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Fluctuation-Enhanced Diamagnetism in Superconductors above the Transition Temperature*

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A theory which describes small-amplitude fluctuations of arbitrary spatial extent in a superconductor has been used to calculate the magnetization in a magnetic field above the transition temperature. The calculations agree quite well with the experimental data. Analytical and numerical work indicates that corrections to the electromagnetic properties because of the large size of the fluctuating pairs play an essential role. The effect of impurity scattering has also been included. For moderately small impurity concentrations, agreement is obtained with a semiempirical suggestion due to Gollub, Beasley, and Tinkham, that a universal behavior should occur in terms of an appropriately scaled magnetic field. Deviations from this behavior are predicted at higher impurity concentrations.

I. INTRODUCTION

There has been considerable recent interest in the question of the magnetic properties of superconductors as the temperature is lowered to the transition temperature. The first calculations of this effect by Schmidt[1] and Schmid[2] concentrated on the diamagnetic susceptibility. They obtained the formula

$$\chi = -\frac{T_c}{6\pi}\left(\frac{e}{\hbar c}\right)^2 \xi(T) \ , \qquad (1.1)$$

where $\xi(T)$ is the coherence length, diverging like $(T - T_c)^{-1/2}$. In the first experimental investigation of this prediction,[3] it was pointed out that since the experiments are done in a finite magnetic field (B) which lowers the nucleation temperature of the transition, a generalization of (1.1) is required which would involve $[T - T_{c2}(B)]^{-1/2}$, where T_{c2} is the nucleation temperature. Such a generalization was then provided by Prange[4] as well as in a paper by Patton, Ambegaokar, and Wilkins (PAW).[5] The theories of Refs. 1, 2, and 4 were based on the quadratic part of the usual Ginsburg-Landau functional for the free energy. In PAW attention was focused on the fact that the previously used functional was only valid for long-wavelength fluctuations, whereas fluctuations of all wavelengths contribute to the magnetization at all but very small values of $(T - T_c)$ and B. On the basis of a cursory examination of the microscopic theory, a modified functional was proposed. This modification was based on two hypotheses, one of them correct and the other not. The correct observation was that in the absence of a magnetic field, in which case the free-energy functional can be diagonalized by expanding the order parameter in terms of plane waves, the eigenvalue of the Gorkov kernel, $E(p^2)$, with p the wave number, changes over from a behavior of the form $E(p^2) \propto p^2$ for $p\xi_0 < 1$ (ξ_0 is the temperature-independent coherence length) to $E(p^2) \to 1$ for $v_F p > \omega_D$, where v_F is the Fermi

velocity and ω_D the Debye frequency. A simple function that was both mathematically tractable and able to simulate this crossover was proposed. This part of PAW seems to us to have been good physics. The physical error in Ref. 5 came from the assumption that since in the slow variation limit the inclusion of a field corresponds to the replacement $p^2 \to k^2 + (eB/\hbar c)(4n+2)$, where k is now the wave number in the direction of the field and n the Landau quantum number, a similar replacement is valid in the general form $E(p^2)$. This is in fact not the nature of microscopic generalizations of the Ginsburg-Landau theory to include rapid variations of the order parameter in all but extremely dirty superconductors.[6] More recent experiments[7] have revealed deviations from the Prange calculations in qualitative accord with the predictions of PAW; but they have at the same time demonstrated the quantitative inadequacies of the latter theory.

In this paper we report on analyses and calculations based on the correct microscopic generalized Ginsburg-Landau functional including also the effect of pairs whose total energy is not twice the chemical potential. We find that we can reproduce the main physical effect, which is a fall in the fluctuation enhanced diamagnetism at a field considerably smaller than the scale set by analyses of the PAW type, namely, $(eB/\hbar c)\xi_0^2 \approx 1$. We have done several calculations for the pure system to explore the origins of this effect. Our conclusion is that it is to be understood in terms of the failure of the naive replacement described above. We point out that terms omitted by this replacement play a large role in the fluctuation magnetization because of a cancellation between other superficially larger terms. Using the insight obtained by this work on the pure system, we have also performed approximate calculations of the effect of impurity scattering on the phenomenon. For smallish values of impurity concentration, $\xi_0/v_F\tau < 3$ (where $v_F\tau$ is the mean free path), our calculations agree with a semiempirical suggestion[7] about a universal dependence of the magnetization when considered as a function of an appropriately scaled magnetic field. For higher concentrations we predict deviations which should of course be experimentally tested.

From our work one can conclude that although the detailed shape of the universal curve depends on the explicit form of the field-free generalized Ginsburg-Landau kernel, $E(p^2)$, the only crucial characteristic of this kernel required to explain the experimental data presently available is that its scale be determined by $p\xi_0 = 1$.

Since the completion of the analysis contained in this paper, and after the first convincing numerical results were obtained but before the calculations were entirely finished, we have received preprints of work by Lee and Payne.[8] This work is very similar in spirit and technique to ours, and we find ourselves in rather complete agreement with it. There remain, however, several differences between the two investigations, for instance in the treatment of impurity effects and in the method of obtaining a convergent expression for the magnetization, which are instructive.

In outline, the program of this paper is as follows. In the next section we describe the analysis leading to the generalized Ginsburg-Landau theory and to an expression for the fluctuation-enhanced magnetization. The numerical results are described in Sec. III. Section IV is devoted to a discussion of the effect of impurities. Three appendices contain mathematical details. In particular, Appendix B contains a fairly detailed discussion of the properties of the eigenvalues of the generalized Ginsburg-Landau operator.

II. ANALYSIS

A. Functional Integral for Free Energy

Our starting point is the Hamiltonian for the Gorkov model in the presence of a constant magnetic field. In standard notation we have

$$H = \frac{1}{2m}\int d^3x\, \psi_\sigma^\dagger(\vec{x})\left(\frac{\hbar}{i}\vec{\nabla} - \frac{e}{c}\vec{A}(\vec{x})\right)^2 \psi_\sigma(\vec{x}) - V\int d^3x\, \psi_\uparrow^\dagger(\vec{x})\psi_\downarrow^\dagger(\vec{x})\psi_\downarrow(\vec{x})\psi_\uparrow(\vec{x})$$

$$\equiv H_0 - \int d^3x\, O^\dagger(\vec{x})\, O(\vec{x}) \quad , \tag{2.1}$$

where we have defined $O(x) \equiv \sqrt{V}\psi_\downarrow(\vec{x})\psi_\uparrow(\vec{x})$. As usual, the attractive interaction will be allowed to act only on particles in a shell of width $\hbar\omega_D$ about the Fermi surface to simulate the dynamical overscreening of the electronic charge due to the sympathetic vibrations of the ionic lattice. The thermodynamic properties of (2.1) follow from the partition function

$$Z_G = \mathrm{Tr} e^{-\beta(H-\mu N)} \quad . \tag{2.2}$$

Making the well-known transformation to the interaction representation, one obtains

$$Z_G = \mathrm{Tr}\{T_s \exp[-\beta(H_0 - \mu N)] \times \exp[\int_0^\beta ds \int d^3x\, O^\dagger(\vec{x}, s^+)\, O(\vec{x}, s)]\} \quad , \tag{2.3}$$

where $O(x, s) = e^{sH_0} O(x) e^{-sH_0}$, T_s orders the operators from left to right in order of increasing s, and s^+ means a number infinitesimally larger than s. Under the operator T_s one may freely commute the O's. It is convenient to introduce the Fourier transforms with respect to s $(0 < s < \beta)$

of these operators:

$$O(\vec{x},s)=\frac{1}{\beta}\sum_{m=-\infty}^{\infty}O_m(\vec{x})e^{-2\pi ims/\beta}\ . \tag{2.4}$$

