such a small interval in X that it is, for practical purposes, unobservable.

In conclusion, we have established the limiting behavior of thermodynamic potentials at the critical point and have given preliminary values for the critical exponents. These satisfy the scaling relation [Eq. (2)], and one has in addition $\gamma_+ = \gamma_+'$ within experimental error. Hence the superfluid and normal regions appear to have at least closely the same critical indices. Experiments with a still more sensitive strain gauge are being attempted with the purpose of obtaining more accurate values of these exponents. Furthermore, a study of small instabilities and the hysteresis effects of the pressure readings will be made.

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[1]For a review see the article by K. W. Taconis and R. DeBruyn Ouboter, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland, Amsterdam, 1964), Vol. 4, p. 38.

[2]E. H. Graf, D. M. Lee, and J. D. Reppy, Phys. Rev. Lett. 19, 417 (1967).

[3]R. B. Griffiths, Phys. Rev. Lett. 24, 715 (1970). In his paper, Griffiths used for the critical exponents the symbols μ [$=\delta^{-1}$] and ϵ [$=\gamma$].

[4]T. Alvesalo, P. Berglund, S. Islander, G. R. Pickett, and W. Zimmermann, Jr., in Proceedings of the Twelfth International Conference on Low Temperature Physics, Kyoto, Japan, September 1970, edited by E. Kanda (to be published).

[5]S. G. Sydoriak and T. R. Roberts, Phys. Rev. 118, 901 (1960).

[6]T. R. Roberts and S. G. Sydoriak, Phys. Fluids 3, 895 (1960).

[7]R. B. Griffiths and J. C. Wheeler, Phys. Rev. A 2, 1047 (1970).

[8]R. B. Griffiths, private communication.

Theory of Fluctuation-Induced Diamagnetism in Superconductors

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A free-energy expression for a pure superconductor is derived microscopically which includes effects of a nonlocal order parameter. In the presence of strong field the simple transformation $\vec{q} \rightarrow \vec{q} + 2e\vec{A}/c$ is no longer valid. Using this free energy, fluctuation-induced diamagnetism of a superconductor above T_c is calculated. The resulting universal behavior for pure superconductors is in good agreement with the experiment of Gollub, Beasley, and Tinkham.

Recently Gollub, Beasley, and Tinkham[1] (GBT) reported observation of universal behavior in the fluctuation-induced diamagnetism of clean superconductors above the transition temperature. This magnetization has been calculated exactly within the framework of the Ginsburg-Landau (GL) theory by Prange.[2] However, the fluctuation spectrum of the (GL) theory overestimates the contribution from short-wavelength fluctuations when a magnetic field B is present. This results in a calculated magnetization which is considerably larger than the measured value[1] when $B > 0.05H_{c2}(0)$. Patton, Ambegaokar, and Wilkins[3] (PAW) had dealt with this problem by introducing an energy-cutoff parameter into the fluctuation spectrum. As a result their magnetization is strongly suppressed below the Prange value if $B \gtrsim mcE/he$ (m = electron mass). Physical arguments[1,3] suggest the choice $E \approx \hbar^2/2m\xi_0^2 \approx e\hbar H_{c2}(0)/mc$. As pointed out by GBT, with this choice of E the PAW theory only begins to suppress the magnetization strongly (to $\sim\frac{1}{2}$ the Prange value) when $B \approx H_{c2}(0)$, when in fact the corresponding measured value is almost zero. Thus, it would seem that some other physical effect must play a part in depressing the magnetization of clean superconductors in a magnetic field. The present calculation treats in detail the nonlocal effects which arise because of the presence of a magnetic field. It is found that once the nonlocal effects are included, the magnetization is suppressed considerably (to $\sim\frac{1}{2}$ the Prange

value) by the time $B \approx 0.06 H_{c2}(0)$. Thus, good agreement with experiment is obtained without the inclusion of an adjustable parameter.

