Magnetic Properties of Intrinsic London Superconductors

KAZUMI MAKI*
The Enrico Fermi Institute for Nuclear Studies, The University of Chicago, Chicago, Illinois

AND

TOSHIO TSUZUKI
Kyoto University, Department of Physics, Kyoto, Japan
(Received 23 November 1964)

We present here a theory of intrinsic London superconductors in the vicinity of the transition point where the transition from the mixed state to the normal state takes place. The equations for local superconductors [i.e., for $\Delta(\mathbf{r})$] for impurity-free metal, deduced previously by Gor'kov, are explicitly solved by using the variational function of Abrikosov. Use is made of the results due to Gor'kov concerning the upper critical field of pure superconductors. It is shown that the mixed state in the immediate subcritical region is expressed in terms of κ_1 and κ_2, which coincide at the critical temperature with κ, the Ginzburg-Landau parameter. The upper critical field is expressed in terms of κ_1, while the slope of the magnetization curve is given in term of κ_2. The explicit calculation of κ_1 and κ_2 shows that κ_2 increases more rapidly than κ_1 as temperature decreases, and diverges at low temperature.

I. INTRODUCTION

THE concept of negative surface energy introduced by Ginzburg and Landau[1] seems to be most useful in accounting for the anomalous magnetic properties of so-called London superconductors. Abrikosov[2] has shown in his remarkable study of the Ginzburg-Landau equations the existence of flux-line structure in superconductors having κ, the Ginzburg-Landau parameter, larger than $1/\sqrt{2}$ in strong magnetic fields.

Unfortunately it turns out that the Ginzburg-Landau theory holds only in a small temperature region close to the critical temperature,[3] and hence it is worthwhile to examine if Abrikosov's picture is valid at lower temperature.

Previously one of the present authors[4] showed that Abrikosov's theory holds quite generally, independently of temperature, in the case of superconducting alloys where the electron mean free path is very short.

The purpose of the present paper is to study the magnetic properties of the mixed state in the immediate subcritical region, by restricting ourselves to the case of intrinsic London superconductors (where the electron mean free path is infinite). Although such superconductors are very scarce in nature, it is still of interest to study these ideal cases which, together with the previous results for alloys, might throw light on the general properties of London superconductors.

The upper critical field below which the normal state becomes unstable has been previously obtained by Gor'kov,[5] by using a homogeneous integral equation for the ordering parameter $\Delta(\mathbf{r})$. In the region where the external field H_0 is slightly smaller than the upper critical field H_{c2}, it is expected that the ordering parameter might still be small. The basic equations required to describe this situation have already been obtained by Gor'kov[3] and our task reduces to solving this set of equations explicitly by a variational method. We find that, as far as we approximate nonlocal kernels by local ones (see Sec. III), Abrikosov's structure in the immediate subcritical region is completely described in terms of two parameters $\kappa_1(T)$ and $\kappa_2(T)$ which coincide at the critical temperature with κ, the Ginzburg-Landau parameter. The upper critical field H_{c2} and the magnetization M are expressed in terms of κ_1 and κ_2 as

$$H_{c2}(T)=\kappa_1(T)\sqrt{2}H_c(T)$$

and

$$-4\pi M=(H_{c2}-H_0)/\{[2\kappa_2^2(T)-1]\beta\}\,,\quad \beta=1.16\,,$$

respectively, where H_c is the thermodynamic critical field and H_0 the external field.

Explicit calculation of κ_1 and κ_2 shows that the relation $\kappa_2(T)\geqq\kappa_1(T)\geqq\kappa$ holds in the present case, and $\kappa_2(T)$ diverges as $[\ln(c/T)]^{1/2}$ at lower temperatures T, which behavior is quite in contrast with the case of alloys.

In the following we use the unit system $\hbar=k_B=C=1$.

II. EQUATIONS FOR LOCAL SUPERCONDUCTORS

In this section we would like to give a general background for subsequent discussions. We shall present the basic equations for local superconductors on the one hand and recapitulate in detail the calculation of the upper critical field due to Gor'kov on the other hand. In the following we use the same notation as used by Gor'kov[3] unless otherwise stated explicitly.

* On leave of absence from Research Institute for Mathematical Sciences, Kyoto University, Kyoto, Japan.

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

[2] A. A. Abrikosov, Zh. Eksperim. i Teor. Fiz. **32**, 1442 (1957) [English transl.: Soviet Phys.—JETP **5**, 1174 (1957)].

[3] L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **36**, 1918 (1959); **37**, 1407 (1959) [English transls.: Soviet Phys.—JETP **9**, 1364 (1959); **10**, 998 (1960)].

[4] K. Maki, Physics **1**, 21, 127 (1964).

[5] L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **37**, 835 (1959) [English transl.: Soviet Phys.—JETP **10**, 593 (1960)].

When the ordering parameter $\Delta(\mathbf{r})$ is small (i.e., $\Delta/\pi T_{c0}\ll 1$, T_{c0} is the critical temperature), which is usually the case if magnetic fields are sufficiently large, we obtain the following equation[3]:

$$\Delta^\dagger(\mathbf{r})=|g|T\sum_n\int G_\omega(\mathbf{r}',\mathbf{r})G_{-\omega}(\mathbf{r}',\mathbf{r})\Delta^\dagger(\mathbf{r}')\,d^3\mathbf{r}'$$

$$-|g|T\sum_n\int\int\int G_\omega(\mathbf{s},\mathbf{r})G_{-\omega}(\mathbf{s},\mathbf{l})G_\omega(\mathbf{m},\mathbf{l})$$

$$\times G_{-\omega}(\mathbf{m},\mathbf{r})\Delta^\dagger(\mathbf{s})\Delta(\mathbf{l})\Delta^\dagger(\mathbf{m})\,d\mathbf{s}^3\,d^3\mathbf{l}\,d^3\mathbf{m}\,,$$

$$\omega=2\pi T(n+\tfrac{1}{2})\,,\qquad(1)$$

where $|g|$ is the coupling constant between electron paris, T is the temperature, and the summation is taken over all integers.

The ordering parameter $\Delta^\dagger(\mathbf{r})$ is defined by

$$\Delta^\dagger(r)=|g|\langle T_\tau\psi_\uparrow{}^\dagger(\mathbf{r},t)\psi_\downarrow{}^\dagger(\mathbf{r},t)\rangle\,,$$

where $\langle T_\tau\cdots\rangle$ means the average of the time-ordered product over Gibbs' ensemble. The Green's function is given by

$$G_\omega(\mathbf{r},\mathbf{r}')=e^{i\varphi(r,r')}G_\omega{}^0(\mathbf{r},\mathbf{r}')\,,$$

where $G_\omega{}^0(\mathbf{r},\mathbf{r}')$ is the Green's function of the electron in the normal metal and its Fourier transform is given by $(i\omega_n-\xi)^{-1}$ with $\xi=(p^2-p_0{}^2)/2m$. The effect of the magnetic field is taken account of in the phase factor $\varphi(\mathbf{r},\mathbf{r}')=e\int_{\mathbf{r}'}{}^{\mathbf{r}}\mathbf{A}(\mathbf{l})\cdot d\mathbf{l}$, where $\mathbf{A}$ is the vector potential and the integral is taken along a straight path connecting $\mathbf{r}$ and $\mathbf{r}'$.