Then we have

$$Z_G=Z_G^0\,\langle T_s\exp[(1/\beta)\textstyle\sum_m\int d^3x\,O_m^\dagger(\vec{x})\,O_m(\vec{x})]\rangle\ , \tag{2.5}$$

where the angular brackets denote an average with respect to the density matrix for the Hamiltonian H_0, in which interactions are neglected but the magnetic field is included, and Z_G^0 is the grand partition function for this Hamiltonian. Now by using the representation (valid under the T_s sign)

$$e^{|O|^2}=\int(d^2\chi/\pi)e^{-|\chi|^2}e^{\chi O^\dagger}e^{\chi^* O} \tag{2.6}$$

for each m and each point $\vec{x}$ one obtains the usual functional integral representation[9]:

$$Z_G/Z_G^0=\Pi_m\int\delta^2\chi_m(\vec{x})\exp[-(1/\beta)\textstyle\sum_m\int d^3x\,|\chi_m(\vec{x})|^2]\times\mathcal{L}(\{\chi_m(\vec{x})\})\ , \tag{2.7}$$

where

$$\mathcal{L}(\{\chi_m(\vec{x})\})\equiv\langle T_s\exp\{(1/\beta)\textstyle\sum_m\int d^3x[\chi_m(\vec{x})\,O_m^\dagger(\vec{x})+\chi_m^*(\vec{x})\,O_m(\vec{x})]\}\rangle\ . \tag{2.8}$$

The functional integral is, as usual, to be thought of as the limit of a multiple integral:

$$\prod_m\delta^2\chi_m(\vec{x})\to\prod_{m,i}\left(\frac{\Delta v_i}{\beta}\right)\frac{d^2\chi_{m,i}}{\pi}\ , \tag{2.9}$$

where i labels discrete volume elements Δv_i. Outside the critical region above the transition temperature we argue that the fluctuations of each χ_m are small. Thus one needs to evaluate the functional $\mathcal{L}$ to terms quadratic in $\chi_m(\vec{x})$. In the diagrammatic expansion[9] for $\mathcal{L}$, this corresponds to keeping the Feynman graph with two vertices, corresponding to $\chi O^\dagger$ and $\chi^* O$. In this approximation, one obtains

$$Z_G/Z_G^0=\Pi_m\int\delta^2\chi_m(\vec{x})\exp[-(1/\beta)\textstyle\sum_m\int d^3x\,d^3x'\times\chi_m^*(\vec{x})K^{(m)}(\vec{x},\vec{x}')\,\chi_m(\vec{x}')]\ , \tag{2.10}$$

where the Hermitian kernel $K^{(m)}(\vec{x},\vec{x}')$ is given in terms of the single-particle Green's function corresponding to the Hamiltonian H_0 as

$$K^{(m)}(\vec{x},\vec{x}')=\delta(\vec{x},\vec{x}')-(v/\beta)\textstyle\sum_l{}'\,G_l(\vec{x},\vec{x}')\times G_{m-l-1}(\vec{x},\vec{x}')\ . \tag{2.11}$$

Above, the prime indicates that one is to sum over the quasienergy indices $\omega_l=(2l+1)\pi/\beta$ subject to the restriction $|\omega_l|<\omega_D$, $|\omega_{m-l-1}|<\omega_D$. This is the natural way, within the spirit of the Gorkov model, to introduce the cutoff referred to below Eq. (2.1).

Equation (2.10) is of course the microscopic version of a generalized Ginsburg-Landau theory for small fluctuations, i.e., up to quadratic terms in the order parameter. However, it includes the full effect of a constant magnetic field and of fluctuations of arbitrarily small spatial extent. These fine general remarks notwithstanding, some further work is required before physical results can be calculated from (2.10). We notice, however, that the functional integral (2.10) is of the Gaussian form beloved by physicists and can be evaluated once the eigenvalues of the kernel (2.11) are known. Thus if one could solve the equation

$$\int K^{(m)}(\vec{x},\vec{x}')\psi_\alpha^m(\vec{x}')\,d^3\vec{x}'=E_\alpha^{(m)}\psi_\alpha^m(\vec{x})\ , \tag{2.12}$$

where α labels the eigenvalues, one could in principle make the expansion $\chi_m(\vec{x})=\sum_\alpha C_\alpha^m\psi_\alpha^m(\vec{x})$ and by a change of integration variables obtain

$$\frac{Z_G}{Z_G^0}=\prod_{m,\alpha}\int\frac{d^2C_\alpha^m}{\beta\pi}\exp\left(-\frac{1}{\beta}\sum_{m,\alpha}E_\alpha^{(m)}|C_\alpha^m|^2\right)=\prod_{m,\alpha}(E_\alpha^{(m)})^{-1}\ . \tag{2.13}$$

The change in free energy due to small fluctuations is thus given in principle by

$$\delta\Omega(\mu,\beta)=\frac{1}{\beta}\sum_{m,\alpha}\ln E_\alpha^{(m)}\ . \tag{2.14}$$

We now turn to the problem of evaluating the eigenvalues.

B. Evaluation of Eigenvalues

To avoid notational complications we shall describe the calculation of the E_α^0. These terms, as we shall see, make the most important contribution to the fluctuation magnetization obtained from (2.13) for not too dirty superconductors. Let us therefore consider Eq. (2.11) with $m=0$. To remove the magnetic field dependence we use the semiclassical approximation, as well as a trick due to Werthamer, [10] and obtain

$$\int d^3x\,K^{(0)}(\vec{x},\vec{x}')\psi_\alpha(\vec{x}')=\psi_\alpha(\vec{x})-(V/\beta)\textstyle\sum_l{}'\int d^3x'\,Q_l(|\vec{x}-\vec{x}'|)\times\exp[-i(\vec{x}-\vec{x}')\vec{\Pi}(\vec{x}_0)]\psi_\alpha(\vec{x}_0)\big|_{\vec{x}_0=\vec{x}}\ , \tag{2.15}$$

where

$$Q_l(\rho)\equiv G_l(\rho;B=0)\,G_{-l-1}(\rho;B=0)=\left(\frac{m}{2\pi\hbar^2\rho}\right)^2\exp\left(\frac{-2|\omega_l|\rho}{\hbar v_F}\right) \tag{2.16}$$

and

$$\vec{\Pi}(\vec{x}) \equiv \left(\frac{1}{i} \vec{\nabla}_{\vec{x}} - \frac{2e}{\hbar c} \vec{A}(\vec{x}) \right) \tag{2.17}$$

The quasienergy ω_l was defined below (2.11) and v_F is the Fermi velocity. The vector potential $\vec{A}$ describing a constant magnetic field, which we take to be in the z direction, may be chosen to have the form $\vec{A}(\vec{x}) = \frac{1}{2}\vec{B} \times \vec{x}$. It is then natural to express the operators $\vec{\Pi}$ in terms of creation and annihilation operators for Landau levels:

$$a \equiv \tfrac{1}{2}\lambda[\Pi_x - i\,\Pi_y], \qquad a^\dagger \equiv \tfrac{1}{2}\lambda[\Pi_x + i\,\Pi_y] \ , \qquad [a, a^\dagger] = 1 \ , \tag{2.18}$$

where $\lambda = (\hbar c/eB)^{1/2}$. The operator Π_z of course commutes with Π_x, Π_y and can be replaced by the wave number in the z direction k. Using spherical coordinates centered at $\vec{x}$ and introducing $\rho \equiv |\vec{x} - \vec{x}'|$ one then finds for the second term on the right-hand side of (2.15) the expression

$$-(V/\beta)\sum_l{}' \int d\Omega \int \rho^2 d\rho\, Q_l(\rho) \exp[-i\rho k \cos\theta] \times \exp[-i(\rho/\lambda)\sin\theta\,(e^{-i\varphi}a + e^{i\varphi}a^\dagger)]\,\psi_\alpha(\vec{x}) \ . \tag{2.19}$$

