Generalized Ginzburg-Landau Theory of Superconducting Alloys*

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The Ginzburg-Landau-Gorkov theory of superconducting alloys is generalized to arbitrary temperatures and magnitudes of the gap parameter $\Delta=|\Delta|\exp i\varphi$. However, the theory is still based on the assumption that the integral equation for the Green's function can be solved in powers of $\mathbf{v}_s=(2e\mathbf{A}-\nabla\varphi)/2m$ and successively higher space derivatives of $|\Delta|$ and $\mathbf{v}_s$. The averaging over the positions of the impurities is carried out by means of the ladder-diagram technique developed by Abrikosov and Gorkov. The results are presented in terms of the free-energy functional. The form of this functional is found to be close to that proposed by Ginzburg-Landau if $|\Delta|$ is close to the BCS gap $\Delta_{\mathrm{BCS}}(T)$ and varies slowly in space. A comparison of the magnitudes of the fourth- and second-order terms in the free-energy functional shows that the local theory is valid if: (1) $|\Delta|$ and $\mathbf{v}_S$ vary slowly over distances ξ; and (2) $\lambda_S=h/2mv_S>\xi$. In the "dirty" limit ($l<<\xi_0$) the length ξ ranges from about $(l\xi_0)^{1/2}$ to $(T_c/T)(l\xi_0)^{1/2}$ as $|\Delta|$ varies from $\Delta_{\mathrm{BCS}}(T)$ to zero.

1. INTRODUCTION

THE Gorkov version[1,2] of the Ginzburg-Landau (GL) equations[3] is applicable only in a very narrow temperature region near T_c since the derivation is based on the assumptions that the static magnetic field and the order parameter Δ vary slowly with position, and further, that the energy gap $|\Delta|$ is small compared to T_c. The Ginzburg-Landau-Gorkov (GLG) equations for the pure superconductor have been generalized by Werthamer[4] and the author[5] to arbitrary temperatures and values of $|\Delta|$ between $\Delta_{\mathrm{BCS}}(T)$ and zero, but the equations are still based on the assumption that an expansion in powers of $\mathbf{v}_s=(2e\mathbf{A}-\nabla\varphi)/2m$ (where $\mathbf{A}$ is the vector potential and φ the phase of Δ) and successively higher space derivatives of $|\Delta|$ and $\mathbf{v}_s$ converges rapidly. A criterion for the validity of the generalized GLG theory has been obtained by comparing the magnitudes of the gauge-invariant fourth- and second-order terms in the free-energy functional.[6]

The purpose of this work is to determine the way in which the generalized GLG equations are modified as the mean free path l becomes finite. One expects that the equations describing the alloy have a much wider range of applicability than those for the pure superconductor, since for a sufficiently short mean free path l the electrodynamics is local over the whole temperature range. Werthamer[7] has solved part of the problem by relating one of the coefficients in the free-energy functional to the current expression obtained by Abrikosov and Gorkov[8] for superconducting alloys in the London limit.

The calculation is performed in analogy with Gorkov's derivation of the GL equations near T_c in the presence of dilute random impurity centers.[2] The essence of the method is to average the gap equation, and the current expression, over the position of each impurity center. The diagram technique of Abrikosov and Gorkov[8] is used to calculate such an average of an expression containing several Green's functions. The main difference between Gorkov's and our problem is that the normal-state Green's functions are replaced by Nambu matrix Green's functions, and accordingly, scalar vertex corrections by matrix vertex corrections.

We calculate also the predominant gauge invariant contributions of the fourth order to the free energy functional, and by comparison with the second-order contributions we obtain the conditions for the validity of the local theory of superconducting alloys.

2. THE DIFFERENTIAL EQUATION FOR THE GAP

In this section we are concerned with the derivation of the differential equation for Δ. From the results obtained for the pure superconductor[4,6] it is clear that it suffices to determine the coefficients of $\nabla^2\Delta$, A^2, and Δ. Then the contribution proportional to $\nabla^2\Delta$ has to be divided into two parts such that one part belongs to the term $(\nabla-2ie\mathbf{A})^2\Delta$, and the other to the term $(\nabla^2|\Delta|^2)\Delta$. Similarly, the contribution proportional to A^2 has to be divided so that one part belongs to the first term cited above, and the other to the term $\Delta^*[(\nabla-2ie\mathbf{A})\Delta]^2$. In the "clean" limit the coefficients must reduce to the results obtained previously.