Similarly the current density is given as

$$\mathbf{j}(\mathbf{r})=\frac{ie}{m}(\nabla_\mathbf{r}-\nabla_{\mathbf{r}'})T\sum_n\int\int G_\omega(\mathbf{r}',\mathbf{s})G_\omega(\mathbf{l},\mathbf{s})$$

$$\times G_{-\omega}(\mathbf{l},\mathbf{r})\Delta^\dagger(\mathbf{l})\Delta(\mathbf{s})\,d^3\mathbf{l}\,d^3\mathbf{s}\,|_{\mathbf{r}=\mathbf{r}'}\,.\qquad(2)$$

The above set of equations has been previously obtained by Gor'kov[3] in his microscopic derivation of the Ginzburg-Landau theory.

For the following discussions it is more convenient to rewrite Eq. (1) into

$$\ln\left(\frac{\gamma\omega_D}{\pi T_{c0}}\right)\Delta^\dagger(\mathbf{r})=\int K_0(\mathbf{r},\mathbf{r}')\Delta^\dagger(\mathbf{r}')\,d^3\mathbf{r}'$$

$$-\int\int\int K_1(\mathbf{r},\mathbf{s},\mathbf{m},\mathbf{l})\Delta^\dagger(\mathbf{s})\Delta(\mathbf{m})\Delta^\dagger(\mathbf{l})\,d^3\mathbf{s}\,d^3\mathbf{m}\,d^3\mathbf{l}\,,\qquad(3)$$

where we made use of the identity

$$1=\frac{mp_0}{2\pi^2}|g|\ln\left(\frac{\gamma\omega_D}{\pi T_{c0}}\right),$$

p_0 is the Fermi momentum, and ω_D is the cutoff frequency. T_{c0} is the critical temperature and $\ln\gamma=C$ the Euler constant.

Two integral kernels are given by

$$(mp_0/2\pi^2)K_0(\mathbf{r},\mathbf{r}')=T\sum\nolimits_n G_\omega(\mathbf{r}'\mathbf{r})G_{-\omega}(\mathbf{r}',\mathbf{r})\qquad(4)$$

and

$$(mp_0/2\pi^2)K_1(\mathbf{r},\mathbf{s},\mathbf{l},\mathbf{m})$$
$$=T\sum\nolimits_n G_\omega(\mathbf{s},\mathbf{r})G_{-\omega}(s,\mathbf{l})\cdot G_\omega(\mathbf{m},\mathbf{l})G_{-\omega}(\mathbf{m},\mathbf{r})\,,\qquad(5)$$

respectively.

As is well known, Gor'kov[5] has shown that there is another critical field besides the thermodynamic critical field corresponding to the limiting field below which the normal state becomes unstable, and he calculated this field by using the following equation:

$$\ln\left(\frac{\gamma\omega_D}{\pi T_{c0}}\right)\Delta^\dagger(\mathbf{r})=\int K_0(\mathbf{r},\mathbf{r}')\Delta^\dagger(\mathbf{r}')d^3r'\,,\qquad(6)$$

which is the linear part of Eq. (3). After a number of integrations he arrived at the following integral equations (see also Sec. A of the Appendix):

$$\Delta(x)\ln\left(\frac{e\gamma\Delta_{00}\delta}{v(eH_0)^{1/2}}\right)=-\frac{(eH_0)^{1/2}}{2}\int_{-\infty}^{\infty}H_T(x,x')\Delta(x')dx'\,,\qquad(7)$$

where

$$H_T(\xi/(eH_0)^{1/2},\,\xi'/(eH_0)^{1/2})$$
$$=\frac{2\pi T}{v(eH_0)^{1/2}}\int_1^\infty\frac{du\,J_0((\xi^2-\xi'^2)(u^2-1)^{1/2})}{u\sinh[(2\pi Tu|\xi-\xi'|/v(eH_0)^{1/2})]}$$
$$\times\theta(|\xi-\xi'|-\delta)\,,$$
$$\theta(a)=1\,,\quad\text{for}\quad a>0$$
$$=0\,,\quad\text{for}\quad a<0\,,\qquad(8)$$

δ ($\simeq v(eH_0)^{1/2}/\omega_D$) is introduced so as to simulate the cutoff of the interaction in momentum space, v is the Fermi velocity, and $\Delta_{00}=\pi T_{c0}/\gamma$ is the ordering parameter at $T=0$°K. In deriving the above equation we assume that the external field H_0 is uniform and directed along the z axis and Δ depends only on x. The exponential e and the charge e should not be confused here. It is easy to see that the latter appears always in dimensionless combinations such as $v(eH_0)^{1/2}/\pi T$ and $(eH_0)^{1/2}x$.

In the light of a recent formulation by Helfand and Werthamer,[6] we know that the eigenfunction of Eq. (7) should be $e^{-eH_0x^2}$ (more generally speaking, Hermitian functions with argument $(2eH_0)^{1/2}x$). We first rewrite Eq. (7) in the form

$$\ln\left(\frac{e\gamma\Delta_{00}\delta}{v(eH_0)^{1/2}}\right)=-\frac{(eH_0)^{1/2}}{2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}dx\,dx'\Delta^\dagger(x)$$
$$\times H_T(x,x')\Delta(x')\Big/\int_{-\infty}^{\infty}|\Delta(x)|^2dx\,.\qquad(9)$$

[6] E. Helfand and N. R. Werthamer, Phys. Rev. Letters 13, 686 (1964).

Substituting $\Delta(x)=e^{-eH_0x^2}$ into Eq. (9) we have

$$\ln\left(\frac{e\gamma\Delta_{00}\delta}{v(eH_0)^{1/2}}\right)=-\frac{(eH_0)^{1/2}}{2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}dx\,dx'e^{-eH_0(x^2+x'^2)}\times H_T(x,x')\bigg/\int_{-\infty}^{\infty}dx\,e^{-2eH_0x^2},$$

$$=-\frac{1}{2}\left(\frac{2}{\pi}\right)^{1/2}\int_{-\infty}^{\infty}d\xi\int_{-\infty}^{\infty}d\xi'e^{-(\xi^2+\xi'^2)}\frac{2\pi T}{v(eH_0)^{1/2}}\int_1^{\infty}\frac{du}{u}\times\frac{J_0((\xi^2-\xi'^2)(u^2-1)^{1/2})\theta(|\xi-\xi'|-\delta)}{\sinh[(2\pi Tu/v(eH_0)^{1/2})|\xi-\xi'|]}. \quad (10)$$

The above expression reduces further to

$$\ln\left(\frac{e\gamma\Delta_{00}\delta}{v(eH_0)^{1/2}}\right)=-\rho^{-1/2}\int_{\delta}^{\infty}d\zeta\int_1^{\infty}\frac{du}{u}\frac{e^{-\frac{1}{4}(u^2+1)\zeta^2}I_0(\frac{1}{4}(u^2-1)\zeta^2)}{\sinh(\rho^{-1/2}\zeta u)}, \quad (11)$$

where $\rho=(v(eH_0)^{1/2}/2\pi T)^2$ and we have made use of identity

$$\int_{-\infty}^{\infty}e^{-ax^2}J_1(bx)\,dx=\left(\frac{\pi}{a}\right)^{1/2}e^{-b^2/8a}I_0\left(\frac{b^2}{8a}\right). \quad (12)$$