Since we are mostly interested in fluctuations above T_c we begin with the linearized Gorkov equation for the order parameter $\Delta^*(\vec{r})$,

$$\Delta^*(\vec{r}) = VkT \sum_n \int d^3r_1 \, Q(\vec{r}_1, \vec{r}) \Delta^*(\vec{r}_1), \tag{1}$$

where $Q_n(\vec{r}_1, \vec{r}) = G_{-\omega}(\vec{r}_1, \vec{r}) G_\omega(\vec{r}_1, \vec{r})$ and G_ω is the normal electron thermal Green's function, with $\omega = 2\pi kT(n+\frac{1}{2})$.[4] Using a lemma derived by Werthamer,[4]

$$\exp[(2ie/\hbar c)\int_{\vec{r}}^{\vec{r}_1} d\vec{s} \cdot \vec{A}(\vec{s})] \Delta^*(\vec{r}_1) = \exp[-i(\vec{r}_1 - \vec{r}) \cdot \vec{\Pi}] \Delta^*(\vec{r}), \tag{2}$$

where $\vec{\Pi} = -\nabla/i - (2e/\hbar c)\vec{A}(\vec{r})$, Eq. (1) can be simplified as follows. We introduce $Q_n(q)$ as the Fourier transform of $Q_n(r)$ for $B = 0$. We then subtract out the divergent part of the integral in Eq. (1) by writing $Q_n(q) = [Q_n(q) - Q_n(0)] + Q_n(0)$. The $Q_n(0)$ contribution is the well-understood BCS gap equation. Let $K(q) = -[kT/N(0)] \sum_n [Q_n(q) - Q_n(0)]$. Equation (1) becomes $\hat{L} \Delta^*(\vec{r}) = 0$, where the operator $\hat{L}$ is defined by

$$\hat{L} = N(0)V[\ln(T/T_c) + \int d^3r_1 d^3q (2\pi)^{-3} \exp(i\vec{q} \cdot \vec{r}_1) K(q) \exp(-i\vec{r}_1 \cdot \vec{\Pi})]. \tag{3}$$

$N(0)$ is the density of states at the Fermi level. Expanding $K(q)$ in powers of q^2 yields the usual GL equation if only the q^2 term is kept. To obtain higher order q^n one must keep the corresponding order in $(\vec{r}_1 \cdot \vec{\Pi})^n / n!$. However different components of Π_i do not commute, and in fact, in the case of constant field B, $[\Pi_x, \Pi_y] = -i(2e/\hbar c)B$. Hence higher-order terms will include not only the combination $\vec{\Pi} \cdot \vec{\Pi} = [\nabla/i + (2e/\hbar c)\vec{A}]^2$, but will also contain terms dependent on $(2eB/\hbar c)^2$ as well. It is thus inconsistent to treat nonlocality in the order parameter (higher orders in q^2) without taking into account nonlocal electrodynamics, the expansion parameter being $\xi_0^2 B 2e/\hbar c$ in both cases.[5] This is why the PAW form for the free energy is not a good approximation. A direct calculation of the $\xi_0^2 2eB/\hbar c$ dependence is a hard counting problem. However, it is clear that the eigenstates of $\hat{L}$ are the Landau states $\langle r | n, k, k' \rangle$, where

$$[\nabla/i + (2e/\hbar c)\vec{A}]^2 | n, k, k' \rangle = [k^2 + (4eB/\hbar c)(n+\tfrac{1}{2})] | n, k, k' \rangle. \tag{4}$$

Using a coherent-state representation the eigenvalues can be calculated as follows: We introduce the operator $a = (\Pi_x - i\Pi_y)(4eB/\hbar c)^{-1/2}$. Then $a, a^\dagger$ are Boson operators obeying $[a, a^\dagger] = 1$. Furthermore, we can write $\exp(-i\vec{r}_1 \cdot \vec{\Pi}) = \exp(-iz_1 \Pi_z - \mu^* a + \mu a^\dagger)$, where $\mu = -\beta^{1/2}(y_1 + ix_1)$ and $\beta = eB/\hbar c$. The operator $\exp(-\mu^* a + \mu a^\dagger)$ is the generator of a translation in the coherent state[6] $|\alpha\rangle = \sum_n \alpha^n \exp(-|\alpha|^2/2)(n!)^{-1/2} \times |n, k, k'\rangle$, i.e.,

$$\exp(-\mu^* a + \mu a^\dagger) | \alpha \rangle = \exp[(\mu\alpha^* - \mu^*\alpha)/2] | \alpha + \mu \rangle. \tag{5}$$