First we concentrate on the coefficient of $\nabla^2\Delta$. For simplicity we shall assume that Δ is real. Then we find with the help of the general method developed in Ref. 5 that this coefficient is proportional to a quantity c which

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[1] L. P. Gorkov, Zh. Eksperim. i Teor. Fiz. **36**, 1918 (1959) [English transl.: Soviet Phys.—JETP **9**, 1364 (1959)].

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[5] L. Tewordt, Phys. Rev. **132**, 595 (1963).

[6] L. Tewordt, Z. Physik **180**, 385 (1964).

[7] N. R. Werthamer, Rev. Mod. Phys. **36**, 292 (1964).

[8] For example, Chap. 7 of A. A. Abrikosov, L. P. Gorkov, and I. E. Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Mechanics*, translation by R. A. Silvermann (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

can be written as

$$c=\sum_n \nabla_q^2 \int d^3p \tfrac{1}{2}\mathrm{Tr}\langle \bar{G}(\mathbf{p}-\mathbf{q})\tau_1 \bar{G}(\mathbf{p}+\mathbf{q})\tau_1\rangle_{\mathrm{av}}|_{\mathbf{q}=0}. \quad (1)$$

Here $\bar{G}(\mathbf{p})$ denotes the Nambu matrix Green's function, averaged over the positions of the impurities, i.e.,

$$\bar{G}(\mathbf{p})=-(i\tilde{\omega}+\epsilon_p\tau_3+\tilde{\Delta}\tau_1)/(\tilde{\omega}^2+\epsilon_p^2+\tilde{\Delta}^2), \quad (2)$$

where $\tilde{\omega}=\omega\eta$, $\tilde{\Delta}=\Delta\eta$, $\omega=(2n+1)\pi\beta^{-1}$, Δ is the gap parameter at position $\mathbf{r}$, $\eta=\{1+[2\tau(\omega^2+\Delta^2)^{1/2}]^{-1}\}$, τ is the collision time, $\epsilon_p=(p^2/2m)-\mu$, and τ_i are the Pauli spin matrices. In the ladder approximation the average of the product of two $\bar{G}$'s occuring in Eq. (1) is determined by

$$\langle \bar{G}(\mathbf{p}-\mathbf{q})\tau_1\bar{G}(\mathbf{p}+\mathbf{q})\rangle_{\mathrm{av}} = \bar{G}(\mathbf{p}-\mathbf{q})[\tau_1+\tau_3\Lambda(\mathbf{p};\mathbf{q})\tau_3]\bar{G}(\mathbf{p}+\mathbf{q}), \quad (3)$$

where the vertex correction Λ satisfies the integral equation

$$\Lambda(\mathbf{p};\mathbf{q})=n\int \frac{d^2p'}{(2\pi)^3}|u(\mathbf{p}-\mathbf{p}')|^2\bar{G}(\mathbf{p}'-\mathbf{q}) \times[\tau_1+\tau_3\Lambda(\mathbf{p}';\mathbf{q})\tau_3]\bar{G}(\mathbf{p}'+\mathbf{q}). \quad (4)$$

The quantity $u(\mathbf{q})$ is the Fourier component of the impurity potential, and n is the impurity concentration. The matrix Λ is decomposed in Nambu space

$$\Lambda=\Lambda_0 1+\Lambda_1\tau_1+\Lambda_2\tau_2 \quad (5)$$

(the τ_3 component turns out to be zero), and accordingly also Eq. (4). The integrations over ϵ_p' can be performed easily in the resulting equations. One sees then immediately that the equation for Λ_0 goes over into the equation for Λ_1 if one sets

$$\Lambda_0(\mathbf{p};\mathbf{q})=(\Delta/i\omega)\Lambda_1(\mathbf{p};\mathbf{q}). \quad (6)$$

