imately constant throughout the superconductor, including the vortex-core regions. This would obviously not be possible if the vortex cores were stationary normal regions, since then the current would bypass them entirely. In fact, the condition for equilibrium of a vortex structure is precisely that the current vanish at the vortex core, since $F = J \times H$; thus pinned vortices will not need to have any current flow in the cores. No such condition is valid for flowing vortices since they must sustain a net Lorentz force. The assumption of uniform current flow also requires that the electric field be concentrated in the vortex-core regions and its magnitude be much larger than $(v/c) \times H$. Anderson[8] has pointed out that there must exist electric fields additional to $(v/c) \times H$ since this field in the presence of the inhomogeneous normal conductivity will not satisfy current conservation, so that space charges must build up; but it is by no means obvious why these might lead to approximate homogeneity of current. The only presently understandable region is that near H_{c2} at reasonable T. At this point uniform E and J must be expected and are not incompatible; the sharp drop in resistivity is probably explained by Tinkham's[9] observation that ρ_n actually drops at the transition point, rather than rising, because of the density-of-states peak.

We finally comment on the question of Hall voltages in type-II superconductors. Inasmuch as the flux lines are described as vortices of superconducting electrons, the lines may move not in the direction of the applied force, but perpendicular to the force.[10] If so, one expects a large Hall voltage in the flux-flow state. In many of our samples we do observe transverse voltages, but they are due primarily to surface impurities and thermal effects. Although some components of these transverse voltages could be interpreted as Hall-type emf, the magnitude is very much smaller than that expected from the vortices moving perpendicular to the force.[11] Our observations, however, do not as yet exclude the possibility of these effects existing in pure crystals.

[1]A. A. Abrikosov, Zh. Eksperim. i Teor. Fiz. 32, 1442 (1957) [translation: Soviet Phys. -JETP 5, 1174 (1957)].
[2]P. W. Anderson and Y. B. Kim, Rev. Mod. Phys. 36, 39 (1964).
[3]C. F. Hempstead and Y. B. Kim, Phys. Rev. Letters 12, 145 (1964).
[4]Y. B. Kim, C. F. Hempstead, and A. R. Strnad, Rev. Mod. Phys. 36, 43 (1964).
[5]J. Volger, F. A. Staas, and A. G. Van Vijfeijken, Phys. Letters 9, 303 (1964).
[6]C. Caroli, P. G. de Gennes, and J. Matricon, Phys. Letters 9, 307 (1964).
[7]B. Rosenblum and M. Cardona, Phys. Rev. Letters 12, 657 (1964).
[8]We are indebted to P. W. Anderson for the theoretical considerations mentioned here.
[9]M. Tinkham, private discussion.
[10]W. F. Vinen, Rev. Mod. Phys. 36, 48 (1964); P. H. Borcherds, C. E. Gough, W. F. Vinen, and A. C. Warren, Phil. Mag. 10, 349 (1964).
[11]The absence of Hall voltages in type-II superconductors was reported earlier by A. I. Schindler and D. J. Gillespie, Phys. Rev. 130, 953 (1963); C. F. Hempstead and Y. B. Kim, Bull. Am. Phys. Soc. 9, 29 (1964).

WEAK TIME DEPENDENCE IN PURE SUPERCONDUCTORS*

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(Received 30 September 1964; revised manuscript received 24 November 1964)

In recent years the equilibrium properties of type-II superconductors have been successfully investigated by means of the Ginzburg-Landau theory.[1] In this theory the state of the superconductor is characterized by an order parameter (energy gap), and an electromagnetic field, both slowly varying with position. One expects a similar characterization to hold also for certain restricted types of time variations, especially if these are slow enough to preclude breakup of Cooper pairs. (The motion of fluxoids through the superconductor should be a case in point.) Because of the time dependence, there appears to be no obvious way of basing such a theory on thermodynamics alone. We therefore use the BCS model[2] in the Gor'kov formulation[3] to derive the necessary time-dependent generalizations. In this paper we restrict ourselves to pure superconductors. We make the following assump-

tions concerning the frequency ω and the wave number q of the disturbance: (a) $\omega < |\Delta|$. For $|\omega| > \Delta$ additional effects due to breakup of Cooper pairs will occur. (b) $q < 1/\xi_0$, the reciprocal coherence length. This restriction (London limit) is discussed at length by Werthamer.[4] (c) $\omega \ll qv_F$, where v_F is the Fermi velocity. This appears to be the case of greatest interest. (d) Pure materials. Mean free path $l > q^{-1}$ (anomalous skin effect). In addition, $\omega\tau > 1$. Condition (d) means that the part of our description concerned with the normal-fluid component will not be purely local.