We now disentangle the noncommuting variables a and $a^\dagger$ by using the relation

$$\exp\{-i(\rho/\lambda)\sin\theta\,[e^{-i\varphi}a + e^{i\varphi}a^\dagger]\} = \exp\{-i(\rho/\lambda)\sin\theta\, e^{i\varphi}a^\dagger\} \exp\{-i(\rho/\lambda)\sin\theta\, e^{-i\varphi}a\} \times \exp\{-(\rho^2/2\lambda^2)\sin^2\theta\} \ . \tag{2.20}$$

Expanding the exponentials involving a and $a^\dagger$ we notice that, because of the integration over the azimuthal angle φ, only terms of the form $(a^\dagger a)^m$ survive. It is thus clear that the Landau levels, which diagonalize the operators $a^\dagger a$ and Π_z, are the required eigenfunctions. The eigenvalues defined in (2.12) are then seen to be given for $m = 0$ by

$$\tilde{E}^{(0)}_{n,k} = 1 - \frac{2\pi V}{\beta} \sum_l{}' \int_{-1}^{1} d(\cos\theta) \int d\rho \times \rho^2 Q_l(\rho) e^{-i\rho k\cos\theta} e^{-(\rho^2/2\lambda^2)\sin^2\theta} \times \sum_{t=0}^{n} \left(\frac{\rho\sin\theta}{\lambda} \right)^{2t} (-1)^t \frac{n!}{(t!)^2(n-t)!} \ , \tag{2.21}$$

where we have replaced α by the quantum numbers for the Landau levels, i.e., $\alpha \to n, k$.

From (2.16) we have for the l sum [restricted as described below (2.11)]:

$$\sum_l{}' Q_l(\rho) = \left(\frac{m}{2\pi\hbar^2\rho} \right)^2 \left(\sinh \frac{2\pi\rho}{\hbar v_F \beta} \right)^{-1} (1 - e^{-2\omega_D \rho/\hbar v_F}) \ . \tag{2.22}$$

The polynomial entering (2.21) is a Laguerre polynomial,

$$L_n(u) = \sum_{t=0}^{n} (-1)^t \frac{n!}{(t!)^2(n-t)!}\, u^t \ . \tag{2.23}$$

Thus, in terms of dimensionless variables defined below, we have

$$\tilde{E}^{(0)}_{n,q} = 1 - N(0)V \int_{-1}^{1} \tfrac{1}{2} d(\cos\theta) \int_0^\infty dx\, (\sinh x)^{-1} \times [(1 - e^{-\Lambda x})\, e^{-iqx\cos\theta} e^{-x^2 b \sin^2\theta/2} \times L_n(x^2 b \sin^2\theta)] \ . \tag{2.24}$$

In writing (2.24) we have scaled lengths with respect to the coherence length $\xi_0 \equiv \hbar v_F \beta/2\pi$, and introduced the dimensionless quantities $q \equiv k\xi_0$ and $b \equiv \xi_0^2/\lambda^2 = (eB/\hbar c)\xi_0^2$. Furthermore, $N(0) \equiv m^2 v_F/2\pi^2\hbar^3$, and $\Lambda \equiv \hbar\omega_D\beta/\pi$ is the cutoff parameter of the BCS theory.

To obtain a law of corresponding states of the type familiar in superconductivity theory it is necessary that physical results should depend only on $\ln\Lambda$; and, indeed, if the dependence on Λ is stronger than this, the Gorkov model Hamiltonian is not justified, since this model does not properly account for the changeover from sympathetic to antisympathetic vibrations of the phonons which occurs when the electron excitation energies are of the order of $\hbar\omega_D$. We shall see that the physical quantity of interest, namely, the magnetization, can indeed be expressed by a law of corresponding states for weak-coupling superconductors in the usual way.

Equation (2.24) may be further simplified by using an integral transformation described in Appendix A:

$$\int_{-1}^{1} \tfrac{1}{2} d(\cos\theta) \int_0^\infty dx\, x^2 F(x)\, e^{-iqx\cos\theta} e^{-x^2 b \sin^2\theta/2} \times L_n(x^2 b \sin^2\theta) = \tfrac{1}{2}(-1)^n \int_0^\infty du\, e^{-u/2} \times L_n(u) H(ub + q^2) \ , \tag{2.25}$$

where

$$H(p^2) = \int_0^\infty dx\, x^2 F(x) \frac{\sin px}{px} = \int \frac{d^3x}{4\pi} F(x) e^{-i\vec{p}\cdot\vec{x}} \ . \tag{2.26}$$

Combining Eqs. (2.24)–(2.26) we obtain

$$\tilde{E}^{(0)}_{n,q} = 1 + (-1)^n \int_0^\infty du\, e^{-u/2} L_n(u) h(ub + q^2) \ , \tag{2.27}$$

where

$$h(p^2) = -\tfrac{1}{2} N(0) V \int_0^\infty dx\, (\sinh x)^{-1} (1 - e^{-\Lambda x}) \frac{\sin px}{px} \ . \tag{2.28}$$

We notice that in the absence of a magnetic field the operators Π_x, Π_y, Π_z would all commute and the eigenvalue would be obtained from (2.15) by Fourier transformation of the kernel (2.22) as

$$\tilde{E}_{\vec{p}}^{(0)} = 1 + 2h(p^2) \ . \tag{2.29}$$

Equation (2.27) thus expresses the way in which the finite-field eigenvalue is obtained from the zero-field one. We notice that the transformation is not simply the naive replacement of p^2 by $q^2 + b(4n+2)$ assumed by PAW. On the other hand it is true that the major contribution to the integral in (2.27) occurs for $u < 4n + \alpha$ where α is a number of the order of 10. Thus, if one considers quantum numbers n, q which are small in the sense $(4bn+q^2)^{1/2} \ll \Lambda$, one only needs the function $h(p^2)$ for $p \ll \Lambda$. In this limit (2.28) may be further simplified by partial integration in a standard way:

$$\frac{2}{N(0)V}\, h(p^2) = \int_0^\infty dx \ln\tanh(\tfrac{1}{2}x)\, \Lambda e^{-\Lambda x} \frac{\sin px}{px} + \int_0^\infty dx \ln\tanh\tfrac{1}{2}x\,(1 - e^{-\Lambda x}) \frac{d}{dx}\left(\frac{\sin px}{px}\right) \ . \tag{2.30}$$

In the first term we introduce a new variable $y = \Lambda x$ and perform the integral in the limit $\Lambda \gg 1$, $\Lambda \gg p$. In the second integral, under the same conditions, we may simply replace Λ by ∞. Thus we obtain

$$2[N(0)\,V]^{-1} h(p^2) \cong \ln\gamma \hbar\omega_D\beta + \int_0^\infty dx\, (\sinh x)^{-1} [1 - \sin px/px] \ , \tag{2.31}$$

where $\gamma = 2e^C/\pi \simeq 1.13$ (C is Euler's constant). The first term in (2.31) may be combined with the 1 in (2.27) using the standard BCS relation $1 = N(0)V \times \ln\gamma \hbar\omega_D\beta_C$ for the transition temperature to obtain[11] for $(nb+q^2)^{1/2} \ll \Lambda$,

$$E_{n,q}^{(0)} = N(0)\,V [\ln T/T_c + (-1)^n \int_0^\infty du\, e^{-u/2} \times L_n(u)\, f(ub+q^2)] \ , \tag{2.32}$$

$$f(p^2) = \frac{1}{2}\int_0^\infty dx\ (\sinh x)^{-1} \left(1 - \frac{\sin px}{px}\right) = \sum_{l=0}^{\infty} \left(\frac{1}{2l+1} - \frac{1}{p}\tan^{-1}\frac{p}{2l+1}\right) \ . \tag{2.33}$$