Using the relation

$$\ln\left(\frac{2(\rho)^{1/2}}{\delta e}\right)=\rho^{-1/2}\int_{\delta}^{\infty}d\zeta\int_1^{\infty}\frac{du}{u\sinh(\rho^{-1/2}\zeta u)}, \quad (13)$$

we finally obtain an implicit equation for the field H_0 at which the nucleation of superconducting correlation begins:

$$\ln(T/T_{c0})+f_0(\rho)=0, \quad (14)$$

where

$$f_0(\rho)=\rho^{-1/2}\int_0^1 d\zeta\int_1^{\infty}\frac{du}{u}\times\frac{1-e^{-\frac{1}{4}(u^2+1)\zeta^2}I_0(\frac{1}{4}(u^2-1)\zeta^2)}{\sinh(\rho^{-1/2}\zeta u)}, \quad (15)$$

and $T_{c0}=\gamma\Delta_{00}/\pi$ is the critical temperature. The asymptotic forms of $f_0(\rho)$ are given as (see Sec. A of the Appendix)

$$f_0(\rho)=(7/6)\zeta(3)\rho-(31/10)\zeta(5)\rho^2+(281/28)\zeta(7)\rho^3,\quad \text{for } \rho\ll1 \quad (16)$$

$$=\ln(2e^{-1}(2\gamma\rho)^{1/2})+\pi^{-2}(\zeta'(2)+[\zeta(2)/2]\ln(2/\pi^2\gamma\rho))\rho^{-1},\quad \text{for } \rho\gg1. \quad (17)$$

The upper critical field is obtained from the above expressions:

$$H_{c2}(T)=\frac{1}{ev^2}\frac{6}{7\zeta(3)}(2\pi T_{c0})^2\times\theta\left\{1+\left[\frac{31}{10}\zeta(5)\left(\frac{6}{7\zeta(3)}\right)^2-\frac{3}{2}\right]\theta\right\},$$

$$\theta=1-T/T_{c0},\quad \text{for } T_{c0}-T\ll T_{c0} \quad (18)$$

$$H_{c2}(T)=\frac{1}{ev^2}\left(\frac{\gamma\Delta_{00}{}^2e^2}{2}\right)\left\{1-\frac{\gamma 8}{\pi^2e^2}\left[\zeta'(2)+\zeta(2)\times\ln\left(2e\left(\frac{2}{\pi}\right)^{1/2}\frac{T}{T_{c0}}\right)\right]\left(\frac{T}{T_{c0}}\right)^2\right\},$$

$$\text{for } T\ll T_{c0}. \quad (19)$$

Defining κ_1 by $\kappa_1(T)=H_{c2}(T)/\sqrt{2}H_c(T)$, we have

$$\kappa_1=1.25\kappa\{1+0.65(T/T_{c0})^2\ln(\text{const}(T/T_{c0}))\},\quad \text{for } T\ll T_{c0} \quad (20)$$

$$=\kappa(1+0.41\theta),\quad \text{for } T_{c0}-T\ll T_{c0}, \quad (21)$$

where

$$\kappa=(3\pi T_{c0}m/e)(2\pi m/7\zeta(3)p_0{}^5)^{1/2}$$

and we made use of the expressions

$$H_c(T)=(2mp_0/\pi)^{1/2}\Delta_{00}\left[1-\frac{\gamma^2}{3}(T/T_{c0})^2\right],\quad \text{for } T\ll T_{c0} \quad (22)$$

$$=\left(\frac{\pi mp_0}{7\zeta(3)}\right)^{1/2}4T_{c0}\theta\left[1-\left(1-\frac{31\zeta(5)}{49\zeta(3)^2}\right)\theta\right],\quad \text{for } T_{c0}-T\ll T_{c0}. \quad (23)$$

The above results have been previously obtained by Gor'kov[5]. He proposed an interpolation formula of the form

$$\sqrt{2}\kappa_1(T)=\kappa\{1.77-0.43(T/T_{c0})^2+0.07(T/T_{c0})^4\}, \quad (24)$$

which is currently used in the analysis of the experimental data.

III. ABRIKOSOV'S MIXED STATE

In the preceding section we have obtained an implicit equation for the upper critical field H_{c2} by assuming $\Delta(r)=e^{-eH_0x^2}$. It should be noted that Eq. (6) has degenerate solutions

$$\Delta(r)=\exp\{iky-eH_0[x-(k/2eH_0)]^2\}$$

for arbitrary k.

When the external magnetic field is slightly smaller than H_{c2} and the ordering parameter is still small, it is quite natural to look for the solution of Eqs. (2) and

(3) by assuming

$$\Delta(r)=\sum_{-\infty}^{\infty} C_n\psi_n(x,y);$$
$$\psi_n(x,y)=\exp\{ikny-eH_0[x-(kn/2eH_0)]^2\}, \quad (25)$$

where C_n and k are constants.

Substituting Eq. (25) into Eq. (2) and after a rather lengthy calculation we find (see Sec. B of the Appendix)

$$j_i(x,y)=\frac{eN}{m(2\pi T)^2}\sum_{n,m} C_n\psi_n C_m{}^\dagger\psi_m{}^\dagger \times B_i\left(x+\frac{kn}{2eH_0}, x+\frac{km}{2eH_0}\right), \quad (26)$$

where $i=x,\ y$

$$B_x(a,b)=\frac{3}{4\pi}\left(\frac{2\pi T}{v}\right)^3\int\frac{d\Omega}{z}\int_0^\infty dx_1\int_0^\infty dx_2 \times A(x_1,x_2;a,b), \quad (27)$$

$$B_y(a,b)=\frac{3}{4\pi}\left(\frac{2\pi T}{v}\right)^3\int i\alpha\frac{d\Omega}{z}\int_0^\infty dx_1\int_0^\infty dx_2 \times A(x_1,x_2;a,b),$$

$$A(x_1,x_2;a,b)=\exp\{-eH_0[(1-i\alpha)(x_1^2+2x_1a) + (1+i\alpha)(x_2^2+2x_2b)]\} \times\left[\sinh\left(\frac{2\pi T}{z}|x_1+x_2|\right)\right]^{-1}, \quad (28)$$

$N=p_0^3/3\pi^2$ is the density of electrons and $z=\cos\theta$, $\alpha=\tan\theta\cos\phi$, and $d\Omega=d\cos\theta\, d\phi$.

It is not difficult to show that j_i defined above satisfies the equation of continuity (see Sec. B of the Appendix) and we can integrate the Maxwell equation $\nabla\times\mathbf{H}=4\pi\mathbf{j}$. The magnetic field is given as

$$H(\mathbf{r})=H_0-\frac{eN}{m(2\pi T)^2}\sum_{n,m} C_n\psi_n C_m{}^\dagger\psi_m{}^\dagger \times C\left(x+\frac{kn}{2eH_0}, x+\frac{km}{2eH_0}\right), \quad (29)$$

where

$$C\left(x+\frac{kn}{2eH_0}, x+\frac{km}{2eH_0}\right) =\int_{-\infty}^{x} B_y\left(x'+\frac{kn}{2eH_0}, x'+\frac{km}{2eH_0}\right)dx'. \quad (30)$$

The above expression for the magnetic field is much simplified if we neglect small nonlocal effects, which amounts to the approximation

$$C\left(x+\frac{kn}{2eH_0}, x+\frac{km}{2eH_0}\right)\cong C(0,0). \quad (31)$$

In this approximation we have

$$H(\mathbf{r})=H_0-\frac{6\pi eN}{m(2\pi T)^2}g(\rho)|\Delta(\mathbf{r})|^2, \quad (32)$$

where

$$g(\rho)=\frac{1}{6\pi}C(0,0)=\frac{df_0(\rho)}{d\rho} \quad (33)$$

and $f_0(\rho)$ has been already defined in Eq. (15).