For purposes of orientation, consider first a pure, uniform superconductor. The linear constitutive relations giving charge ρ and current j due to scalar and vector potentials φ and A are[5] (setting $\hbar = 1$)

$$\rho = -\frac{3\rho_0 e^2}{k_F^2}\varphi + \frac{3\rho_n e^2}{ck_F^2}\frac{\omega(qA)}{q^2},$$

$$j = -\frac{\rho_s e^2}{m^2 c}A_t - \frac{3\rho_n e^2 \omega q}{k_F^2}\frac{}{q^2}\varphi + \frac{3e^2}{k_F^2 c}\left[\rho_n + 2|\Delta|^2\frac{\partial\rho_n}{\partial|\Delta|^2}\right]\frac{\omega^2}{q^2}A_l,$$

where ρ_S and ρ_n (with $\rho_S + \rho_n = \rho_0$) are the superfluid and normal mass densities, respectively the latter being given, in the usual notation, by[6]

$$\rho_n = -\tfrac{4}{3}k_F^2 N(0)\int_0^\infty d\epsilon \frac{\partial f(E)}{\partial E},$$

k_F being the Fermi momentum. A_l is the longitudinal part of A. Further small terms of order $(\omega/qk_F)^2$ in the transverse part of A also occur in j, but are not required in the following analysis. (Small dissipative terms of order (ω/qk_F) arising at finite temperatures in the limit $l \to \infty$ due to the presence of real excitations will also be neglected.) These equations lack gauge invariance, as they presuppose a constant gap. In the presence of φ and A, the gap acquires a space- (R-) and time- (T-)dependent phase, whose inclusion in ρ and j insures gauge invariance. If $\Delta^+ = |\Delta| \times \exp(2ieW/c)$, then φ, A must be replaced by

$$\bar{\varphi} = \varphi + (1/c)(\partial W/\partial T),$$

$$\bar{A} = A - \nabla W.$$

The presence of W in ρ and j means that an extra equation is needed to ensure charge conservation: a differential equation for the energy gap. We now depart from small-signal theory in the following limited sense: $|\Delta|$ is slowly varying. φ, A, and W need not be small; only the gauge-invariant combinations $\bar{\varphi}$ and $\bar{A}$ must be small. Our procedure for establishing the necessary equations is to solve the integral form of the Gor'kov equations[3] for the Green's functions G and F in powers of $\bar{\varphi}$ and $\bar{A}$ and in successively higher space and time derivatives of $|\Delta|$, all to lowest nontrivial orders. We note a certain difficulty with regard to time variation: We define G as

$$G(1,2) = \frac{\mathrm{Tr}\{\exp(-\beta H_0)[\Psi(r_1,t_1)\Psi^\dagger(r_2,t_2)]_+\}}{\mathrm{Tr}\exp(-\beta H_0)},$$

where H_0 is the Hamiltonian excluding time-dependent fields, and Ψ is the electron-annihilation operator in the Heisenberg representation:

$$\Psi(r_1 t_1) = U(t_1 t_0)\Psi(r_1 t_0)U^{-1}(t_1 t_0),$$

where U is the time-evolution operator in the presence of time-varying fields. Integral equations for G and F can be established once the boundary conditions are known. We follow Kadanoff and Baym[7] in supposing the fields and the gap to be analytic functions of time in the strip $0 > \mathrm{Im}t > -\beta$. Then the boundary conditions on G are

$$G(0,t') = -G(-i\beta,t'),$$

and similarly for F. It is then not difficult to establish the following integral equation for the Green's function (for brevity we use the matrix notation of Nambu[8]):

$$\mathcal{G}(1,1') = \mathcal{G}_0(1-1') - \int \mathcal{G}_0(1-2)\left\{\vec{\Delta}(2) - \vec{\Delta}\left[e\varphi(2) - \frac{e^2}{2mc^2}A^2(2)\right]\tau_3 - \frac{e}{2mci}\left[\vec{\nabla}_2 \cdot A(2) + A(2)\cdot\vec{\nabla}_2\right]\right\}\mathcal{G}(2,1'), \quad (1)$$

where $\mathcal{G}_0(1-1')$ is the BCS-Gor'kov Green's function for a uniform superconductor with a gap Δ. $\vec{\Delta}(2)$ is the matrix

$$\vec{\Delta}(2) = \begin{pmatrix} 0 & \Delta(2) \\ \Delta^+(2) & 0 \end{pmatrix}.$$