In Eq. (2.32) all the Λ dependence is contained in T_c as is usual in the theory of weak-coupling superconductors. Let us, however, examine the asymptotic behavior of Eqs. (2.27) and (2.28) and Eqs. (2.32) and (2.33) for large quantum numbers. This behavior is most easily displayed by using a formula derived in Appendix B [Eq. (B7)]:

$$\tfrac{1}{2}(-1)^n \int_0^\infty du\, e^{-u/2}\, L_n(u)\, g(u) \to g(\tilde{u}) + 2\frac{\partial^2}{\partial\tilde{u}^2}\, g(\tilde{u}) + \frac{4}{3}\,\tilde{u}\,\frac{\partial^3}{\partial\tilde{u}^3}\, g(\tilde{u}) + \cdots \Big|_{\tilde{u}=4n+2} \ . \tag{2.34}$$

For large argument $f(p^2)$ behaves like $\frac{1}{2}\ln p$ (Appendix B). Thus we have

$$E_{nq}^{(0)} \to \tfrac{1}{4}\pi N(0)\, V\Lambda[q^2 + (4n+2)b] \tag{2.35}$$

If this behavior continued for arbitrarily large values of the quantum numbers it would follow that the sum of terms with $m = 0$ in (2.14) would diverge like $\int p^2\, dp \ln(\ln p^2)$. On the other hand, whereas the expression (2.27) reduces to (2.35) in the region $1 \ll (4bn+q^2)^{1/2} \ll \Lambda$, for quantum numbers large in the sense $(4bn+q^2)^{1/2} \gg \Lambda$, one finds from the asymptotic behavior of (2.28) [$h(p^2) \propto p^{-1}$] and the first term of (2.34) the behavior

$$\tilde{E}_{nq}^{(0)} \to 1 - \tfrac{1}{4}\pi N(0)\, V\,[q^2 + (4n+2)b]^{-1/2} \ . \tag{2.36}$$

This expression still does not quite lead to a finite value for the free energy,[12] but the divergence is now weaker, i.e., $\int p\, dp$. It is likely that this divergence would be removed by a more careful treatment of electron energies far from the Fermi surface and by the detailed form of the electron-phonon interaction. But we have to realize that within the model being treated here (2.14) is an infinite quantity if the n sums are allowed to run to arbitrarily large values.

The generalization of the above calculation to the eigenvalues for $m \neq 0$ is straightforward and only requires appropriate changes of the range of the sum in (2.11). The result for $m \ll \Lambda$ is

$$\tilde{E}_{nq}^{(m)} = 1 + (-1)^n \int_0^\infty du\, e^{-u/2}\, L_n(u)\, h^{(m)}(ub+q^2) \ , \tag{2.37}$$

where

$$h^{(m)}(p^2) = -N(0)\,V \int_0^\infty dx\, (\sinh x)^{-1}\, e^{-|m|x} \times [1 - e^{-\Lambda x}]\, \frac{\sin px}{px} \ . \tag{2.38}$$

For moderate values of the quantum numbers, namely, in the sense of the inequality given above (2.32), formulas of the form (2.32), (2.33) hold:

$$E_{nq}^{(m)} = N(0)\,V [\ln T/T_c + (-1)^n \int_0^\infty du\, e^{-u/2}\, L_n(u) \times f^{(m)}(ub+q^2)] \ , \tag{2.39}$$

where

$$f^{(m)}(p^2) = \frac{1}{2}\int_0^\infty dx\, (\sinh x)^{-1} \left(1 - e^{-|m|x}\, \frac{\sin px}{px}\right)$$

$$= 2\sum_{l=0}^{\infty}\left[\frac{1}{2l+1} - \frac{1}{p}\tan^{-1}\frac{p}{2l+1+|m|}\right]. \quad (2.40)$$

In further calculations we shall not make use of the explicitly cutoff-dependent eigenvalues $\tilde{E}_{nq}^{(m)}$, i.e., Eqs. (2.27) and (2.37), but will express physical quantities as convergent sums over the $E_{nq}^{(m)}$'s, i.e., Eqs. (2.32) and (2.39), and take care that only moderate values of $(4nb+q^2)^{1/2}$ enter. What is meant by moderate in this context of course depends on the value of Λ, which must be chosen on physical grounds. Taking typical values of ω_D and T_c, we estimate $\Lambda \sim 30$ for weak-coupling superconductors. We shall not consider deviations from a law of corresponding states for strong-coupling superconductors, but methods for studying this question are available.[13]

C. Evaluation of Magnetization

With the knowledge of the eigenvalues $E_{n,q}^{m}$ we return to the expression for the change in free energy due to fluctuations, Eq. (2.14). Taking into account the degeneracy of the Landau levels, we have

$$\delta\Omega = \frac{1}{\beta}(\text{vol})\frac{eB}{\pi\hbar c}\sum_{m=-\infty}^{\infty}\sum_{n=0}^{\infty}\int_{-\infty}^{\infty}\frac{\xi_0 dq}{2\pi}\ln\tilde{E}_{n,q}^{(m)}. \quad (2.41)$$

The magnetization per unit volume is given by the derivative

$$M = -\frac{1}{(\text{vol})}\frac{\partial}{\partial B}(\delta\Omega). \quad (2.42)$$

As was pointed out in Sec. IIB, the contribution to (2.41) from large quantum numbers diverges. To avoid this difficulty we consider the contribution to $\delta\Omega$ of a *fixed number of modes*, assuming and numerically verifying that the modes with lowest quantum numbers contribute most to the magnetization (2.42). We must now be careful about taking the derivative with respect to B because when this quantity is varied the changing degeneracy of the modes requires that we change the (finite) upper limit of the n sum. Thus we must take the derivative in the following way. Let

$$(B_0+\Delta B)N = C, \quad B_0(N+1) = C. \quad (2.43)$$

For $B = B_0$ we sum from $n=0$ to $n=N$, i.e., we count $(N+1)$ modes; for $B = B_0+\Delta B$ we sum from $n=0$ to $n=N-1$, i.e., over N modes. Since the degree of degeneracy is proportional to B_0 in the first case and $B_0 = \Delta B$ in the second, the number of states included in both cases is the same (proportional to C). Thus

$$-\left(\frac{\pi\beta\hbar c}{e}\right)M = \sum_{m=-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{\xi_0 dq}{2\pi}\lim_{N\to\infty}\left[\frac{1}{\Delta B}\left(\sum_{n=0}^{N-1}(B_0+\Delta B)\times \ln E_{nq}^{(m)}(B_0+\Delta B) - \sum_{n=0}^{N} B_0 \ln E_{nq}^{(m)}(B_0)\right)\right]. \quad (2.44)$$

From (2.43) we have

$$(B_0+\Delta B)/\Delta B = N+1, \quad \Delta B/B_0 = 1/N. \quad (2.45)$$

Using these expressions in (2.44) and making a Taylor series expansion of $E_{nq}^{m}(B_0+\Delta B)$ in ΔB one finds

$$M = -\frac{e}{\pi\beta\hbar c}\sum_{m=-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{\xi_0 dq}{2\pi}\lim_{N\to\infty}\sum_{n=0}^{N-1}\left\{(n+1)\ln\frac{E_n}{E_{n+1}} + \frac{B}{E_n}\frac{\partial E_n}{\partial B} + \frac{1}{2N}\left[\frac{B}{E_n}\frac{\partial E_n}{\partial B} + B\frac{\partial}{\partial B}\left(\frac{B}{E_n}\frac{\partial E_n}{\partial B}\right)\right]\right\}, \quad (2.46)$$

where terms of order N^{-2} have been neglected within the square bracket, and the indices m, q omitted. For numerical calculations based on the eigenvalues given in Eqs. (2.32) and (2.39) it is convenient to use difference formulas for the derivatives in (2.46). This can be done by converting the B derivatives into derivatives with respect to the integration variable u and transferring these to act on the function $e^{-u/2}L_n(u)$. Then using a recursion relation [Appendix B, Eq. (B3d)], one obtains for arbitrary fixed m and q the relation

$$2B\frac{\partial E_n}{\partial B} = (n+1)E_{n+1} - E_n - (n-1)E_{n-1}. \quad (2.47)$$