We can further carry out the similar calculation as given by Abrikosov.[2] First we note that in the presence of the magnetic field $H(\mathbf{r})$, the following integral

$$I=\left\langle\Delta(\mathbf{r})\left\{\ln\left(\frac{\gamma\omega_D}{\pi T_{c0}}\right)\Delta^\dagger(\mathbf{r})-\int K_0(\mathbf{r},\mathbf{r}')\Delta^\dagger(\mathbf{r}')d^3\mathbf{r}'\right\}\right\rangle_{\rm av}$$

reduces to

$$I=\left\langle\Delta(\mathbf{r})\left[\ln\frac{T}{T_{c0}}+f_0\left(\frac{v^2eH(\mathbf{r})}{(2\pi T)^2}\right)\right]\Delta^\dagger(\mathbf{r})\right\rangle_{\rm av}$$
$$=\frac{ev^2}{(2\pi T)^2}(H_{c2}-H_0)g(\rho)\langle|\Delta|^2\rangle_{\rm av} +\frac{\pi N}{6m(\pi T)^2}\left(\frac{3ev}{2\pi T}g(\rho)\right)^2\langle|\Delta|^4\rangle_{\rm av}, \quad (34)$$

thanks to a general relation[7] between the change of the eigenvalue and the expectation value of the change of the integral operator. Neglecting a small nonlocal effect associated with the integral $\int\int\int\int d^3\mathbf{r}\, d^3\mathbf{s}\, d^3\mathbf{l}\, d^3\mathbf{m} \times K_1(\mathbf{r,s,l,m})\Delta(\mathbf{r})\Delta^\dagger(\mathbf{s})\Delta(\mathbf{l})\Delta^\dagger(\mathbf{m})$, we finally obtain (see Appendix C)

$$\frac{ev^2}{(2\pi T)^2}(H_{c2}-H_0)g(\rho)\langle|\Delta|^2\rangle_{\rm av}+\frac{1}{8(\pi T)^2} \times\left\{\frac{4\pi N}{3m}\left(\frac{3ev}{2\pi T}g(\rho)\right)^2-f_1(\rho)\right\}\langle|\Delta|^4\rangle_{\rm av}=0, \quad (35)$$

where

$$f_1(\rho)=\frac{1}{\pi}\int\frac{d\Omega}{z^3}\int_0^\infty\frac{t^2dt}{\sinh(t/z)} \times\int_0^1 du\int_0^u dv\, e^{-\rho t^2\Lambda(u,v;\alpha)}, \quad (36)$$

and

$$\Lambda(u,v;\alpha)=[\tfrac{1}{2}((1-u)^2+v^2)-i\alpha\tfrac{1}{2}((1-u)^2-v^2) +\tfrac{1}{4}(1+\alpha^2)]. \quad (37)$$

---

[7] This relation is well known in quantum mechanics. If $\mathbf{K}(\alpha)$ is an Hermite operator depending on a parameter α and $|k,\alpha\rangle$ is its eigenvector (i.e., $\mathbf{K}(\alpha)|k,\alpha\rangle=k_\alpha|k,\alpha\rangle$) we have the following relation:

$$\langle k,\alpha|\mathbf{K}(\alpha+\delta\alpha)|k,\alpha\rangle=\langle k,\alpha|k_{\alpha+\delta\alpha}|k,\alpha\rangle,$$

for an infinitesimally small change of α.

Asymptotically we have

$$f_1(\rho)=7\zeta(3)-(62/3)\zeta(5)\rho+(10541/120)\zeta(7)\rho^2, \quad \text{for} \quad \rho\ll 1 \tag{38}$$

$$=4\rho^{-1}\{(\ln(1+\sqrt{2}))^2\ln(24\gamma\rho)+\text{const}\}+O(\rho^{-2}), \quad \text{for} \quad \rho\gg 1. \tag{39}$$

Using the above expressions, we can readily derive the expressions for the magnetic induction as well as the free energy.

$$B=\bar{H}=H_0-(H_{c2}-H_0)/[2\kappa_2^2(T)-1]\beta \tag{40}$$

and

$$\Delta F=\frac{1}{8\pi}\left[B^2-\frac{(H_{c2}-B)^2}{(2\kappa_2^2-1)\beta+1}\right], \tag{41}$$

where[8]

$$\beta=\langle|\Delta|^4\rangle_{\text{av}}/(\langle|\Delta|^2\rangle_{\text{av}})^2=1.159$$

and (42)

$$\kappa_2(T)=[3mf_1(\rho)/8\pi N]^{1/2}[(3ev/2\pi T)g(\rho)]^{-1}.$$

Asymptotic expressions for κ_2 are

$$\kappa_2=\tfrac{1}{3}\kappa e(7\zeta(3)/2\gamma)^{1/2}\ln(1+\sqrt{2})(\ln(T_{c0}/T))^{1/2}$$
$$=1.22\kappa(\ln(T_{c0}/T))^{1/2}, \quad \text{for} \quad T\ll T_{c0} \tag{43}$$
$$=\kappa(1+2.36\theta), \quad \text{for} \quad T_{c0}-T\ll T_{c0}. \tag{44}$$

It is interesting to note that κ_2 increases rapidly as the temperature decreases, and it diverges as $[\ln(T_{c0}/T)]^{1/2}$ at $T=0°\text{K}$. Interpolating the value κ_2 to intermediate temperatures we expect $\kappa_2\geqq\kappa_1$ to hold always. Incidently McConville and Serin[9] discovered a rapid increase of κ_2 in their recent measurement of the jump of the specific heat along the transition line in pure niobium samples.

IV. CONCLUDING REMARKS

In the above sections we have seen, restricting ourselves to the immediate subcritical region where the ordering parameter is still small, that Abrikosov's theory has a rather wide applicable region if one introduces two parameters κ_1 and κ_2 instead of a single κ. In the derivation of the final results Eqs. (40) and (41), we have systematically approximated nonlocal integral kernels by local ones. The errors involved in such approximations are found to be a few percent, independently of temperatures.

The most interesting result of the present study is that κ_2 is always larger than κ_1. This situation is in contrast to one we met in the case of alloys, where we have $\kappa_1\geqq\kappa_2$. The following asymptotic expressions for the case of alloys are compared with Eqs. (21) and (44).

$$\kappa_1=\kappa(1+0,13\theta),$$
$$\kappa_2=\kappa(1-0,39\theta), \quad \text{for} \quad T_{c0}-T\ll T_{c0}. \tag{45}$$

[8] E. H. Kleiner, L. M. Roth, and S. H. Antler, Phys. Rev. 133, A1226 (1964).