Using Eqs. (3) and (5) and performing the integrals[7] we obtain[8]

$$\hat{L} \langle \vec{r} | n, k, k' \rangle = g_n(k, \beta) \langle \vec{r} | n, k, k' \rangle, \tag{6}$$

where

$$g_n(k, \beta) = N(0)V\{\ln(T/T_c) + [(-1)^n/2] \int_0^\infty e^{-\frac{1}{2}x} L_n(x) K((k^2 + \beta x)^{1/2}) \, dx\}. \tag{7}$$

Equations (6) and (7) imply that the effect of a constant B field is taken care of to all orders if the Gor'kov kernel K for zero field is folded with a function of area unity. If $K(q)$ is approximated by q^2 one recovers the GL form $k^2 + 4\beta(n+\frac{1}{2})$ by using recursion relations for $L_n(x)$ in Eq. (7).

We choose the free-energy functional to be $f(\Delta) = f_0 + V^{-1} \int d^3r \, \Delta^*(\vec{r}) \hat{L} \Delta(\vec{r})$. The functional $f(\Delta)$ has the property that its variation leads to Eq. (1) and it reduces to the GL free energy when $\Delta(\vec{r})$ varies only slightly over distances of the order of $\hbar v_F / 4\pi kT$. Following Schmid[9] the total free energy F can be written in terms of the eigenvalues $g_n(k, \beta)$:

$$F = F_0 + \frac{VkT}{\pi} \frac{eB}{hc} \sum_n \int dk \, \ln[g_n(k, \beta)]. \tag{8}$$

We have also calculated F directly by extending Hubbard's[10] method of expressing the partition function as a functional integral involving a free-energy functional. The results agree with Eq. (8) except for corrections which can be shown to be small for clean superconductors. This will be reported in

detail elsewhere.

We now proceed to calculate the magnetization:

$$M=-\frac{\partial F}{\partial B}=-\frac{VkT}{\pi}\frac{e}{hc}\sum_n\int dk\left\{\ln[g_n(k,\beta)]+\beta\frac{\partial}{\partial\beta}\ln[g_n(k,\beta)]\right\}. \tag{9}$$

Next we note that $\partial g_n/\partial\beta$ can be calculated from Eq. (7) by making a change of variable $y=\beta x$ and differentiating inside the integral sign. Using recursion relations for L_n, we rearrange[11] each term in the series in Eq. (9),

$$M=\frac{VkT}{\pi}\frac{e}{hc}\sum_{n=0}\int dk\frac{n+1}{2}\left[2\ln\left(\frac{g_{n+1}}{g_n}\right)-\frac{g_{n+1}}{g_n}+\frac{g_n}{g_{n+1}}\right]. \tag{10}$$

We now have a recipe such that given an appropriate kernel $K(q)$ for zero field we can obtain the magnetization after some numerical integrations. The kernel we shall use is that given by Werthamer[4]:

$$K(q)=\tilde{K}(y)=\sum_{n=0}^{\infty}\{(n+\tfrac{1}{2})^{-1}-[\tan^{-1}(y/(n+\tfrac{1}{2}))]/y\}, \tag{11}$$

where $y=\alpha_0 q$ and $\alpha_0=\hbar v_F/4\pi kT$. For $y<\frac{1}{2}$, the function $\tilde{K}(y)$ has an expansion in y^2, the lowest-order term being that retained in the familiar GL theory. For large y, $\tilde{K}(y)$ grows logarithmically.

At this point we can understand the universal behavior in the pure limit. The properties of the superconductor enter only through the parameters α_0 and T_c. Introducing the variables $k'=\alpha_0 k$ and $b=\alpha_0^2\beta$, one concludes from Eqs. (7), (10), and (11) that $-MB^{-1/2}/T$ is a universal function of b and $\epsilon=(T-T_c)/T_c$.