If we now choose Δ to be the value of the gap at $R = \frac{1}{2}(r_1 + r_1')$ and $T = \frac{1}{2}(t_1 + t_1')$, iteration of

this equation provides an expansion in the variation of Δ and the fields. The resulting equations can be continued onto the real time axis. Employing the London gauge for simplicity we find the following results:

$$\rho = \frac{3e}{k_F^2}\left[i\frac{\rho_s}{4|\Delta|^2}\left(\Delta\frac{\partial\Delta^+}{\partial T} - \Delta^+\frac{\partial\Delta}{\partial T}\right) - \rho e\varphi\right], \tag{2}$$

$$\vec{j} = -\frac{e}{2m^2}\frac{\rho_s}{|\Delta|^2}\left[\frac{i}{2}\left(\Delta\frac{\partial\Delta^+}{\partial\vec{R}} - \Delta^+\frac{\partial\Delta}{\partial\vec{R}}\right) + \frac{2e}{c}|\Delta|^2\vec{A}\right] - \frac{3e}{k_F^2}\left[\rho_n\nabla_R L\left(e\frac{\partial\varphi}{\partial T}\right) + \frac{i}{2}\frac{\partial\rho_n}{\partial|\Delta|^2}\left(\Delta\nabla_R L\frac{\partial^2\Delta^+}{\partial T^2} - \Delta^+\nabla_R L\frac{\partial^2\Delta}{\partial T^2}\right)\right]. \tag{3}$$

Here L is the inverse Laplace operator defined, for the infinite medium, by

$$Lf(\vec{R},T) = \frac{1}{4\pi}\int d\vec{R}'\frac{f(\vec{R}',T)}{|\vec{R}-\vec{R}'|}; \quad \nabla^2 L = -\delta(\vec{R}-\vec{R}'). \tag{3a}$$

The second term of j is entirely due to the presence of excitations in the superconductor. The most interesting and tractable case is close to T_c where Δ is small, and we only give the gap equation for small Δ. The corresponding approximations to ρ and j are to retain all terms of order Δ^2 in (2) and (3). Thus

$$\rho_s = N(0)\alpha|\Delta|^2; \quad \rho_n = \rho - \rho_s. \tag{4}$$

The gap equation is then

$$N(0)\Delta^+\left[\ln\frac{T}{T_c} - \frac{3\alpha}{4k_F^2}|\Delta|^2\right] = D_R(\Delta^+) + D_T(\Delta^+), \tag{5}$$

where

$$D_R(\Delta^+) = \frac{1}{8m^2}\left(\frac{\rho_s}{|\Delta|^2}\right)_{\Delta=0}\left(\vec{\nabla} - \frac{2ie}{c}\vec{A}\right)^2\Delta^+, \tag{6}$$

$$D_T(\Delta^+) = -\frac{3}{8k_F^2}\left(\frac{\rho_s}{|\Delta|^2}\right)_{\Delta=0}\left(\frac{\partial}{\partial T} + 2ie\varphi\right)^2\Delta^+ - \frac{3}{4k_F^2}\left(\frac{\partial\rho_n}{\partial|\Delta|^2}\right)_{\Delta=0}\left(\frac{\partial^2}{\partial T^2} + 2ie\varphi\frac{\partial}{\partial T} - 2e^2\varphi^2\right)\Delta^+. \tag{7}$$

We have written (6) and (7) in this form to indicate the origin of the terms. Charge conservation is given by these equations provided we omit nonlocal terms in div$j$ of the form $(\vec{\nabla}_R\Delta)\cdot\vec{\nabla}_R L(\partial^2\Delta^+/\partial T^2)$. Such terms will arise from higher iterations of (1) than the first that we have considered.

It is of interest to compare these results with those of Ambegaokar and Kadanoff.[9] Assuming as they do a constant $|\Delta|$, the charge-conservation condition at $T=0$ is a wave equation for W with a velocity $v_F/\sqrt{3}$. At $T=0$ only the first term in (7) remains. At higher temperatures the charge-conservation equation as shown by (6) and (7) is no longer a wave equation but is still of hyperbolic form. The change in the form of the equation is determined approximately by the temperature where

$$\frac{\rho_s}{|\Delta|^2} + 2\frac{\partial\rho_n}{\partial|\Delta|^2} = 0.$$

To take plasma effects into account to lowest order ($\omega_p = \infty$) we must have $\rho = 0$, which determines φ in terms of W (see Anderson and Dayem,[10] who examine a consequence of this). For consistency in a nonlinear theory the condition $\rho = 0$ should actually be written to one order higher in the potentials and derivatives of the gap.

The authors gratefully acknowledge helpful conversations with V. Ambegaokar, P. W. Anderson, and N. R. Werthamer. Similar calculations have been made by V. Ambegaokar, N. D. Mermin, and J. Wilkins, to whom we are indebted for pointing out an error in our work.

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*Work supported by U. S. Air Force Grant No. AF-AFOSR-610-64.

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[1]V. L. Ginzburg and L. D. Landau, Zh. Eksperim. i Teor. Fiz. 20, 1064 (1950).

[2]J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).