[9] T. McConville and B. Serin, Phys. Rev. Letters 13, 365 (1964).

A recent calculation of H_{c2} by Helfand and Werthamer[6] shows that the temperature dependence of κ_1 changes gradually and monotonically from its value at $l=\infty$ to that at $l=0$ as the electronic mean free path decreases. The present calculation suggests that the temperature dependence of κ_2 might be much more sensitive to the impurity concentration (or the electronic mean free path) than that of κ_1. In this respect, detailed measurements of the slope of the magnetization curve at the transition point are quite desirable.

We shall conclude this section with a brief discussion of the validity of the general Ginzburg-Landau approach (i.e., the possibility of expanding the free energy in powers of the square of the order parameter Δ).

Assuming that such an expansion is possible, we obtain formally

$$\Delta F=a\langle|\Delta|^2\rangle_{\text{av}}+b\langle|\Delta|^4\rangle_{\text{av}}+c\langle|\Delta|^6\rangle_{\text{av}}, \tag{46}$$

where a, b, and c are the functions of the temperature and the external field.

In the case of Abrikosov's mixed state in pure superconductors we have

$$a=(mp_0/(2\pi)^2)(ev^2/(2\pi T)^2)(H_{c2}-H_0)g(\rho), \tag{47}$$

$$b=\frac{1}{4}\frac{mp_0}{(2\pi)^2}\frac{1}{(2\pi T)^2}\left\{\frac{4\pi N}{3m}\left(\frac{3ev}{2\pi T}g(\rho)\right)^2-f_1(\rho)\right\}. \tag{48}$$

As we have already seen, b (or $\rho f_1(\rho)$) diverges as $\ln(T_{c0}/T)$ at lower temperatures. The close examination of c shows that c diverges even more badly. Therefore, in order to obtain a reliable expression for ΔF at extremely low temperatures, we have to sum an infinite series of diverging terms. Such a summation is in fact possible and we find at $T=0$

$$\Delta F=a\langle|\Delta|^2\rangle_{\text{av}}+b'\ln(\text{const}\,T_{c0}/\langle|\Delta|^2\rangle_{\text{av}}^{1/2})\langle|\Delta|^4\rangle_{\text{av}}. \tag{49}$$

Roughly speaking, the above expression is obtained from Eq. (40) by simply replacing $\ln(T_{c0}/T)$ in the coefficient b by $\ln(T_{c0}/\langle|\Delta|^2\rangle_{\text{av}}^{1/2})$. The above equation indicates that the formal expansion of Eq. (40) becomes invalid at lower temperatures. On the other hand, in the case of alloys we have seen that the expansion (40) is always possible if $|\Delta|^2$ is small at all temperatures. This different situation for the case of alloys reflects the existence of the gapless region in fields close to the upper critical field where the excitation spectrum of quasiparticles is strongly modified.[4,10]

As far as real superconductors are concerned, the electron has a finite lifetime τ and we expect that at extremely low temperatures where $\tau T\ll 1$, the factor $\ln(T_{c0}/T)$ may be replaced by $\ln(\tau T_{c0})$ and $\kappa_2(T)$ remains finite even at $T=0°\text{K}$.

The recent measurement of the jump of the specific heat along the transition line in pure niobium samples[8] seems in qualitative agreement with the present theory.

[10] P. G. deGennes, Phys. Condensed Matter 3, 79 (1964).

We should, however, point out that there is a serious disagreement concerning the temperature dependence of the uper critical field,[9,11] of which the origin is not clear.

In summary we conclude that Abrikosov's picture holds quite generally, independently of the temperature and the electronic mean free path, if we use two parameters. Deviation from the original Abrikosov theory is most easily seen in the temperature dependence of $\kappa_2(T)$ [or $(\partial M/\partial H)|_{H_0=H_{c2}}$], which behaves quite differently depending on whether the electronic mean free path is short or long.

APPENDIX

In the following we shall calculate explicitly the quantities corresponding to the diagrams given in Fig. 1. We use the Green's function given by

$$G_\omega(\mathbf{r},\mathbf{r}')=e^{i\varphi(\mathbf{r},\mathbf{r}')}\int\frac{d^3p}{(2\pi)^3}e^{i\mathbf{p}\cdot(\mathbf{r}-\mathbf{r}')}\frac{1}{i\omega-\xi},$$

where

$$\xi=(p^2-p_0^2)/2m,\quad \omega=2\pi T(n+\tfrac{1}{2}),$$

and

$$\varphi(\mathbf{r},\mathbf{r}')=\tfrac{1}{2}eH_0(x+x')(y-y').$$

We assume here that the magnetic field is uniform and directed along the z axis.

A. The Calculation of the Diagram (a)

$$\begin{aligned}K&=T\sum_n\int d\mathbf{r}'^3\,G_\omega(\mathbf{r}',\mathbf{r})G_{-\omega}(\mathbf{r}',r)\Delta^\dagger(\mathbf{r}')\\&=T\sum_n\int d^3\mathbf{r}'\int\frac{d^3\mathbf{p}}{(2\pi)^3}\int\frac{d^3\mathbf{q}}{(2\pi)^3}\frac{e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')+ieH_0(x+x')(y-y')}}{(i\omega-\xi)(i\omega+\xi+\mathbf{v}\cdot\mathbf{q})}\Delta(x',y')\\&=T\sum_n\frac{mp_0}{(2\pi)^3}\int d\Omega\int d^3\mathbf{r}'\int\frac{d^3\mathbf{q}}{(2\pi)^3}\frac{e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')+ieH_0(x+x')(y-y')}}{2i\omega+\mathbf{v}\cdot\mathbf{q}}\Delta(x',y'),\end{aligned}\qquad\text{(A1)}$$

where we have integrated over ξ after replacing $d^3\mathbf{p}$ by $mp_0d\xi d\Omega$.

Taking the polar axis in the direction of x

$$(\text{i.e.,}\quad \mathbf{v}\cdot\mathbf{q}=v(q_x\cos\theta+q_y\sin\theta\cos\phi+q_z\sin\theta\sin\phi)),$$

we can carry out further integrations. We have finally a simple expression for the case where $\Delta(x',y')$ depends only on x';

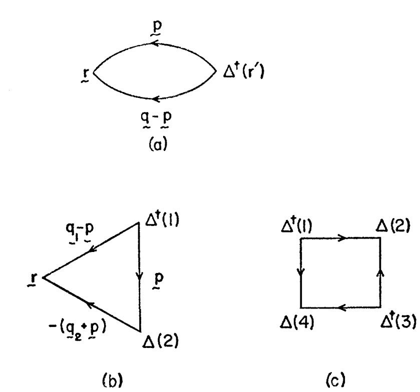

FIG. 1. (a) The diagram corresponding to the coefficient of Δ in Eq. (1). (b) The diagram corresponding to the expression of the current density. (c) The diagram corresponding to the coefficient of $|\Delta|^2\Delta$ in Eq. (1).