Starting from Eq. (11) for $\tilde{K}(y)$ the function $MB^{-1/2}/T$ can be calculated. An interesting approach is to note that in Eq. (7) the x integration only extends out to $x\approx 4n+10$. Furthermore for small b the k integration in Eq. (10) is important only out to $k\approx(bn)^{1/2}$, and the sum over n is important out to $bn\approx 1$. Hence for small b only the part of $\tilde{K}(y)$ for $y\lesssim 1$ is sampled. In this region $\tilde{K}(y)$ can be approximated by a function of the form

$$P=1-\exp(-\gamma y^2), \tag{12}$$

where $\gamma=7\zeta(3)/3=2.8$ is picked to fit the coefficient of y^2 in the Taylor series for $\tilde{K}$. Using this approximate form for $\tilde{K}(y)$, the integrals in Eqs. (7) and (10) can be performed. The field-dependent

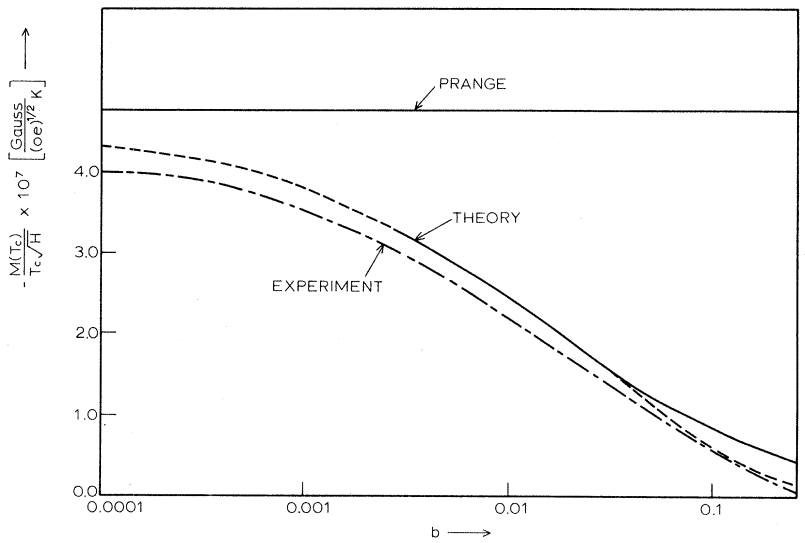

FIG. 1. The field dependence of $-M(T_c)/H^{1/2}T_c$ vs b for pure superconductors. Solid curve, the numerical calculation using $K(q)$ given by Eq. (11); dashed curve, the result using substitute kernel given by Eq. (12); and dash-dot curve, the experimental curve of GBT. In terms of scaling field H_S defined in Eq. (2) of GBT, $b=0.008H/H_S$.

part of the free energy turns out to be convergent,

$$F = F_0' - (VkT\beta/2\pi^2\alpha_0)\sum_{m=1}^{\infty}(\pi/\gamma)^{1/2}m^{-3/2}D_\epsilon{}^m(1-z^m)^{-1}, \quad (13)$$

where $D_\epsilon{}^{-1} = (1+2\gamma b)[1+\ln(1+\epsilon)]$ and $z = (1-2\gamma b)/(1+2\gamma b)$. Note that $2b\gamma = B/H_{c2}(0)$, where $H_{c2}(0)$ is the upper critical field at $T=0$ as calculated from GL theory. The expression for $MB^{-1/2}T$ can easily be calculated from Eq. (13) in the form of an infinite sum. The resulting universal curve for $T=T_c$ is shown in Fig. 1. It is interesting to note that if nonlocal electrodynamics were not taken into account one would have essentially the PAW theory, and with our interpretation of γ one would obtain a curve of roughly similar shape but which is shifted by a factor of about 10 to the right. Nonlocal electrodynamics thus has the effect of suppressing short-wavelength fluctuations somewhat earlier than one expects just from examining the Gor'kov kernel for zero field.