In this way one obtains two coupled equations for Λ_1 and Λ_2 which are given by

$$\Lambda_1(\mathbf{p};\mathbf{q})=nN(0)\int \frac{d\Omega\mathbf{p}'|u(\mathbf{p}-\mathbf{p}')|^2}{4\eta(\omega^2+\Delta^2)^{1/2}}\left[\omega^2+\Delta^2+\left(\frac{\mathbf{p}'\cdot\mathbf{q}}{m\eta}\right)^2\right]^{-1}\left[-\omega^2+(\omega^2+\Delta^2)\Lambda_1(\mathbf{p}';\mathbf{q})+\omega\left(\frac{\mathbf{p}'\cdot\mathbf{q}}{m\eta}\right)\Lambda_2(\mathbf{p}';\mathbf{q})\right], \quad (7)$$

$$\Lambda_2(\mathbf{p};\mathbf{q})=nN(0)\int \frac{d\Omega\mathbf{p}'|u(\mathbf{p}-\mathbf{p}')|^2}{4\eta(\omega^2+\Delta^2)^{1/2}}\left[\omega^2+\Delta^2+\left(\frac{\mathbf{p}'\cdot\mathbf{q}}{m\eta}\right)^2\right]^{-1} \times\left[\omega\left(\frac{\mathbf{p}'\cdot\mathbf{q}}{m\eta}\right)-\frac{(\omega^2+\Delta^2)}{\omega}\left(\frac{\mathbf{p}'\cdot\mathbf{q}}{m\eta}\right)\Lambda_1(\mathbf{p}';\mathbf{q})+(\omega^2+\Delta^2)\Lambda_2(\mathbf{p}';\mathbf{q})\right]. \quad (8)$$

Here $N(0)$ denotes the density of states at the Fermi surface, $d\Omega\mathbf{p}'$ is the solid angle element in the direction of $\mathbf{p}'$, and $p=p'=p_F$. Inserting Eqs. (3) and (5) into Eq. (1) and carrying out the traces and integrations over ϵ_p, one obtains

$$c=\frac{N(0)}{4\pi}\sum_n \nabla_q^2\int \frac{d\Omega\mathbf{p}}{\eta(\omega^2+\Delta^2)^{1/2}}\left[\omega^2+\Delta^2+\left(\frac{\mathbf{p}\cdot\mathbf{q}}{m\eta}\right)^2\right]^{-1}\left[-\omega^2+(\omega^2+\Delta^2)\Lambda_1(\mathbf{p};\mathbf{q})+\omega\left(\frac{\mathbf{p}\cdot\mathbf{q}}{m\eta}\right)\Lambda_2(\mathbf{p};\mathbf{q})\right]\Big/_{\mathbf{q}=0}. \quad (9)$$

If we carry out the differentiations with respect to $\mathbf{q}$ in Eq. (9) we encounter the quantities $(\Lambda_i)_{\mathbf{q}=0}$, $(\nabla_q\Lambda_i)_{\mathbf{q}=0}$, and $(\nabla^2\Lambda_i)_{\mathbf{q}=0}$. These quantities can be determined from Eqs. (7) and (8). In this way we obtain from Eq. (9) the final result

$$c=\frac{2p_F^2N(0)}{m^2}\left[\sum_{n=0}^{\infty}\frac{\pi}{(\omega^2+\Delta^2)^{3/2}\eta_{\mathrm{tr}}} -\sum_{n=0}^{\infty}\frac{\pi\Delta^2}{(\omega^2+\Delta^2)^{5/2}\eta_{\mathrm{tr}}}\right]. \quad (10)$$

The quantity η_{tr} differs from η in that τ is replaced by the transport collision time τ_{tr}. Note that τ_{tr} arises from the vertex correction $\Lambda_2\tau_2$ which takes into account essentially the p-wave scattering by the impurity. In the limit $\tau_{\mathrm{tr}}\to\infty$, or $\eta_{\mathrm{tr}}\to 1$, the first and second terms in brackets reduce to the functions $\beta^3 g$ and $(\frac{2}{3})\Delta^2\beta^5 g'$, respectively, where $g=g_1'$. The function g_1 has been introduced by Bardeen,[9] and the primes denote derivatives with respect to $|\Delta\beta|^2$.