[11] E. S. Rosenblum, S. H. Antler, and K. H. Gooen, Rev. Mod. Phys. 36, 77 (1963).

$$K=T\sum_n \frac{mp_0}{(2\pi)^2}\int_{-1}^{1} d\cos\theta\int_0^{2\pi} d\phi\int_{-\infty}^{\infty} dx'\int \frac{d^3\mathbf{q}}{(2\pi)}\frac{e^{iq_x(x-x')}\delta(q_z)\delta(q_y-eH_0(x+x'))}{2i\omega+\mathbf{v}\cdot\mathbf{q}}\Delta(x')$$

$$=T\sum_n \frac{mp_0}{(2\pi)^2}\int_{-1}^{1} d\cos\theta\int_0^{2\pi} d\phi\int_{-\infty}^{\infty} dx' e^{-(2/v)|\omega(x-x')/\cos\theta|+ieH_0(x^2-x'^2)\tan\theta\cos\phi}\Delta(x')$$

$$=\frac{2\pi m\rho_0}{(2\pi)^2}T\int_1^{\infty}\frac{du}{u}\int_{-\infty}^{\infty} dx'\frac{J_0(eH_0(x^2-x'^2)(u^2-1)^{1/2})}{\sinh((2\pi Tu/v)|x-x'|)}, \tag{A2}$$

where $u=(\cos\theta)^{-1}$.

Thus Eq. (6) reduces to

$$\ln\left(\frac{\gamma\omega_D}{\pi T_{c0}}\right)\Delta(x)=\pi T\int_1^{\infty}\frac{du}{u}\int_{-\infty}^{\infty} dx'\frac{J_0(eH_0(x^2-x'^2)(u^2-1)^{1/2})}{\sinh[(2\pi Tu/v)|x-x'|]}\theta(|x-x'|-\delta)\Delta(x'). \tag{A3}$$

In the above expression we have introduced a cutoff δ in the interaction range in order to avoid a spurious divergence of the integral. The cutoff distance δ is determined so as to simulate the cutoff in the frequency of the ordinary pair interaction. Comparing the two sides of Eq. (A3) at $T=T_{c0}$, we find $\omega_D=v/e\gamma\delta$.

Now let us turn to the evaluation of the asymptotic expression of $f_0(\rho)$.

(a) *$\rho\ll 1$.* In this limit $f_0(\rho)$ is rewritten as

$$f_0(\rho)=\int_0^{\infty} d\zeta\int_1^{\infty}\frac{du}{u}\frac{1-e^{-\frac{1}{4}(u^2+1)\rho\zeta^2}I_0(\frac{1}{4}(u^2-1)\rho\zeta^2)}{\sinh(\zeta u)}. \tag{A4}$$

Expanding the integral in powers of ρ, we obtain

$$f_0(\rho)=\frac{7}{6}\zeta(3)\rho-\frac{31}{10}\zeta(5)\rho^2+\frac{281}{28}\zeta(7)\rho^3. \tag{A5}$$

(b) *$\rho\gg 1$.* (A4) is transformed as

$$f_0(\rho)=\lim_{\epsilon\to 0}\left\{\int_\epsilon^{\infty} d\zeta\int_1^{\infty}\frac{du}{u\sinh(\zeta u)}-\int_\epsilon^{\infty} d\zeta\int_1^{\infty}\frac{du}{u^2}e^{-\frac{1}{4}(u^2+1)\rho\zeta^2}I_0(\tfrac{1}{4}(u^2-1)\rho\zeta^2)\Big[\zeta^{-1}+2\zeta u^2\sum_1^{\infty}(-1)^n((n\pi)^2+(\zeta u)^2)^{-1}\Big]\right\},$$

$$=\lim_{\epsilon\to 0}\left\{-(\ln\epsilon+1)-\frac{1}{2}\int_1^{\infty}\frac{du}{u}\frac{1}{2\pi}\int_0^{2\pi} d\phi\ln\left(\frac{4}{\epsilon\gamma\rho(u^2+1-(u^2-1)\cos\phi)}\right)\right.$$
$$\left.-2\sum_1^{\infty}(-1)^n\int_0^{\infty} d\zeta\,\zeta\int_0^{\infty} du\, e^{-\frac{1}{4}(u^2+1)\rho\zeta^2}I_0(\tfrac{1}{4}(u^2-1)\rho\zeta^2)\frac{1}{(n\pi)^2+(\zeta u)^2}\right\},$$

$$=\ln\left(\frac{2(2\gamma\rho)^{1/2}}{e}\right)-2\sum_1^{\infty}(-1)^n\int_0^{\infty} dt\int_0^{\infty} d\zeta\,\zeta\int_0^{\infty} du\, e^{-\frac{1}{4}(u^2+1)\rho\zeta^2-t[(n\pi)^2+(\zeta u)^2]}I_0(\tfrac{1}{4}(u^2-1)\rho\zeta^2),$$

$$=\ln\left(\frac{2(2\gamma\rho)^{1/2}}{e}\right)-\sum_1^{\infty}(-1)^n\int_0^{\infty} dt\, e^{-t(n\pi)^2}\int_1^{\infty} du\left\{\left(\frac{u^2-1}{4}\rho+u^2t\right)^2-\left(\frac{u^2-1}{4}\rho\right)^2\right\}^{-1/2},$$

$$=\ln\left(\frac{2(2\gamma\rho)^{1/2}}{e}\right)-\sum_1^{\infty}(-1)^n\int_0^{\infty} dt\frac{e^{-t(n\pi)^2}}{(\rho(\rho+2t))^{1/2}}\ln\left(\frac{(\rho+2t)^{1/2}+\sqrt{\rho}}{(\rho+2t)^{1/2}-\sqrt{\rho}}\right), \tag{A6}$$

where we have made use of the identity

$$\int_0^{\infty} dx\, e^{-ax}I_0(bx)=(a^2-b^2)^{-1/2},\quad \mathrm{Re}a>\mathrm{Re}b.$$

The last expression can be expanded in powers of ρ^{-1} and $\rho^{-1}\ln\rho$.

B. The Calculation of Diagram (b)

$$j=\frac{ie}{m}(\nabla_{\mathbf{r}}-\nabla_{\mathbf{r}'})T\sum_n\int\int d^3\mathbf{r}_1\,d^3\mathbf{r}_2\,G_\omega(\mathbf{r}',\mathbf{r}_2)G_\omega(\mathbf{r}_1,\mathbf{r}_2)G_{-\omega}(\mathbf{r}_1,\mathbf{r})\Delta^\dagger(\mathbf{r}_1)\Delta(\mathbf{r}_2)\,|_{\mathbf{r}'=\mathbf{r}}$$

$$=\frac{e}{m}T\sum\int d^3\mathbf{r}_1\int d^3\mathbf{r}_2\int\frac{d^3\mathbf{p}}{(2\pi)^3}\int\frac{d^3\mathbf{q}_1}{(2\pi)^3}\int\frac{d^3\mathbf{q}_2}{(2\pi)^3}\mathbf{p}\cdot\frac{e^{i\mathbf{q}_1\cdot(\mathbf{r}-\mathbf{r}_1)-i\mathbf{q}_2\cdot(\mathbf{r}-\mathbf{r}_2)-ieH_0\Lambda_1}}{(i\omega-\xi)(i\omega+\xi-\mathbf{v}\cdot\mathbf{q}_1)(i\omega+\xi+\mathbf{v}\cdot\mathbf{q}_2)}\Delta^\dagger(\mathbf{r}_1)\Delta(\mathbf{r}_2)$$