[3]E.g., A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaloshinski, Methods of Quantum Field Theory in Statistical Mechanics, translated by R. A. Silverman (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963), Chap. 7.

[4]N. R. Werthamer, Phys. Rev. 132, 663 (1963).

[5]See reference 3, Chap. 7, Sec. 37.2. However, the discussion there applies to Pippard superconductors, while the present problem is meaningful only in the London limit.

[6]J. Bardeen, Phys. Rev. Letters 1, 399 (1958).

[7]L. P. Kadanoff and G. Baym, Quantum Statistical Mechanics, (W. A. Benjamin, Inc., New York, 1962), Chap. 8.
[8]Y. Nambu, Phys. Rev. 117, 648 (1960).
[9]V. Ambegaokar and L. P. Kadanoff, Nuovo Cimento 22, 914 (1961).
[10]P. W. Anderson and A. H. Dayem, Phys. Rev. Letters 13, 195 (1964).

MAGNETIC ORDERING AND CRITICAL THICKNESS OF ULTRATHIN IRON FILMS*

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Early theoretical work[1,2] showed plane nets of atoms to be nonferromagnetic although such arrays in applied fields could result in stable ferromagnetic systems.[3] Experimental investigations,[4-6] which were encouraged by later theoretical work,[7,8] showed that the magnetization decreased relative to bulk value for films which were less than ≈100 lattice parameters thick and appeared to substantiate the spin-wave treatment of Klein and Smith.[7] However, more recent experiments[9-11] have shown that the earlier experimental work was subject to serious error, and that for particles as small and films as thin as 15 Å, the magnetization was essentially equal to bulk value. Thus, the question still remained: At what point does the saturation magnetization show an appreciable thickness dependence?

A major difficulty in thin-film research is the achievement of magnetic saturation for films thinner than ≈20 Å. It occurred to us[12] that the use[13] of the Mössbauer effect in Fe^{57} circumvents this problem and offers a new technique to examine the thickness dependence. We have measured the resonance-absorption spectra of Fe films of 1.2-120Å average thickness at 4.2°K and in the range 298-823°K. Three quantities are derivable from these spectra as a function of film thickness (D) and temperature (T): (1) the magnetic field at the Fe^{57} nucleus $H_n(D, T)$ [$H_n(D, T)$ for bulk Fe^{57} is very nearly proportional to the saturation magnetization $M_S(D, T)$[13,14]]; (2) Curie temperature $T_C(D)$; and (3) quadrupole splitting $2\epsilon(D, T)$ [$=\frac{1}{2}|e^2qQ|$].[15] We conclude from our data that $T_C(D)$ and $2\epsilon(D, T)$, as well as $H_n(D, T)$[$\approx M_S(D, T)$], undergo an abrupt change for films of about two lattice parameters average thickness. This implies the existence of a critical thickness in Fe films.

In order to have enough Fe^{57} to produce observable resonance absorption, samples consisting of alternating layers of Fe (92% Fe^{57}) and SiO were prepared by evaporation in a vacuum system at $\approx 3\times10^{-8}$ Torr. The layers were formed by exposing a quartz cover glass alternately to heated sources containing the Fe and SiO for fixed and reproducible time increments. The SiO evaporation rate was such that the Fe films were separated by 50 Å or more of SiO substrate. The top Fe film was covered with ≈500 Å of Al or SiO. The total Fe thickness was measured by chemical analysis and x-ray emission spectrometry[16] (by far the more accurate). The Fe film thickness was determined by dividing the total Fe thickness by the number of layers. Resonance-absorption spectra were obtained from a Mössbauer spectrometer using a stainless-steel source.[17]

The room-temperature spectra obtained from all samples were of two types: (1) a "six-line" pattern characteristic of the magnetic hyperfine spectrum of metallic iron,[13] and (2) a "two-line" pattern. The six-line spectra were observed only for films of 6 Å or greater thickness; the two-line spectra were obtained only for films of 4.6 Å or smaller thickness. In the six-line spectra, $H_n(D,298°K)$ is essentially equal to bulk value $H_n(\infty,298°K)$ for film thicknesses of 15 Å or greater. For thinner films $H_n(D,298°K)$ decreases slightly and becomes ≈4% less than the room-temperature bulk value at 6 Å. The 6Å film exhibited a quadrupole coupling $\epsilon(6\text{ Å},298°K) = 0.06 \pm 0.02$ mm/sec. No quadrupole coupling was observed in thicker films.

The two-line spectra obtained from films of 1.2-4.6Å thickness consist of two partially resolved lines of equal intensity with a separation of 0.6 mm/sec. The shape of the two-line spectra does not correspond to a collapsed hyperfine pattern.[13] Therefore, $H_n(D, T)$ for films 4.6 Å or thinner must be less than the