Now we determine the coefficient of A_iA_j. With the help of the general method developed in Ref. 5 we find that this coefficient is proportional to a quantity a_{ij} which can be written as

$$a_{ij}=\sum_n\int d^3p\tfrac{1}{2}\mathrm{Tr}\langle \bar{G}(\mathbf{p})p_i\bar{G}(\mathbf{p})p_j\bar{G}(\mathbf{p})\tau_1\rangle_{\mathrm{av}}. \quad (11)$$

In calculating the average of the product of three $\bar{G}$'s one has first to take into account the vertex corrections which arise from impurity interaction lines of the ladder type "bridging" each vertex p_i and p_j separately, and second to consider interaction lines "bridging" both vertices p_i and p_j simultaneously. However, one recognizes that the latter contribution is equivalent to a

[9] J. Bardeen, Rev. Mod. Phys. 34, 667 (1962).

contribution due to interaction lines "bridging" the vertex τ_1. The vertex correction at a vertex p_i has been calculated previously by Abrikosov and Gorkov.[8] In matrix notation the result is that the matrix p_i 1 is replaced by

$$p_i 1 \rightarrow p_i[(1+\Lambda_0)1-\Lambda_1\tau_1], \tag{12}$$

where

$$\Lambda_0=[\Delta^2/(\omega^2+\Delta^2)][(\eta/\eta_{tr})-1]; \quad \Lambda_1=(i\omega/\Delta)\Lambda_0. \tag{13}$$

For the vertex τ_1 we find that it is replaced by

$$\tau_1 \rightarrow (1-\Lambda_1')\tau_1+\Lambda_0' 1, \tag{14}$$

where

$$\Lambda_1'=\frac{\omega^2}{(\omega^2+\Delta^2)}(1-\eta); \quad \Lambda_0'=\frac{\Delta}{i\omega}\Lambda_1'. \tag{15}$$

If one inserts the corrected vertices into Eq. (11) and carries out the traces and the integrations over ϵ_p, one obtains the result

$$a_{ij}=\langle p_i p_j\rangle_F N(0)\left[\sum_{n=0}^{\infty}\frac{\pi\Delta}{(\omega^2+\Delta^2)^{3/2}\eta_{tr}} -\sum_{n=0}^{\infty}\frac{\pi\Delta^3}{(\omega^2+\Delta^2)^{5/2}\eta_{tr}}\left(1+\frac{1}{2\eta_{tr}}\right)\right]. \tag{16}$$

Here $\langle p_i p_j\rangle_F$ means the average of $p_i p_j$ over the Fermi surface. In the limit $\eta_{tr}\rightarrow 1$ the first and second terms inside the brackets of Eq. (16) reduce to $\Delta\beta^3 g$ and $\Delta^3\beta^5 g'$, respectively.

Finally, we remark that the coefficient of Δ in the gap equation is the same as for the pure superconductor since the following equality holds

$$\sum_n \int d^3p \tfrac{1}{2}\mathrm{Tr}(\bar{G}\tau_1)=\sum_n \int d^3p \tfrac{1}{2}\mathrm{Tr}(G\tau_1). \tag{17}$$

3. THE FREE-ENERGY FUNCTIONAL

The results obtained in the previous section for the coefficients of $\nabla^2\Delta$, A^2, and Δ suffice to construct the complete differential equation for the gap parameter. It is also possible to construct the corresponding free-energy functional $F\{\Delta,\Delta^*,\mathbf{A}\}$. This follows essentially from the fact that the coefficient of Δ^3 in the expression for a_{ij} [Eq. (16)] is equal to the derivative, with respect to Δ^2, of the coefficient of Δ. The result is

$$F=\int d^3r\left\{\frac{(\mathbf{H}-\mathbf{H}_a)^2}{8\pi}+N(0)\left[w(|\Delta\beta|^2) +\tfrac{1}{6}(v_F\beta)^2 g_\tau(|\Delta\beta|^2)|(\nabla-2ie\mathbf{A})\Delta|^2 +\frac{1}{36}(v_F\beta)^2\beta^2 f_\tau(|\Delta\beta|^2)(\nabla|\Delta|^2)^2\right]\right\}, \tag{18}$$

where

$$g_\tau(|\Delta\beta|^2)=\sum_{n=0}^{\infty}\frac{\pi}{[(\omega\beta)^2+|\Delta\beta|^2]^{3/2}\eta_{tr}}, \tag{19}$$

$$f_\tau(|\Delta\beta|^2)=-\frac{3}{2}\sum_{n=0}^{\infty}\frac{\pi}{[(\omega\beta)^2+|\Delta\beta|^2]^{5/2}\eta_{tr}}. \tag{20}$$