Considerable insight into the nature of (2.46) and into the role of the "nonlocal" terms can be obtained by approximating the eigenvalues in the manner suggested by Eq. (2.34). Using this formula in (2.32) or (2.39) we obtain

$$E_n \approx N(0)V[\ln T/T_c + 2f(\tilde{u}b+q^2) + 4b^2 f''(\tilde{u}b+q^2) + \tfrac{8}{3}b^2(\tilde{u}b)f'''(\tilde{u}b+q^2) + \cdots], \quad (2.48)$$

where the primes mean derivatives with respect to the argument and $\tilde{u} = 4n+2$ as before. For sufficiently small b's one might be tempted to argue that the nonlocal terms, being explicitly proportional to b^2, are of little consequence. It is important, however, to note that large cancellations occur between the first two terms of (2.46). Thus, if one substitutes (2.48) into the first two terms in the curly brackets of (2.46), writes $n+1 = \frac{1}{4}\tilde{u} + \frac{1}{2}$, and makes a Taylor series expansion of E_{n+1} about $\tilde{u}$, one finds that large terms of the form $\tilde{u}bf'$ cancel and that the relevant comparison is then between bf' and $b(\tilde{u}b)f''$. Even for quite small b, these numbers are not of different orders of magnitude because the sum and integral in (2.46) sample values of $ub+q^2 \lesssim 1$.

Another useful observation is to note if one substitutes the first two terms of (2.48), i.e., the local approximation, on the right-hand side of

(2.47) and makes Taylor series expansions, one already finds the contribution of the third term in (2.48), i.e., the first nonlocal correction, to the left-hand side. Since, as is readily verified by explicit substitution, the first nonlocal term makes no contribution to the logarithm in (2.46), we see that the difference formula (2.47) simulates in a nice way the first nonlocal effects. We were led to this observation as a result of numerical work described in Sec. III, and we have then used it to simplify our discussion of impurity effects.

Before turning to these topics, we made contact with known analytical results for *very* small fields and temperatures near T_c. In this region even the values of the argument $(ub+q^2)^{1/2}$ contributing to (2.46) are small and one may use the small argument expansion of $E_{nq}^{(0)}$ (Appendix B)

$$E_{nq}^{(0)} = N(0)V\{\ln T/T_c + \tfrac{2}{3}\lambda(3)[q^2+(4n+2)b]+\cdots\}$$

$$= \tfrac{8}{3}N(0)V\lambda(3)[\alpha+(K^2+n+\tfrac{1}{2})+\cdots], \qquad (2.49)$$

where

$$\alpha \equiv \frac{3\ln(T/T_c)}{8\lambda(3)\,b} \quad , \qquad K \equiv \frac{q}{2\sqrt{b}} \quad ,$$

and

$$\lambda(n) = \sum_{l=0}^{\infty} (2l+1)^{-n} \quad .$$

The $m \neq 0$ terms are ineffective in this limit because they have the same form as (2.49) except for a finite constant in the square bracket. Thus their effect is simulated by (2.49) at a temperature $T \gg T_c$ which is not the limit of interest. Substituting (2.49) into (2.46) we obtain

$$X(b,t) \equiv -\frac{\pi\beta M}{\sqrt{B}}\left(\frac{\hbar c}{e}\right)^{3/2}$$

$$= \int_{-\infty}^{\infty}\frac{dK}{\pi}\lim_{N\to\infty}\sum_{n=0}^{N-1}\left[\frac{n+\frac{1}{2}}{\alpha+K^2+n+\frac{1}{2}}\left(1+\frac{1}{2N}\right)\right.$$

$$\left. -(n+1)\ln\frac{\alpha+K^2+n+\frac{3}{2}}{\alpha+K^2+n+\frac{1}{2}}\right] . \qquad (2.50)$$

The sum corresponding to the second term in the square bracket of (2.46) makes no contribution for large N in this limit, but it can be seen from this expression that the $1/2N$ term is needed to ensure the convergence of the K integral: If the sum is carried out first and the limit $N\to\infty$ taken the result then behaves like K^{-2} for large K. The further evaluation of (2.50) involves some fairly delicate questions of convergence. One can however reduce it to the form

$$X(b,t) = 3\zeta(-\tfrac{1}{2},\ \alpha+\tfrac{1}{2}) - \alpha\zeta(\tfrac{1}{2},\ \alpha+\tfrac{1}{2}) \quad , \qquad (2.51)$$

where $\zeta(n,q)$ is the generalized Riemann ζ function. At $T=T_c(\alpha=0)$ this then reduces to the small-b limit[4,5]:

$$X(b,1) = \frac{3}{4\pi}\left(1-\frac{1}{\sqrt{2}}\right)\zeta\left(\frac{3}{2}\right) \approx 1.826. \qquad (2.52)$$

III. NUMERICAL RESULTS: PURE LIMIT

Several varieties of numerical calculations have been performed to test the ideas of Sec. II and to make comparison with experiment.

Our first calculation was a full numerical calculation based on the eigenvalues given in Eqs. (2.32) and (2.33) and Eqs. (2.39) and (2.41) with the formula (2.46), with (2.47) used to evaluate the derivatives. The eigenvalues were calculated numerically for intermediate values of the quantum numbers. Asymptotic expansions (Appendix B). were used for small and large $q^2+(4n+2)b$. At the chosen crossover points between the integrated values and the expansions the agreement was better than 2×10^{-5}. The values of X [defined in Eq. (2.50)] so obtained are shown in Fig. 1. The contributions of the terms with $m=1$ and $m=2$ were also calculated. They were found to be completely negligible. Calculations of the magnetization at finite temperatures are shown in Fig. 2.

The experimental results of Gollub, Beasley, and Tinkham[7] are also shown in Fig. 1. The falloff for values of b considerably less than 1 is reproduced by our calculation.

We have compared our calculation with the result published by Lee and Payne, [8] and at first seemed to have an apparent inconsistency. For small values of b, Lee and Payne do an approximate calculations in which, in our notation, the function $f(p^2)$ in (2.33) is approximated by

$$\tilde{f}(p^2) = 1 - e^{-\gamma p^2/4} \quad . \qquad (3.1)$$

The parameter γ is chosen so that the coefficients of p^2 in $f(p)$ and $\tilde{f}(p)$ agree. It is easy to verify that this implies that the coefficient of p^4 in $\tilde{f}(p)$ is 0.6 times the corresponding coefficient of $f(p)$. Thus the approximation underestimates the quartic and first nonlocal term and would be expected to deviate from the small-b limit more slowly than the exact calculation. As read from the printed graph, however, the result of Lee and Payne was found to lie *below* our curve for small b. We therefore redid the approximate Lee-Payne calculation taking some care not to subtract large terms and found a slightly different curve which does in fact lie above ours, except at the lowest value of b, for which we expect that because of poor convergence our calculation is too high.

We also recalculated PAW, which corresponds to an exponential approximation like (3.1) but neglecting nonlocal terms, and verified that the

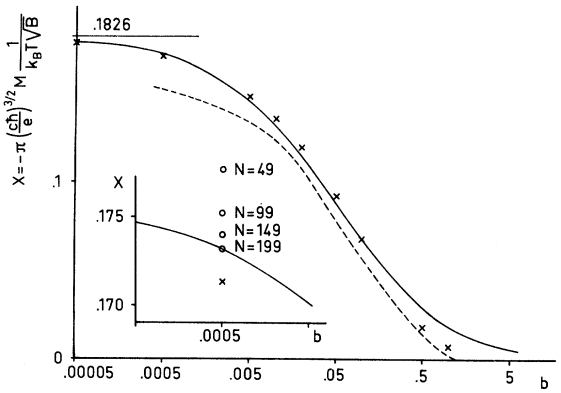

FIG. 1. Magnetization as a function of the magnetic field (solid line) and comparison with the approximate kernel results of Lee and Payne (crosses). The dashed line is the experimental curve of Gollub, Beasley, and Tinkham. The neighborhood of the point $b=0.005$ is shown enlarged ten times with the results of the numerical calculation given for different numbers of terms in the sum over the Landau quantum number.

deviations from the small-b limit set in at a b approximately a factor of 10 higher. The falloff is also more precipitous than in our numerical calculations based on the correct kernel.