$$=\frac{e}{m}T\sum\frac{mp_0}{(2\pi)^2}\int d\Omega\int d^3\mathbf{r}_1\int d^3\mathbf{r}_2\int\frac{d^3\mathbf{q}_1}{(2\pi)^3}\int\frac{d^3\mathbf{q}_2}{(2\pi)^3}\mathbf{p}\cdot\frac{e^{i\mathbf{q}_1\cdot(\mathbf{r}-\mathbf{r}_1)-i\mathbf{q}_2\cdot(\mathbf{r}-\mathbf{r}_2)-ieH_0\Lambda_1}}{(2i\omega-\mathbf{v}\cdot\mathbf{q}_1)(2i\omega+\mathbf{v}\cdot\mathbf{q}_2)}\Delta^\dagger(\mathbf{r}_1)\Delta(\mathbf{r}_2),\tag{A7}$$

where

$$\Lambda_1=(x_1+x_2)(y_2-y_1)+\tfrac{1}{2}[(y-y_1)(x-x_2)+(y-y_2)(x_1-x)].$$

Substituting $\Delta(\mathbf{r})=\sum_n C_n e^{ikny}\psi_n(x)$, where $\psi_n(x)=\exp[-eH_0(x-kn/2eH_0)^2]$, we obtain

$$j_i=[eN/m(2\pi T)^2]\sum_{n,m}C_nC_m{}^\dagger J_{n,m,i},\tag{A8}$$

$$J_{n,m,x}=\frac{2mp_0}{N}T^2e^{ik(n-m)y}\int\frac{d\Omega}{4\pi}\int_{-\infty}^{\infty}dx_1\int_{-\infty}^{\infty}dx_2\theta((x_1-x)(x-x_2))\frac{e^{i\alpha eH_0\Lambda_2}\psi_n(x_1)\psi_m(x_2)}{\sinh((2\pi T/vz)|x_1-x_2|)},\tag{A9}$$

$$J_{n,m,y}=\frac{2mp_0}{N}T^2e^{ik(n-m)y}\int\frac{d\Omega}{4\pi}\int_{-\infty}^{\infty}dx_1\int_{-\infty}^{\infty}dx_2\theta((x_1-x)(x-x_2))\frac{i\alpha e^{i\alpha eH_0\Lambda_2}\psi_n(x_1)\psi_m(x_2)}{\sinh((2\pi T/vz)|x_1-x_2|)},\tag{A10}$$

where $z=\cos\theta$, $\alpha=\tan\theta\cos\phi$, $d\Omega=d\cos\theta\,d\phi$,

$$\Lambda_2=\left\{\left(x_1-\frac{kn}{2eH_0}\right)^2-\left(x_2-\frac{km}{2eH_0}\right)^2+\frac{k(n-m)}{eH_0}x-\left(\frac{k}{2eH_0}\right)^2(n^2-m^2)\right\},$$

and

$$\begin{aligned}\theta(a)&=1\quad\text{for}\quad a>0,\\&=0\quad\text{for}\quad a<0.\end{aligned}\tag{A11}$$

It is easy to see that the above expressions satisfy the equation of continuity $\partial j_x/\partial x+\partial j_y/\partial y=0$.

Equations (A9) and (A10) are further simplified as

$$J_{n,m,x}=\frac{2mp_0}{N}T^2e^{ik(n-m)y}\int\frac{d\Omega}{4\pi}\int_0^{\infty}dx_1\int_0^{\infty}dx_2\left\{\psi_n(x+x_1)\psi_m(x-x_2)e^{i\alpha eH_0\Lambda_2'}\Big/\sinh\left(\frac{2\pi T}{vz}|x_1+x_2|\right)+\begin{pmatrix}x_1\to-x_1\\x_2\to-x_2\end{pmatrix}\right\},\tag{A12}$$

and

$$J_{n,m,y}=\frac{2mp_0}{N}T^2e^{ik(n-m)y}\int\frac{d\Omega}{4\pi}i\alpha\int_0^{\infty}dx_1\int_0^{\infty}dx_2\left\{\psi_n(x+x_1)\psi_m(x-x_2)e^{i\alpha H_0\Lambda_2'}\Big/\sinh\left(\frac{2\pi T}{vz}|x_1+x_2|\right)+\begin{pmatrix}x_1\to-x_1\\x_2\to-x_2\end{pmatrix}\right\},\tag{A13}$$

where

$$\Lambda_2'=\{x_1^2-x_2^2+2x_1(x-kn/2eH_0)+2x_2(x-km/2\rho H_0)\}.\tag{A14}$$

We finally obtain

$$J_{n,m,i}=e^{ik(n-m)y}\psi_n(x)\psi_m(x)B_i(x+kn/2eH_0,\,x+km/2eH_0)\quad\text{for}\quad i=x,y,\tag{A15}$$

where B_i is given in Eq. (27).

C. The Calculation of Diagram (c)

$$R=T\sum_n\iiiint d^3\mathbf{r}_1\,d^3\mathbf{r}_2\,d^3\mathbf{r}_3\,d^3\mathbf{r}_4\,G_\omega(\mathbf{r}_1,\mathbf{r}_2)G_{-\omega}(\mathbf{r}_3,\mathbf{r}_2)G_\omega(\mathbf{r}_3,\mathbf{r}_4)G_{-\omega}(\mathbf{r}_1,\mathbf{r}_4)\Delta^\dagger(\mathbf{r}_1)\Delta(\mathbf{r}_2)\Delta^\dagger(\mathbf{r}_3)\Delta(\mathbf{r}_4).\quad\text{(A16)}$$

Substituting in the above expression

$$\Delta(x)=\sum_{n=-\infty}^{\infty}C_ne^{ikny}\psi_n(x)$$

we obtain after a similar calculation to that given in the preceding subsections

$$R=(mp_0/(2\pi)^2v^2)T\sum_{n,m,p}C_n{}^\dagger C_m{}^\dagger C_{n+p}C_{m-p}S_{n,n+p,m,m-p}\,,\quad\text{(A17)}$$

$$S_{n_1,n_2,n_3,n_4}=\int\frac{d\Omega}{z^3}\iiiint dx_1\,dx_2\,dx_3\,dx_4\,\theta(1,3\,;2,4)\times\frac{e^{i\alpha eH_0\Lambda_3}}{\sinh((2\pi T/vz)|x_1+x_3-x_2-x_4|)}\psi_{n_1}(x_1)\psi_{n_2}(x_2)\psi_{n_3}(x_3)\psi_{n_4}(x_4)\,,\quad\text{(A18)}$$

where

$$\theta(1,3\,;2,4)=1\,,\quad\text{for}\quad x_1,\,x_3>x_2,\,x_4$$
$$\text{or}\quad x_1,\,x_3<x_2,\,x_4\,,$$
$$=0\quad\text{otherwise};$$
$$z=\cos\theta\,,\quad\alpha=\tan\theta\,\cos\phi\,,\quad d\Omega=d\,\cos\theta\,d\phi$$

and

$$\Lambda_3=\left(x_1-\frac{kn_1}{2eH_0}\right)^2+\left(x_3-\frac{kn_3}{2eH_0}\right)^2-\left(x_2-\frac{kn_2}{2eH_0}\right)^2-\left(x_4-\frac{kn_4}{2eH_0}\right)^2-\left(\frac{k}{2eH_0}\right)^2(n_1{}^2+n_3{}^2-n_2{}^2-n_4{}^2).\quad\text{(A19)}$$