The function w in Eq. (18) can be obtained by a quadrature from the function g_1 (see Ref. 6). In the limit $\tau_{tr}\rightarrow\infty$ the function g_τ reduces to g, and f_τ to g'. However, in general, f_τ is different from g_τ'.

Requiring that the functional F be stationary with respect to both Δ^* and $\mathbf{A}$ leads to the gap and the Maxwell equations. Since the coefficient of $\mathbf{A}$ in the latter equation determines the London penetration depth λ_T of weak fields at temperature T, the following relation must hold:

$$\lambda_T^{-2}=2\lambda_L^{-2}|\Delta\beta|^2 g_\tau(|\Delta\beta|^2)|_{\Delta=\Delta_{BCS}}, \tag{21}$$

where $\lambda_L=(4\pi Ne^2/m)^{-1/2}$. In fact, this result agrees with that obtained formerly by Abrikosov and Gorkov.[8] On the other hand, Werthamer[7] has used this relationship to determine g_τ from Abrikosov and Gorkov's expression.

In the limiting case $l\ll\xi_0$, we can easily sum the series over n in Eqs. (19) and (20). The results are

$$g_{\mathrm{dirty}}=\frac{\pi}{4}(\tau_{tr}/\beta)[\tanh(\tfrac{1}{2}|\Delta\beta|)/\tfrac{1}{2}|\Delta\beta|], \tag{22}$$

$$f_{\mathrm{dirty}}=\frac{3}{2}g'_{\mathrm{dirty}}=\frac{3\pi}{64}\left(\frac{\tau_{tr}}{\beta}\right)\left(\frac{1}{x}\frac{d}{dx}\frac{\tanh x}{x}\right)_{x=\frac{1}{2}|\Delta\beta|}. \tag{23}$$

For applications of the free-energy functional it is convenient to measure lengths in units λ_T and to introduce reduced variables

$$\psi=\Delta/\Delta_{BCS}; \quad \mathbf{h}=\mathbf{H}/\sqrt{2}H_c; \quad \mathbf{a}=\mathbf{A}/\sqrt{2}\lambda_T H_c. \tag{24}$$

Inserting further the expressions (22) and (23) into Eq. (18), and making use of the relation (21) and the equality $H_c^2/8\pi=-N(0)w(|\Delta_{BCS}\beta|^2)$, we obtain

$$F_{\mathrm{dirty}}=\frac{H_c^2}{4\pi}\int d^3r\left\{(\mathbf{h}-\mathbf{h}_a)^2-\frac{1}{2}\frac{w(\chi_0^2|\psi|^2)}{w(\chi_0^2)} +\frac{\tanh(\frac{1}{2}\chi_0|\psi|)}{|\psi|\tanh(\frac{1}{2}\chi_0)}|(\kappa^{-1}\nabla-i\mathbf{a})\psi|^2 +\frac{\chi_0^3}{64\tanh(\frac{1}{2}\chi_0)}\left(\frac{1}{x}\frac{d}{dx}\frac{\tanh x}{x}\right)_{x=\frac{1}{2}\chi_0|\psi|}(\kappa^{-1}\nabla|\psi|^2)^2\right\},$$

where $\kappa=\sqrt{2}2e\lambda_T^2 H_c(T)$ and $\chi_0=\Delta_{BCS}(T)\beta$.