To examine the effect of the nonlocal terms we did another calculation, the result of which at first somewhat surprised us. We used the first two terms of Eq. (2.48) in our computer program for evaluating the magnetization and found a curve agreeing quite well with the full numerical calculation shown in Fig. 1. We understood this result as explained in Sec. IIC as due to the simulation of the nonlocal terms by the difference formula (2.47).

To further verify these ideas we did two more calculations. First we put the exponential approximation into our computer program using the difference formula. We obtained a result agreeing rather well with Lee and Payne's approximate calculation. Then we redid the local approximation with the eigenvalues given by the first two terms of Eq. (2.48), this time however evaluating the derivatives explicitly. This complete suppression of nonlocal terms led to a result that fell off slowly with b. All these calculations are represented in Fig. 3.

IV. EFFECTS OF IMPURITIES

The modification of the analysis of Sec. II to include the effects of scattering from impurities is a fairly straightforward excercise in standard techniques. We consider only s-wave scattering. Then for the kernel that enters (2.10) one finds, in the absence of magnetic fields,

$$K^{(m)}(\vec{x},\vec{x}') = \delta(\vec{x},\vec{x}') - (V/\beta)\sum_l{}' \tilde{Q}_l^{(m)}(|\vec{x}-\vec{x}'|)\ , \tag{4.1}$$

where $\tilde{Q}_l$ obeys the integral equation

$$\tilde{Q}_l^{(m)}(|\vec{x}-\vec{x}'|) = Q_l^{(m)}(|\vec{x}-\vec{x}'|) + \frac{\hbar}{2\pi\tau N(0)}\int d^3x_1 Q_l^{(m)}(|\vec{x}-\vec{x}_1|) \times \tilde{Q}_l^{(m)}(|\vec{x}_1-\vec{x}'|)\ . \tag{4.2}$$

Here $Q_l^{(m)}$ is determined by (2.11) with, however, the G's appropriate to the impure system, and τ is the scattering life-time. To include a constant magnetic field one must add phase factors as in (2.15). Then using standard methods and those described in Sec. II one obtains for $m \ll \frac{1}{2}\Lambda$

$$E_{nq}^{(m)} = N(0)V\left\{\ln\frac{T}{T_c} + 2\sum_{l=0}^{\Lambda/2}\left[\frac{1}{2l+1} - \frac{1}{[I(l,n,q,m)]^{-1}-\rho}\right]\right\}\ , \tag{4.3}$$

where

$$I(l,n,q,m) = \tfrac{1}{2}(-1)^n\int_0^\infty du\, e^{-u/2}L_n(u)(ub+q^2)^{-1/2}$$

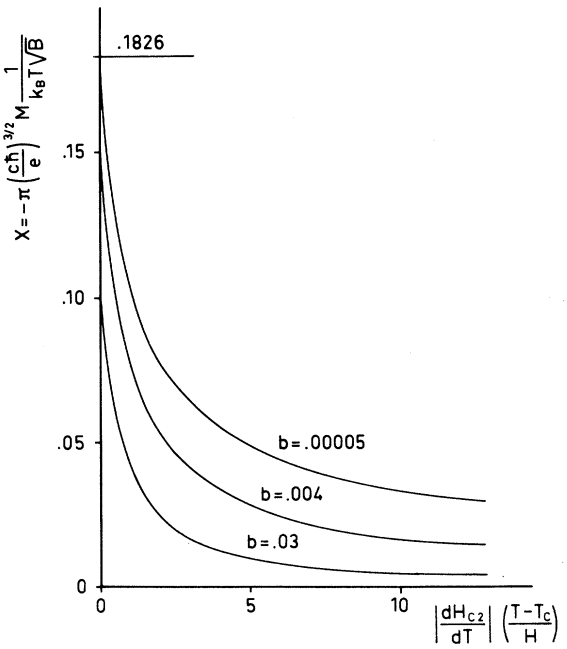

FIG. 2. Magnetization as a function of the temperature for different magnetic fields.

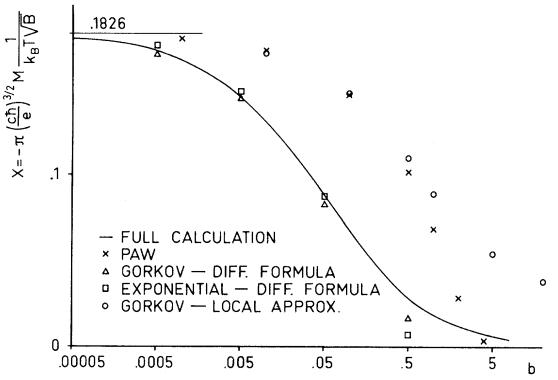

FIG. 3. Illustration of the equivalence of the difference formula for the derivative with respect to the magnetic field and the Laguerre-polynomial integration in producing the early falloff of the magnetization. The exponential and the Gorkov kernel in the local approximation, using the difference formula, are displayed together with the full calculation based on the Gorkov kernel.

$$\times \tan^{-1}\left[\frac{(ub+q^2)^{1/2}}{2l+1+|m|+\rho}\right] . \qquad (4.4)$$

Here the only symbol not previously defined is $\rho \equiv \hbar\beta/2\pi\tau = \xi_0/v_F\tau$, the natural parameter for measuring the impurity concentration. A formula equivalent to Eq. (4.3) is also contained in the most recent preprint we have received from Lee and Payne where it is used for a full numerical calculation. The work described in the last two sections has, however, suggested to us an approximate way of exploring the role of impurity scattering. We neglect nonlocal effects everywhere except that in evaluating derivatives with respect to B we use the difference formula for I:

$$2b\,\frac{\partial I(n)}{\partial b} = (n+1)I(n+1) - I(n) - nI(n-1) . \qquad (4.5)$$

To further simplify the evaluation of the magnetization we make two additional approximations. First, we approximate the local part of I as follows ($\tilde{u} = 4n+2$):

$$I_{\rm loc} = (\tilde{u}b+q^2)^{-1/2}\tan^{-1}\left[\frac{(\tilde{u}b+q^2)^{1/2}}{2l+1+|m|+\rho}\right]$$

$$\approx \frac{1}{2l+1+|m|+\rho}\left[1+\frac{\tilde{u}b+q^2}{3(2l+1+|m|+\rho)^2}\right]^{-1} . \qquad (4.6)$$

Secondly, we take only the $l=0$ term from (4.3). Neither of these approximations qualitatively changes the local part of the kernel. When (4.3) with these approximations is substituted into (2.46), one finds that for large N the terms explicitly proportional to $(2N)^{-1}$ make no contribution to the sum. The integral over q can then be done by the method of residues and the *finite* n sum reduced after considerable fairly tedious algebra to a form involving terms of the type $(A+n)^{-1/2}$. From this sum one has to subtract a term coming from the upper limit of the finite sum. One can verify that the subtraction removes the dependence of the finite sum on its upper limit when this is allowed to become large. The finite-sum form can be readily evaluated by numerical computation. We have done such computations both omitting the $m \neq 0$ terms and summing the first 100 such terms. We notice from (4.6) that the natural measure of the field in the presence of impurity scattering, as far as the eigenvalues are concerned, is $b/(1+\rho)^2$. The results, which are shown in Fig. 4, indicate that if the field is scaled in this way a universal behavior is found for $\rho < 3$. The inset to Fig. 4 indicates the breakdown of universality as ρ is increased. It is interesting that the deviation is in the opposite sense with and without the inclusion of excited pair fluctuations ($m \neq 0$).