The substitute kernel we used is expected to be very good for relatively small b. We have also carried out a numerical calculation using the exact kernel $\tilde{K}(y)$ for $b \geq 0.003$. This is the solid curve shown in Fig. 1, and it coincides over the range $0.003 < b < 0.05$ with the approximate curve. Since the approximate theory should be best for small b we conclude that it is accurate for all b

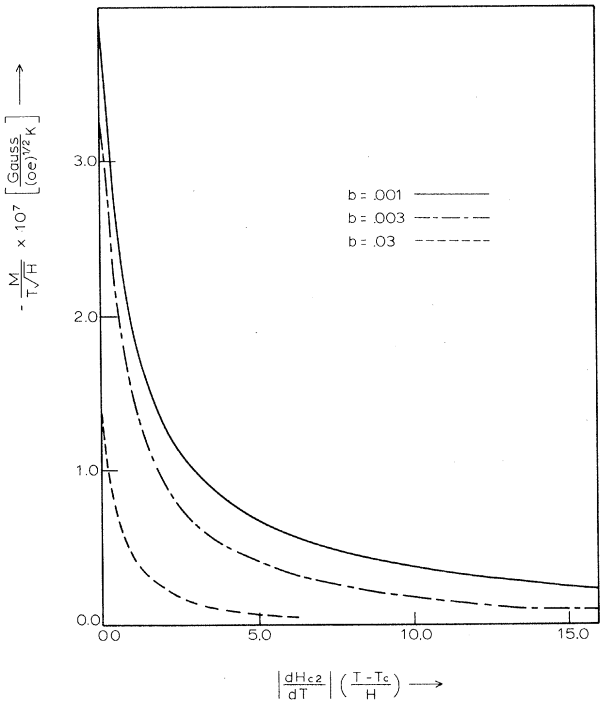

FIG. 2. Temperature dependence of $-M/H^{1/2}T$ for three values of the parameter b.

< 0.05. The experimental points from GBT are also plotted and the agreement is quite satisfactory.

For pure superconductors scaling in the temperature is unnecessary. However, the scaling introduced by Prange[2] is convenient in that the magnetization as a function of temperature varies less rapidly with b. The Prange scaling can be expressed in terms of b and ϵ as $(\partial H_{c2}/\partial T)(T-T_c)/H = 0.177\epsilon/b$. In Fig. 2, $-MB^{1/2}/T$ is plotted as a function of this parameter.[12] Comparison with the data of GBT shows satisfactory agreement.

Finally we would like to point out that in the "dirty" limit ($\xi_0 \gg l$) it has been shown by Maki[13] that what we have referred to as nonlocal electrodynamics is not important for $ql \ll 1$. This partially accounts for the rather drastic increase in the GBT scaling field in the presence of impurity. We have extended the present work to arbitrary scattering length l. This work will be reported in a later publication.

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[1]J. P. Gollub, M. R. Beasley, and M. Tinkham, Phys. Rev. Lett. 25, 1646 (1970).

[2]R. E. Prange, Phys. Rev. B 1, 2349 (1970).

[3]B. R. Patton, V. Ambegaokar, and J. W. Wilkins, Solid State Commun. 7, 1287 (1969).

[4]N. R. Werthamer, in *Superconductivity*, edited by R. D. Parks (Marcel Dekker, New York, 1969).

[5]Physically nonlocal electrodynamics in the present sense means that the phase change given in Eq. (2) is uncertain up to $2eB/\hbar c$ times ξ_0^2, the dimension of the kernel K. Hence nonlocality arises from the strength of the field B and is different from the situation below T_c where nonlocality arises from spatial variation of B.

[6]See R. J. Glauber, Phys. Rev. 131, 2766 (1963).

[7]I. S. Gradshteyn and I. M. Ryzhik, *Tables of Integrals, Sums, Series, and Products*, translation edited by A. Jeffrey (Academic, New York, 1965), p. 847.

[8]The $n=k=k'=0$ version of this equation has been obtained by E. Helfand and N. R. Werthamer, Phys. Rev. 147, 288 (1966).

[9]A. Schmid, Phys. Rev. 180, 527 (1969).