4. TERMS OF THE FOURTH ORDER

In Ref. 6 we have determined the complete set of gauge-invariant contributions of the fourth order to the

free-energy functional of a pure superconductor. In the case of alloys we will restrict our attention to the contributions of the types $|(\nabla-2ie\mathbf{A})^2\Delta|^2$ and $|(\nabla-2ie\mathbf{A})\Delta|^4$. The coefficients of these terms can be determined most easily by making use of the relation $j_i\sim\delta F/\delta A_i+\ldots$ and the fact that the coefficient of the contribution to j_i which is proportional to $A_jA_kA_l$ is equal to (apart from a numerical factor)

$$d_{ijkl}=\sum_n\int d^3p\tfrac{1}{2}\mathrm{Tr}\langle\bar{G}p_j\bar{G}p_k\bar{G}p_l\bar{G}p_i\rangle_{\mathrm{av}}. \quad (26)$$

The first contribution to Eq. (26), denoted by $d_{ijkl}^{(1)}$, can be calculated by replacing all four vertices p_i, p_j, p_k, p_l, by the corrected vertices given in Eqs. (12) and (13).

But in addition one has to consider the contributions due to impurity interaction lines of the ladder type which are "bridging" simultaneously either the vertices p_j, p_k, or p_k, p_l. The expression for the first contribution, denoted by $d_{ijkl}^{(2)}$, is given by

$$d_{ijkl}^{(2)}=\langle p_ip_l\rangle_F\langle p_jp_k\rangle_FN(0)\sum_n\int d\epsilon_p\tfrac{1}{2}\mathrm{Tr}\{\bar{G}\tau_3\bar{\Lambda}\tau_3G\times[(1+\Lambda_0)-\Lambda_1\tau_1]\bar{G}[(1+\Lambda_0)-\Lambda_1\tau_1]\}, \quad (27)$$

where the vertex correction $\bar{\Lambda}$ is determined by the equation

$$\bar{\Lambda}=\frac{1}{2\pi\tau}\int d\epsilon_p\{\bar{G}[(1+\Lambda_0)-\Lambda_1\tau_1]\bar{G}\times[(1+\Lambda_0)-\Lambda_1\tau_1]\bar{G}+\bar{G}\tau_3\bar{\Lambda}\tau_3\bar{G}\}. \quad (28)$$

The second contribution differs from Eq. (27) in that $\langle p_ip_l\rangle_F\langle p_jp_k\rangle_F$ is replaced by $\langle p_ip_j\rangle_F\langle p_kp_l\rangle_F$.

Again we express the results in terms of the corresponding contribution to the free-energy functional which shall be denoted by $F^{(4)}$. We find

$$F^{(4)}=\int d^3rN(0)\frac{1}{12}(v_F\beta)^4\{f_{ijkl}^{(2)}(O_iO_j\Delta)(O_kO_l\Delta)^*+\beta^2f_{ijkl}^{(3)}(O_i\Delta)(O_j\Delta)(O_k\Delta)^*(O_l\Delta)^*\}, \quad (29)$$

where $\mathbf{O}=(\nabla-2ie\mathbf{A})$, and ($\nu=1,2$)

$$f_{ijkl}^{(\nu)}=\frac{1}{15}f^{(\nu)}(\delta_{ij}\delta_{kl}+\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk})+\frac{1}{9}\delta_{ij}\delta_{kl}\tilde{f}^{(\nu)}, \quad (30)$$

$$f^{(2)}(|\Delta\beta|^2)=-\frac{3}{2}\sum_{n=0}^{\infty}\frac{\pi}{[(\omega\beta)^2+|\Delta\beta|^2]^{5/2}\eta_{\mathrm{tr}}^2\eta}, \quad (31)$$

$$f^{(2)}(|\Delta\beta|^2)=-\frac{3}{2}\sum_{n=0}^{\infty}\frac{\pi}{[(\omega\beta)^2+|\Delta\beta|^2]^{5/2}\eta_{\mathrm{tr}}^2}\cdot\frac{(\eta-1)}{\eta}. \quad (32)$$

One obtains similar expressions for $f^{(3)}$ and $\tilde{f}^{(3)}$, apart from an additional factor $-[(\omega\beta)^2+|\Delta\beta|^2]^{-1}$. In the limit $\eta\to1$, the functions $\tilde{f}^{(2)}$ and $\tilde{f}^{(3)}$ reduce to the results obtained in Ref. 6, while $f^{(2)}$ and $f^{(3)}$ go to zero. However, in the limit $l\ll\xi_0$ the latter functions become predominant since they acquire one extra factor (ξ_0/l). The results for these functions in the "dirty" limit are

$$f_{\mathrm{dirty}}^{(2)}=-6(\tau_{\mathrm{tr}}/\beta)^2g,\quad f_{\mathrm{dirty}}^{(3)}=-4(\tau_{\mathrm{tr}}/\beta)^2g'. \quad (33)$$