It should be apparent that the scaling field we have been led to, namely,

$$b_{\rm scal} = \frac{b}{(1+\rho)^2} = \left(\frac{eB}{\hbar c}\right)\xi^2 , \qquad (4.7)$$

where ξ is the Pippard coherence length

$$\frac{1}{\xi} = \frac{1}{\xi_0} + \frac{1}{v\tau} , \qquad (4.8)$$

is precisely that proposed by Gollub *et al.* on the basis of their experiments. The published data of these authors show an alloy for which they estimate a ρ value of 3.12. This is about the largest value at which we would expect the simple scaling

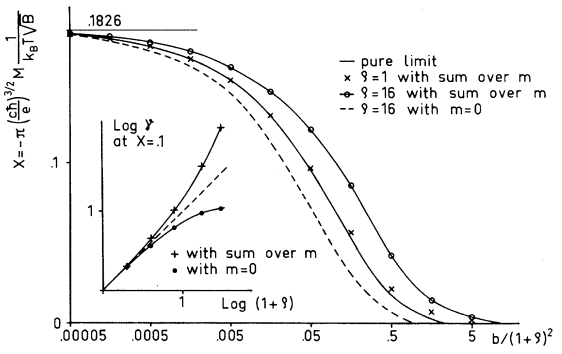

FIG. 4. Effect of impurities. Magnetization as a function of the scaled magnetic field $b' = b/(1+\rho)^2$ for various concentrations of impurities with and without inclusion of the $m \neq 0$ terms. In the lower left-hand corner the logarithm of the scaling factor γ is plotted against $\log_{10}(1+\rho)$. Here γ is the scaling factor, with respect to the singly scaled field $b/(1+\rho)$, which would make the almost congruent magnetization curves fall on each other.

to work.

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APPENDIX A

In this Appendix we wish to prove the integral transformation used in Sec. IIB, namely,

$$\int_{-1}^{1}\frac{d(\cos\theta)}{2}\int_0^\infty d\rho F(\rho)\exp[-i\rho k\cos\theta]\times\exp\left(-\frac{\rho^2}{2\lambda^2}\sin^2\theta\right)L_n\left(\frac{\rho^2\sin^2\theta}{\lambda^2}\right)$$
$$=\tfrac{1}{2}\lambda^2(-1)^n\int_0^\infty dv\times e^{-v\lambda^2/2}L_n(v\lambda^2)H(v+k^2)\ , \quad \text{(A1)}$$

where

$$H(p^2)=\int_0^\infty d\rho F(\rho)\frac{\sin p\rho}{p\rho}\ . \quad \text{(A2)}$$

To prove this we use the following representation for the Laguerre polynomial on the left-hand side of (A1):

$$L_n(x)=\oint\frac{dz}{2\pi i}\frac{1}{z}\left(1+\frac{1}{z}\right)^n e^{-zx}\ . \quad \text{(A3)}$$

Then one can obviously write for the left-hand side of (A1) (call it I)

$$I=\oint\frac{dz}{2\pi i}\frac{1}{z}\left(1+\frac{1}{z}\right)^n B(k^2,\lambda,z)\ , \quad \text{(A4)}$$

where $B(k^2,\lambda,z)$ is an integral over ρ and θ which may be read off from (A1). Now by using

$$\tfrac{1}{2}\sin\theta\, e^{-i\rho k\cos\theta}=(2i\rho k)^{-1}\frac{\partial}{\partial\theta}e^{-i\rho k\cos\theta} \quad \text{(A5)}$$

and integrating by parts one finds that the integral B considered as a function of k^2 obeys the following differential equation:

$$B(k^2,\lambda,z)=H(k^2)+\frac{2(2z+1)}{\lambda^2}\frac{\partial}{\partial k^2}B(k^2,\lambda,z)\ , \quad \text{(A6)}$$

where $H(k^2)$ is given by (A2) and is not a function of λ or z. Furthermore, from the integral representation of B one finds that $B(k^2)\to 0$ as $k^2\to\infty$. The solution of (A6) having this property is

$$B(k^2,\lambda,z)=\frac{\lambda^2}{2(2z+1)}e^{\lambda^2k^2/2(2z+1)}\times\int_{k^2}^\infty dv\, e^{-\lambda^2v/2(2z+1)}H(v)\ . \quad \text{(A7)}$$

Now the required contour integral in z can be done:

$$\oint\frac{dz}{2\pi iz}\left(1+\frac{1}{z}\right)^n e^{-\lambda^2u/2(2z+1)}(2z+1)^{-1}=e^{-\lambda^2u/2}(-1)^nL_n(u\lambda^2)\ . \quad \text{(A8)}$$

By using (A7) and (A8) in (A4) one obtains the right-hand side of (A1), which proves the required identity.

APPENDIX B

In order to develop asymptotic expansions for the eigenvalues $E_{n,q}^{(m)}$ encountered in the text it is necessary to learn to deal with integrals of the form

$$I(\{g\},n)\equiv\int_0^\infty du\, R_n(u)g(u)\ , \quad \text{(B1)}$$

where

$$R_n(u)\equiv(-1)^ne^{-u/2}L_n(u)\ . \quad \text{(B2)}$$

Some properties of these functions are listed below:

$$\int_0^\infty R_n(u)R_m(u)du=\delta_{mn}\ , \quad \text{(B3a)}$$

$$\int_0^\infty R_n(u)du=2\ , \quad \text{(B3b)}$$

$$uR_n=(n+1)R_{n+1}+(2n+1)R_n+nR_{n-1}\ , \quad \text{(B3c)}$$

$$u\frac{dR_n}{du}=-\tfrac{1}{2}(n+1)R_{n+1}-\tfrac{1}{2}R_n+\tfrac{1}{2}nR_{n-1}\ , \quad \text{(B3d)}$$

$$\left(\frac{d}{du}u\frac{d}{du}-\frac{u}{4}\right)R_n(u)=(n+\tfrac{1}{2})R_n(u)\ . \quad \text{(B3e)}$$

We remark that Eq. (2.47) follows in an obvious way from Eq. (B3d).

Before treating the general case (B1) we consider $g(u)=u^p$ where p is an arbitrary integer:

$$I_p(n)=\int_0^\infty du\ R_n(u)u^p=(-1)^{n+p}\left(\frac{\partial}{\partial y}\right)^p\int_0^\infty e^{-xy}L_n(x)dx$$
$$=(-1)^{n+p}\left(\frac{\partial}{\partial y}\right)^p\left(\frac{y-1}{y^{n+1}}\right)\Bigg|_{y=1/2}\ . \quad \text{(B4)}$$

Thus we have for example

$$I_0(n)=2\ ,\quad I_1(n)=2(4n+2)\ ,\quad I_2(n)=2[(4n+2)^2+4]\ ,$$
$$I_3(n)=2[(4n+2)^3+20(4n+2)]\ ,\ldots\ . \quad \text{(B5)}$$

From the last form of (B4) one can derive the more general expression

$$\tfrac{1}{2}I_p(n)=(4n+2)^p+(4n+2)^{p-2}\left[\frac{2p!}{(p-2)!}+\frac{4}{3}\frac{p!}{(p-3)!}\right]$$

$$+(4n+2)^{p-4}\left[6\frac{p!}{(p-4)!}+\frac{88}{15}\frac{p!}{(p-5)!}+\frac{8}{9}\frac{p!}{(p-6)!}\right]$$

$$+\cdots . \qquad \text{(B6)}$$

Thus, by formally decomposing $g(u)$ in (B1) into powers of u, using (B6), and reassembling the series, one obtains

$$\frac{1}{2}\int_0^\infty R_n(u)g(u)=g(\tilde{u})+\left(2\frac{\partial^2}{\partial\tilde{u}^2}+\frac{4}{3}\tilde{u}\frac{\partial^3}{\partial\tilde{u}^3}\right)g(\tilde{u})$$

$$+\left(6\frac{\partial^4}{\partial\tilde{u}^4}+\frac{88}{15}\tilde{u}\frac{\partial^5}{\partial\tilde{u}^5}+\frac{8}{9}\tilde{u}^2\frac{\partial^6}{\partial\tilde{u}^6}\right)g(\tilde{u})+\cdots , \qquad \text{(B7)}$$

where $\tilde{u}=4n+2$.

