a^3$$

with a expressed in angstroms, so that for $a \lesssim 500$ Å we may approximate the solution to Eq. (22) by

$$|a\rangle = (1-\hat{K})|a_0\rangle \tag{23}$$

in which case the coefficients a_{2m+1} are given by

$$\begin{aligned} a_{2m+1} &= -\frac{4B_0 a}{\pi^2}\sum_n (1-\hat{K})_{2m+1,2n+1}(2n+1)^{-2} \\ &= -\tfrac{1}{2}B_0 a + \frac{4B_0 a}{\pi^2}\sum_n \hat{K}_{2m+1,2n+1}(2n+1)^{-2}\,. \end{aligned} \tag{24}$$

The magnetic susceptibility κ is defined by

$$\frac{\kappa}{\kappa_0} = \frac{1}{a}\int_0^a dz \frac{B_0 - B(z)}{B_0} \tag{25}$$

with $\kappa_0 = -1/4\pi$. We obtain for the susceptibility the result

$$\begin{aligned} \frac{\kappa}{\kappa_0} &= \frac{8}{\pi^2}\sum_{n,m}\hat{K}_{2m+1,2n+1}(2n+1)^{-2} \\ &= \frac{8a^2}{\pi^4}\sum_{n,m}[K_{2m+1,2n+1} - K_{00}^{-1}(K_{2m+1,0}K_{0,2n+1})] \\ &\quad\times(2n+1)^{-2}(2m+1)^{-2}\,. \end{aligned} \tag{26}$$

The summations over m and n may be carried out, thus reducing the calculation of the susceptibility to the evaluation of several double integrals:

$$\frac{\kappa}{\kappa_0} = \frac{3}{16}\left(\frac{a}{\lambda}\right)^2\left(\frac{a}{\xi_0}\right)\left[K_{MN} - \frac{K_{M0}K_{0N}}{K_{00}}\right], \tag{27}$$

where

$$K_{MN}=\int_0^1 dx(1-2x)\int_0^1 dx'(1-2x')K(x,x'), \quad (28)$$

$$K_{M0}=K_{0N}=\int_0^1 dx\int_0^1 dx'(1-2x')K(x,x'), \quad (29)$$

$$K_{00}=\int_0^1 dx\int_0^1 dx'\left[\ln\left(\frac{\xi_0}{a}\right)^2-(2C+1)+K(x,x')\right], \quad (30)$$

and

$$K(x,x')=-\ln|x-x'|^2 -2[K_0(\eta e^{i\pi/\Delta}(xx')^{1/2})+K_0(\eta e^{-i\pi/\Delta}(xx')^{1/2})] +2\frac{a}{\xi_0}(x+x'+|x-x'|). \quad (31)$$

For $\eta\leq 2$ which corresponds to $a\lesssim 100$ Å we may expand the Bessel functions which occur in Eq. (31). The integrations Eq. (28) through Eq. (30) may then be carried out analytically. The resultant expression for the magnetic susceptibility is plotted on Fig. 1. The result is considerably lower than that predicted by the nonlocal Pippard theory[5] as calculated by Schrieffer.[4] On the other hand, in common with Pippard we find that $\kappa\propto a^3/\xi_0\lambda^2$ for very thin films. Results for thicker films, say in the range 100 to 500 Å will probably require numerical solution with computers.

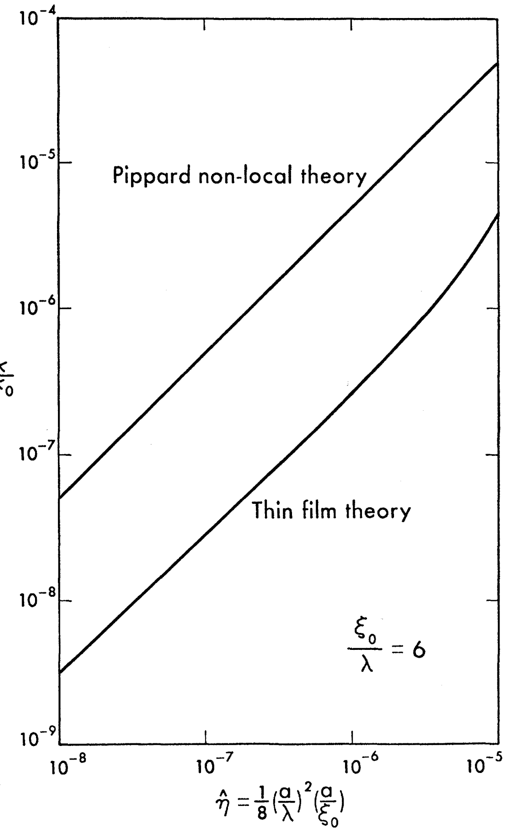

FIG. 1. Magnetic susceptibility.

4. DISCSUSION

This theory of the weak-field magnetic susceptibility of thin superconducting films has only been evaluated for rather thin films (less than 100 Å). Effects of impurities have been completely ignored and the electronic wave function made to vanish at the boundaries. There is at present no relevant experimental data on samples of this kind. The closest are Toxen's for the critical fields of pure indium films, which are considerably larger, i.e., of the order of 300 Å.[6] Toxen[7] has also analyzed his measurements with the aid of the Ginzburg-Landau theory,[8] obtaining a connection between the weak-field susceptibility and the critical field. For very thin films the relation is

$$h_c/H_c=(\tfrac{1}{2}\kappa/\kappa_0)^{-1/2}, \quad (32)$$

where h_c and H_c are thin film and bulk critical fields, respectively. As previously stated, the main numerical result of this paper is that κ/κ_0 is an order of magnitude smaller than previous estimates. If Toxen's expression Eq. (32) is now combined with our result, critical fields about 3 times larger are predicted. It would therefore be of interest to have measurements on such very thin films as well as to extend the present calculations to larger films.

No account has been taken of the effect of impurities distributed throughout the volume of the sample or of the scattering from the boundaries. These must be considered in evaluating the conjecture often made that size and impurity effects are similar, and that they can be described by an effective correlation length $\xi=\xi(\xi_0,a,l)$, where l is the mean free path for impurity scattering.[5] Even from the present simplified but completely "microscopic" theory one does find that the finite size cannot be completely described in this way: that is, one finds significant size effects in the magnetic susceptibility even when the energy gap is the same as in a bulk medium. This arises from the rather different dependence of the energy and of the susceptibility on the pair-correlation function of the film.

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