The conditions for the validity of the local theory can be obtained by comparing for instance the contribution of the type $|(\nabla-2ie\mathbf{A})^2\Delta|^2$ in Eq. (29) with the term $|(\nabla-2ie\mathbf{A})\Delta|^2$ in Eq. (18). We shall denote the magnitude of the ratio of the coefficients of these two terms by ξ^2. Then these conditions turn out to be (1) $|\xi^2\nabla_i\nabla_j|\Delta||<|\xi\nabla|\Delta||<|\Delta|$; (2) $|\xi\nabla_iQ_j|<|\mathbf{Q}|$; (3) $\xi|\mathbf{Q}|<1$. Here $\mathbf{Q}=2e\mathbf{A}-\nabla\varphi$, and φ is the phase of Δ.

In the limiting case $l\ll\xi_0$ the quantity ξ^2 becomes

$$\xi_{\mathrm{dirty}}{}^2=\frac{4\pi}{3\gamma}(v_F\tau_{\mathrm{tr}}\xi_0)\left(\frac{T_c}{T}\right)g(|\Delta\beta|^2)\frac{(\frac{1}{2}|\Delta\beta|)}{\tanh(\frac{1}{2}|\Delta\beta|)}. \quad (34)$$

The function of $|\Delta\beta|$ occuring on the right-hand side of Eq. (34) is close to the constant $a_2=[7\zeta(3)/8\pi^2]$ for $|\Delta\beta|\ll1$, and tends to $(4|\Delta\beta|)^{-1}$ for $|\Delta\beta|\gg1$. Thus the length ξ_{dirty} ranges from about $(l\xi_0)^{1/2}$ to $(T_c/T)(l\xi_0)^{1/2}$ as $|\Delta|$ varies from $\Delta_{\mathrm{BCS}}(T)$ to zero.

5. DISCUSSION

The results of the local theory of superconducting alloys are contained essentially in the expression Eq. (18) for the free-energy functional. The stationary value of this functional yields the Gibbs free-energy difference between the superconducting and normal phases.

The comparison of the fourth-order terms in Eq. (29) with the second-order terms in Eq. (18) has led us to the introduction of a characteristic length ξ, and of gauge-invariant variables $|\Delta|$ and $\mathbf{Q}=2e\mathbf{A}-\nabla\varphi$ instead of $\Delta=|\Delta|\exp(i\varphi)$ and $\mathbf{A}$. The meaning of $\mathbf{Q}$ becomes clear if one expresses the current density $\mathbf{j}$ and the kinetic energy density E_k [third term in Eq. (18)] in terms of $\mathbf{Q}$. Then one finds

$$\mathbf{j}=-(e/m)\rho_s\mathbf{v}_s,\quad E_k=\tfrac{1}{2}\rho_s[\mathbf{v}_s{}^2+((\nabla|\Delta|)^2/4m^2|\Delta|^2)], \quad (35)$$

where

$$\mathbf{v}_s=\mathbf{Q}/2m=(2e\mathbf{A}-\nabla\varphi)/2m \quad (36)$$

and

$$\rho_s/\rho_0=\lambda_L{}^2/\lambda^2=2|\Delta\beta|^2g_\tau(|\Delta\beta|^2. \quad (37)$$

Thus, we have to interpret ρ_s and $(\rho_0-\rho_s)$ as the superfluid and normal mass densities,[9] and $\mathbf{v}_s$ as the superfluid velocity. From the Maxwell equation we find that λ is the local penetration depth for $\mathbf{v}_s$.

Then the conditions for the validity of the local theory can be stated as follows: (1) The gap $|\Delta|$ must vary slowly over distances ξ. (2) The superfluid velocity

$\mathbf{v}_s$ must vary slowly over distances ξ, or equivalently $\lambda > \xi$; one finds that in the "clean" and "dirty" limits this condition is satisfied at all temperatures if $\lambda_L > \xi_0$ and $\lambda_L > l$, respectively, which is equivalent in both cases to $\kappa > 1$. (3) The superfluid velocity v_s must be sufficiently low, more precisely, $\pi/mv_s > \xi$.