[10]J. Hubbard, Phys. Rev. Lett. 3, 77 (1959); B. Mühl-

schlegel, J. Math. Phys. 3, 522 (1962); T. M. Rice, J. Math. Phys. 8, 158 (1967).

[11]We note that if $v_F q \gg \omega_D$, the exact $N(0)VK(q) \to 1 - N(0)V \ln(T/T_c)$, whereas due to the assumption of a delta-function interaction in the Gor'kov theory the $K(q)$ we introduced does not have this property. Hence the true $g_n(k,\beta)$ approaches unity for large n and k, and the sum and integral in Eq. (9) are convergent. The rearrangement of terms is then valid. The rearrangement that was used here leads to convergence before the part $K(q)$ for $v_F q \gtrsim \omega_D$ becomes important.

[12]We should point out that b has temperature dependence through the parameter $\alpha_0 = \hbar v_F/4\pi kT$. Hence for $\epsilon \simeq 1$, constant b is not the same as constant field B. However, because of the slowly varying nature of the magnetization curve, this adjustment is small under most circumstances.

[13]K. Maki, Physics 1, 21 (1964).

Existence of a Gap in the Electronic Density of States of a Tetrahedrally Bonded Solid of Arbitrary Structure

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Rigorous bounds for the density of electronic states are given for an idealized model of a group-IV semiconductor based on the tight-binding method. These include inner bounds which define a minimum gap in the density of states. The importance of this development lies in its independence of periodicity. It applies not only to crystalline structures made up of tetrahedral bonds but also the random tetrahedral network which recent studies have suggested for amorphous Si and Ge.

Recent experiments[1,2] have shown that amorphous Si and Ge appear to have a gap in the electronic density of states rather similar to that found in the corresponding diamond cubic crystals. This is a surprising result in view of the inevitable high degree of structural disorder, whatever the detailed structure of the amorphous phase is assumed to be. Studies of the radial distribution function[3-5] have in fact suggested a *random tetrahedral network* model for such solids. It seems that infinite networks can be constructed such that nearest neighbors are in perfect tetrahedral coordination (apart from small deviations of bond lengths and angles from ideal values) and yet the distribution of further neighbors is highly disordered. Amorphous semiconductors as prepared in the laboratory are thus considered to have such a perfectly tetrahedrally bonded structure with a distribution of voids[3] or other defects dependent on the preparation.

The occurrence of a band gap in such a system has stimulated widespread theoretical interest but most rigorous results in this area[6,7] have so far been obtained for models in which disorder is imposed on a basic *periodic* system. The relevance of such models to the amorphous semiconductor problem is at best oblique. Here we shall address ourselves to the problem as it stands without using periodicity in any way. A rather idealized tight-binding formulation of the problem will be used, but as far as the structure is concerned, we use only the assumed tetrahedral coordination of nearest neighbors, so that the results obtained apply to diamond, wurtzite, and related crystal structures and also the ideal random-network model for amorphous phases. We shall show that this model indeed entails a gap for all such structures.

We assume a Hamiltonian of the form

$$H = \sum_{i,j} V_1 |\varphi_i\rangle\langle\varphi_j| + \sum_{k,l} V_2 |\varphi_k\rangle\langle\varphi_l|. \quad (1)$$

The functions φ may be visualized as directed hybridized orbitals of the familiar sp^3 type. The first summation is over pairs of different orbitals i and j associated with the same atom. There are of course four per atom and they are assumed to be directed toward the nearest neighbors. The second summation is over pairs of orbitals belonging to nearest neighbors and associated with the same bond (e.g., $1, 1'$ in Fig. 1). To keep things as simple as possible, we treat these orbitals as orthogonal as is commonly done in such models.

Schrödinger's equation gives

$$(H-E)\psi = 0 \quad (2)$$

for an eigenstate of the Hamiltonian, assumed to be expandable in terms of φ_i. A zero density of states at E is to be deduced if either (2) has no solution or, in the limit of an infinite system, the eigenstate ψ cannot be normalized (i.e., it diverges at infinity). Let us then assume the ex-