For $n\geq 20$, we used the first three terms of (B7) for the evaluation of the integrals in (2.37) thus getting asymptotic expansions for $E_{nk}^{(m)}$ from those of $f^{(m)}(p^2)$. The accuracy has been checked by direct numerical integration and was found to be better than 1 part in 10^5 for all relevant b. For $n\geq 20$ and small k^2 (B7) is not accurate enough and the integration was done numerically.

Next we consider the function $f(p^2)$ of (2.33). From the power series of the arctan we obtain

$$f(p^2)=\sum_{n=1}^{\infty}(-1)^{n-1}\frac{\lambda(2n+1)}{2n+1}p^{2n},$$
$$\lambda(2n+1)\equiv\sum_{m=0}^{\infty}(2m+1)^{-2n-1} \qquad \text{(B8a)}$$

converging for $p^2<1$. For numerical computations it is convenient to keep the first few arctan unexpanded. We use

$$f(p^2)=\sum_{l=0}^{L-1}\left(\frac{1}{2l+1}-\frac{1}{p}\tan^{-1}\frac{p}{2l+1}\right)$$

$$+\sum_{n=1}^{\infty}(-1)^{n+1}\frac{C_L(n)}{2n+1}p^{2n}. \qquad \text{(B8b)}$$

This expansion has the radius of convergence $p^2=(2L+1)^2$, and the coefficients

$$C_L(n)=\lambda(2n+1)-\sum_{l=0}^{L-1}(2l+1)^{-2n-1}$$

are very rapidly decreasing with n. In particular[14]

$$C_2(1)=1.476\,275\,32\times10^{-2},$$
$$C_2(2)=4.085\,364\,58\times10^{-4},$$
$$C_2(3)=1.430\,128\,16\times10^{-5},$$
$$C_2(4)=5.399\,204\,25\times10^{-7},$$
$$C_2(5)=2.102\,182\,14\times10^{-8},$$
$$C_2(6)=8.299\,475\,02\times10^{-10}$$

were used for numerical integration.

For large values of p^2, we used[15]

$$f(p^2)=(1/p)\,\mathrm{Im}\ln\Gamma(\tfrac{1}{2}+\tfrac{1}{2}ip\,|-\tfrac{1}{2}\psi(\tfrac{1}{2}), \qquad \text{(B8c)}$$

which yields the asymptotic formula

$$f(p^2)=\tfrac{1}{4}\ln p^2+\sum_{n=0}^{\infty}\frac{A(n)}{p^{2n}}, \qquad \text{(B8d)}$$
$$A(0)=\tfrac{1}{2}(C+\ln 2-1)=0.135\,181\,42,$$
$$A(1)=\tfrac{1}{12},\ A(2)=\tfrac{7}{360},\ A_3=\tfrac{31}{1260},\ A_4=\tfrac{127}{1680}.$$

For numerical integration we used (B8b) for $p^2<8$ and (B8d) for $p^2\geq 8$.

For $m\neq 0$ similar formulas can be derived, starting from

$$f^{(m)}(p^2)=\sum_{l=0}^{\infty}\left(\frac{1}{2l+1}-\frac{1}{p}\tan^{-1}\frac{p}{2l+|m|+1}\right).$$

Combining the first three terms of (B7) and (B8b) or (B8d) we got asymptotic expressions for $E_{n,q}$; for instance, for

$$p^2=q^2+b(4n+2)\geq 15(1+2.5b)$$

we used

$$E_{n,q}^{(0)}=0.270\,362\,84+\tfrac{1}{2}\ln p^2+\frac{1}{6p^2}$$
$$+\left(\frac{7}{180}-b^2\right)\frac{1}{p^4}+\frac{4b^2}{3}\frac{b(4n+2)}{p^6}$$
$$+\left(\frac{31}{630}+\frac{2b^2}{3}\right)\frac{1}{p^6}-\frac{4b^2}{3}\frac{b(4n+2)}{p^8}. \qquad \text{(B9)}$$

APPENDIX C

When we derived our expression for the magnetization

$$X\sim\int_{-q_{\max}}^{q_{\max}}dq\left\{\sum_{n=0}^{N-1}\left[\frac{(n+1)E_{n+1}-E_n-nE_{n-1}}{E_n}\right.\right.$$
$$\left.\left.\times\left(1+\frac{1}{2N}\right)+2\ln E_n\right]-2N\ln E_n\right\} \qquad \text{(C1)}$$

we took into account a finite number of fluctuation modes only, thereby postponing all convergence problems which are connected with the ultraviolet divergence of the fluctuation free energy within our approximations. We conjecture that this divergence would in fact be removed by a more detailed treatment of the electron-phonon interaction and other limiting effects, and that it is not a genuine failure of statistics.

We should like to emphasize, however, that the large N limit of (C1) exists with the Ginsburg-Landau eigenvalues E_{nq}, in which case the $1/2N$ term is not negligible as well as with the Gorkov eigenvalues or with those of (2.27). In all these cases the keeping of the $N\ln E_N$ term is essential in assuring the existence of the limit.

To take this limit with the Gorkov eigenvalues is physically justified only if almost all contributions come from a $q \sim N$ region for which $v_F q < \omega_D$. We checked this numerically and found that for $N = 30$ and corresponding $q^2 < q_{max}^2 = 8bN$, accuracy within a few percent of the final limit was obtained.

While it is of no consequence for the convergence in the mathematical sense, it is important for this physically required (and computationally convenient) fast convergence to keep *all* $1/2N$ terms in the expression for X.

Finally, we can use (C1) to justify the rearrangement by which Lee and Payne[8] make their divergent sum convergent. The $N \ln E_n$ term from the "b derivative" of the upper limit of the sum is again essential. We rearrange the finite sum into

$$\sum_{0}^{N-1} (n+1)\left(\frac{E_{n+1}}{E_n} - \frac{E_n}{E_{n+1}} - \ln\frac{E_n}{E_{n+1}}\right) \tag{C2a}$$

$$-N\left(\frac{E_n - E_{n-1}}{E_n}\right) + \frac{1}{2N}\sum_{n=0}^{N-1} \frac{(n+1)E_{n+1} - E_n - nE_{n-1}}{E_n}\,, \tag{C2b}$$

where (C2a) is the convergent expression used by Lee and Payne, (C2b) vanishes for $N \to \infty$ if E_n increases no more strongly than linearly with n.

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Spin-Orbit Effects in Alloys in Porous Glass with H_{c2} above 200 kG

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The critical field H_{c2} was measured for a Pb–40 at.%–Bi alloy in porous-glass samples with pore diameters in the range 20–60 Å. Werthamer *et al.* have calculated H_{c2}, including the effect of electron paramagnetism and spin-orbit scattering. This theory fits the data for the 32- and 60-Å samples, giving the spin-flip scattering length of the order of the grain diameter. For the 20-Å samples the theory does not fit the results. It is suggested that the behavior of this sample is largely "one dimensional."

INTRODUCTION

This paper describes the results of measurements of H_{c2} performed on samples of porous glass containing Pb–40 at.% Bi. Electron-microscope pictures show that the metal in the glass has a grainy appearance.[1] Earlier measurements on pure elements indicate that the grains are weakly coupled.[2] Transmission probabilities τ for transmission of electrons through the intergranular weak link are in the range 0.1–0.03. The actual value of τ is characteristic of the metal, for lead $\tau \sim 0.1$.[2] The electron mean free path l in such a system is $l = d\tau$ where d is the grain diameter. Typical values of l are less than the interatomic spacing.[2] Each glass has a characteristic value