The above integration can be further carried out and we have

$$S_{n_1,n_2,n_3,n_4}=(v^3/(2\pi T)^2)e^{-C(n_i)}s(n_1,n_2,n_3,n_4)\,,\quad\text{(A20)}$$

where

$$C(n_i)=(k^2/4eH_0)\{n_1{}^2+n_2{}^2+n_3{}^2+n_4{}^2-\tfrac{1}{4}(n_1+n_2+n_3+n_4)^2\}$$
$$=(k^2/4eH_0)[(n_1-n_3)^2+(n_2-n_4)^2]\,,\quad\text{(A21)}$$

$$s(n_1,n_2,n_3,n_4)=\frac{1}{2\pi(eH_0)^{1/2}}\int\frac{d\Omega}{z^3}\int_0^\infty\frac{t^2dt}{\sinh(t/z)}\int_0^1du\int_{-u}^{u}\frac{dv}{2}e^{-\rho t^2\Lambda(u,v,\alpha)}\cosh[(\rho)^{1/2}t\Sigma(u,v,\alpha\,;n_i)]\,,\quad\text{(A22)}$$

$$\Lambda(u,v,\alpha)=\{\tfrac{1}{2}((1-u)^2+v^2)-\tfrac{1}{2}i\alpha((1-u)^2-v^2)+\tfrac{1}{4}(1+\alpha^2)\}\,,\quad\text{(A23)}$$

and

$$\Sigma(u,v,\alpha\,;n_i)=(k/2(eH_0)^{1/2})\{(1-i\alpha)(1-u)(n_1-n_3)+(1+i\alpha)v(n_2-n_3)\}\,.\quad\text{(A24)}$$

As we shall show below, s depends on n_i very weakly and it is a good approximation to put $s(n_1,n_2,n_3,n_4)\simeq s(0,0,0,0)$.

In this approximation we have

$$R=\frac{mp_0}{(2\pi)^2}\frac{1}{(2\pi T)^2}\frac{1}{2(eH_0)^{1/2}}f_1(\rho)\sum_{n,m,p}C_n{}^\dagger C_m{}^\dagger C_{n+p}C_{m-p}\times\exp\left\{-\frac{k^2}{4eH_0}[(n-m)^2+(n-m+2p)^2]\right\}$$
$$=(mp_0/(2\pi)^2)(2\pi T)^{-2}(\sqrt{\pi})^{-1}f_1(\rho)\langle|\Delta(\mathbf{r})|^4\rangle_{\text{av}}\,,\quad\text{(A25)}$$

where

$$f_1(\rho)=2(eH_0)^{1/2}s(0,0,0,0)\quad\text{(A26)}$$

and given in Eq. (36).

Finally we shall estimate the error involved in the above approximation. As the general discussion is complicated, we consider only asymptotic behaviors. Using the technique we used in subsection (b) we find

$$s(n_1,n_2,n_3,n_4)=\frac{1}{2\pi(eH_0)^{1/2}}\left\{7\zeta(3)-\frac{62}{3}\zeta(5)\rho+\frac{10541}{120}\zeta(7)\rho^2\right.$$

$$\left.-\frac{127}{60}\zeta(7)\rho^2\left[\frac{k^2}{4eH_0}((n_1-n_3)^2+(n_2-n_4)^2)+2\left(\frac{k^2}{4eH_0}\right)^2(n_1-n_3)^2(n_2-n_4)^2\right]\right\},\quad \text{for}\quad \rho\ll 1,\qquad \text{(A27)}$$

$$=\frac{1}{2\pi(eH_0)^{1/2}}4\rho^{-1}\ln(24\gamma\rho)\left\{[\ln(1+\sqrt{2})]^2\right.$$

$$\left.-\left[\frac{1}{2}+\frac{\ln(1+\sqrt{2})}{2\sqrt{2}}-(\ln(1+\sqrt{2}))^2\right]\frac{k^2}{4eH_0}((n_1-n_3)^2+(n_2-n_4)^2)\right\}$$

$$=\frac{1}{2\pi(eH_0)^{1/2}}4\rho^{-1}\ln(24\gamma\rho)\left\{0.77-0.04\frac{k^2}{4eH_0}[(n_1-n_3)^2+(n_2-n_4)^2]\right\},\quad \text{for}\quad \rho\gg 1.\qquad \text{(A28)}$$

Thus we see that in both limiting cases the effect of nonlocality of the kernel K_1 [i.e., the term containing the additional factor (n_1-n_3) and/or (n_2-n_4) in coefficient of $e^{-C(n_i)}$] is quite negligible. This fact suggests that it is a plausible approximation to replace nonlocal kernels by equivalent local ones, as we have done in the derivation of Eq. (35).

PHYSICAL REVIEW VOLUME 139, NUMBER 3A 2 AUGUST 1965

Thermal Expansion and Other Anharmonic Properties of Crystals*

DUANE C. WALLACE
Sandia Laboratory, Albuquerque, New Mexico
(Received 1 March 1965)

The temperature dependences of the thermodynamic functions, as derived from lattice dynamics, are examined for the limit of low temperature and also for high temperatures (those above a high characteristic temperature). Particular attention is given to the effects of anharmonic terms in the lattice potential energy. Detailed calculations are reported for central-potential models for fcc, bcc, and hcp lattices. In particular, the normal-mode frequencies and Grüneisen parameters were calculated for a large number of points in the Brillouin zone as a function of volume; and the specific heat, compressibility, thermal-expansion coefficient, and macroscopic Grüneisen parameter were calculated as functions of temperature and volume. At fixed volume the isothermal compressibility shows little temperature dependence and the explicit anharmonic contribution is small; at zero pressure the compressibility increases with increasing temperature and the explicit anharmonic contribution is again small. The thermal-expansion coefficient exhibits similar behavior at high temperatures. The anharmonic specific heat is proportional to temperature at high temperatures, and also depends strongly on the volume. The effective Debye temperatures and the macroscopic Grüneisen parameters exhibit a wide variety of temperature and volume dependences. Approximations are developed for quantities which determine the behavior of thermodynamic functions at low and high temperatures, and approximate relations between several anharmonic properties are found. These approximations are tested by comparison with accurate calculations for the central-potential models.

I. INTRODUCTION

THE purpose of the present paper is to report the results of a study of the thermodynamic properties of crystal lattices. The study is based on the lattice-dynamics free energy, and particular attention is given to the effects of the anharmonic terms in the lattice potential energy. Detailed calculations of thermodynamic functions for models based on central-potential interactions among the ions have been carried out for fcc, bcc, and hcp lattices. Even though the central-potential models are probably inadequate for an accurate description of most real materials, it is believed that the qualitative behavior of these models is representative of real crystals.

In order to study the statistical thermodynamics of a system, the first step is to define a mechanical problem of motion for the system. If the thermodynamic properties are to be studied as a function of configuration, then it is necessary to formulate the mechanical problem in such a way as to allow the configuration to be varied. Indeed, this is necessary in principle in order to define a

* This work was supported by the U. S. Atomic Energy Commission.