For the pure superconductor ξ ranges from about the BCS coherence distance ξ_0 to $(T_c/T)\xi_0$ as $|\Delta|$ varies between $\Delta_{\rm BCS}(T)$ and zero. In the limiting case $l \ll \xi_0$ the length ξ ranges from about $(l\xi_0)^{1/2}$ to $(T_c/T)(l\xi_0)^{1/2}$ as $|\Delta|$ varies between $\Delta_{\rm BCS}(T)$ and zero. Thus we see that even in the "dirty" limit the local theory can never be applied in the high-field–low-temperature region since the length ξ becomes very large.

In Eq. (25) we have given the explicit expression of the free-energy functional, in terms of reduced variables ψ and $\mathbf{a}$ and the GL parameter κ, for the limiting case $l \ll \xi_0$. As $T \to T_c$ this functional reduces to the GL functional. But also in the low temperature region the form of the functional becomes close to that of GL, provided that $|\psi|$ is close to 1 and $|\nabla|\psi|^2/\kappa| < 1$. This follows because an expansion of the second term inside the brackets of Eq. (25) yields[10]

$$-w(\chi_0^2|\psi|^2)\,|\,2w(\chi_0^2) = -\tfrac{1}{2} + \tfrac{1}{4}(1-|\psi|^2)^2 + \cdots, \quad (38)$$

where the dots denote higher powers of the deviation $(1-|\psi|^2)$, and the coefficients of the terms $|(\kappa^{-1}\nabla - i\mathbf{a})\psi|^2$ and $(\nabla|\psi|^2/\kappa)^2$ become 1 and $-\frac{1}{8}$, respectively, in the limit $|\psi| \to 1$. In many applications of Eq. (25) one will obtain sufficient accuracy if one expands all the functions about $|\psi|^2 = 1$ in powers of $(1-|\psi|^2)$, up to some low order.

The local theory may be used, for instance, to investigate the structure of the outer and intermediate region of a vortex line. However, in the core region the theory becomes invalid since $|\Delta|$ does not vary slowly over distances ξ, and since v_s becomes too large. We may use the fourth-order terms (fourth-order in powers of v_s, $|\nabla|\Delta||$, etc.) in Eq. (29) to test the validity of the local theory, and to calculate corrections, as one approaches the core region. Near the center of the line where $|\Delta|/T_c \ll 1$ a nonlocal theory like that developed by Maki[11] becomes valid, provided that $l \ll \xi_0$.

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[10] This was pointed out by L. Neumann (private communication). [But note that the coefficient in the second term of Eq. (38) is $\frac{1}{4}$ while this coefficient is $\frac{1}{2}$ in the limit $T \to T_c$.]

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Energy Levels of Dy^{2+} in the Cubic Hosts of CaF_2, SrF_2, and BaF_2

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The absorption and fluorescence spectrum of Dy^{2+} in the cubic hosts of CaF_2, SrF_2, and BaF_2 was investigated. The crystal-field components of the $^5I_7$ and $^5I_8$ states were established and the cubic field parameters for the three hosts were deduced. The laser transition in the CaF_2:Dy^{2+} system was identified and some of the laser characteristics were delineated. The $4f$-$4f$ transitions of Dy^{2+} were found to be of magnetic dipole origin. The nonradiative processes in the above systems are discussed.

I. INTRODUCTION

In recent years, rare earths were successfully reduced to the divalent state in solid hosts not containing oxygen by subjecting the trivalent rare-earth doped crystals to x rays[1] or γ irradiation.[2,3] This technique is successful not only in reducing ions that are near the half-filled or completely filled $4f$ shells, such as Sm^{2+}, Eu^{2+}, and Yb^{2+}, but all the other rare-earth ions that have until recently only been studied in the trivalent state. The CaF_2 host is eminently suitable for photoreduction techniques, and divalent rare earths in this host have been studied by a number of authors.[4–6] Divalent rare earths occupying the divalent Ca site in CaF_2 are especially accessible for theoretical studies, since the local symmetry about the impurity ions is

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