The bulk critical field $H_{c b}$ of a $\mathrm{Sn}-5 \%$ In alloy is approximately equal to that of pure tin, ${ }^{26} 304$ Oe. For tin we take $\lambda_{L}=355 \AA$ and $\xi_{0}=2300 \AA \AA^{27}$ From $l^{*}$ we compute $\left(l_{\infty}\right)_{H}$ using Eq. (A8), and from $\left(l_{\infty}\right)_{H}$ we compute $\left(l_{R}\right)_{H}$ using Eq. (A7) ; the latter is quoted in Table I for comparison with the value derived from the normal-state resistance measurements. (We quote $l_{R}$ rather than $l_{\infty}$ since $l_{R}$ gives a better measure of the total surface-plus-volume scattering for comparison with the Strässler-Wyder theory, in which all scattering is treated by means of a mean free path. Evidently the concept of a mean free path is a bit indefinite in dealing with small real nonideal samples.) We note that the values based on superconducting properties agree well with the values determined from the normalstate resistance. There is no large systematic difference, which is reassuring. The close agreement is perhaps fortuitous, however, since the conductivity of tin is anisotropic by $50 \%$, and there may be preferential crystal orientation in thin films. Further, the $\rho l$ value inferred from size-effect measurements is 1.9 times as large as the anomalous skin-effect value used above. Thus, $l_{300}$ could range anywhere between 88 and $200 \AA$. If it were in the upper end of this range, it would lead to $l / \xi_{0}$ values in better agreement with those required for a fit to the Strässler-Wyder theory. We do not

[^0]think such a large $l$ value is likely, however, since it would destroy the agreement with $\left(l_{R}\right)_{H}$, it would be based on a less reliable and less appropriate technique (size effect versus anomalous skin effect), and further, the sweeping approximations of the Strässler-Wyder theory might well introduce an error as large as a factor of 2 in the appropriate choice of $l / \xi_{0}$.

The theory to which the tunneling data are compared requires that $\Delta$, the order parameter, be constant across the film. For our films $d \approx \xi_{T}$, so it is not immediately obvious that this requirement will be fulfilled. One of $u^{28}$ has calculated the spatial dependence of $\Delta$ for a thin film in a parallel magnetic field, using a variational approach. This calculation shows that for $\mathrm{Sn}-\mathrm{In} 1$ at $H_{c \|}$ the total variation of $\Delta$ across the film should be $\sim 6 \%$. Thus, we expect the theory to be reasonably applicable.
Because of the requirement that $\Delta$ be spatially constant, the film thickness cannot be too great. In fact, if $d$ is much greater than $\xi_{T}$, surface superconductivity appears, and $\Delta$ may become much smaller in the interior of the film than on the surface. The films also cannot be very thin, since in that case the irregularities in the shape of the film and the nature of the surfaces have an effect on the density of states that is not easily calculable. The films studied in these experiments have thicknesses chosen to lie between these two limits.

[^1]
# Bulk $\left(\boldsymbol{H}_{c 2}\right)$ and Surface $\left(\boldsymbol{H}_{c 3}\right)$ Nucleation Fields of Strong-Coupling Superconducting Alloys* 

Gert Eilenberger $\dagger$ and Vinay Ambegaokar<br>Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York

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#### Abstract

The linearized self-consistency equation, in the electron-phonon model, for the nucleation of superconductivity in the presence of a magnetic field is studied. It is found that near the transition temperature this integro-differential equation is susceptible to analysis. The main results are that the ratio of surface to bulk nucleation fields is predicted to have the weak-coupling value of 1.695 , thus not confirming a recent experimental suggestion of a value near 1.9 for strong-coupling superconductors. The slope $\left(\partial H_{c z} / \partial T\right)_{T_{c}}$ is worked out both in terms of integrals over the parameters of the bulk-strong-coupling theory and in terms of other experimental quantities. Comparison of this last result with existing experiments on pure lead is attempted, with good success. In the Appendix an implicit equation for $H_{c 2}(T)$ for all $T$ is derived, but the numerical work necessary to solve this equation has not been undertaken.


## 1. INTRODUCTION

IN this paper we discuss the theory of critical magnetic fields for the nucleation of superconductivity in dilute alloys of materials in which the coupling between electrons and lattice vibrations is strong.

With a view to understanding some recent experiments discussed below, we have derived and studied

[^2]the linearized self-consistency equation for the order parameter of a strong-coupling superconductor in an external magnetic field, allowing for spatial variations. We have found that this equation is rather more amenable to analysis than one might have imagined. The solution can always be written as the product of a position-dependent and a frequency-dependent function. Near the critical temperature $\left(T_{c}\right)$ the position dependent part obeys a linearized Ginsburg-Landau equation, with its well-known solutions for surface and bulk nucleation. The ratio of the surface $\left(H_{c 3}\right)$ to bulk
( $H_{c 2}$ ) nucleation fields is thus predicted to have the value 1.695 calculated by St. James and de Gennes ${ }^{1}$ for the case of weak coupling. The strong-coupling effects appear, however, in the slopes of $H_{c 2}$ and $H_{c 3}$ versus $T$ just below $T_{c}$. These slopes can be expressed as ratios of integrals involving the parameters of the strong-coupling theory. Further inspection shows that apart from very small corrections all of the effects of the strong coupling can be expressed in terms of other experimental parameters. When this has been done, our result for $\left(\partial H_{c 2} / \partial T\right)_{T_{\theta}}$ is obtained as a product of two factors:
(1) The weak-coupling formula for $\left(\partial H_{c 2} / \partial T\right)_{T_{c}}$ in which, however, the Fermi velocity and the impurity lifetime must be understood as being properly renormalized to account for the effects of the electronic band structure and the Coulomb and electron-phonon interactions.
(2) A factor which reduces to 1 in the weak-coupling limit and is made up of the ratios $\Delta^{2}{ }_{\text {obs }} / \Delta^{2}{ }_{\mathrm{BCS}}$ and $H^{2}{ }_{c, \text { obs }} / H^{2}{ }_{c, \mathrm{BCS}}$, where $\Delta_{\text {obs }}$ and $H_{c, \text { obs }}$ are the empirical gap and bulk critical fields, and $\Delta_{\mathrm{BCS}}, H_{c, \mathrm{BCS}}$ the values given by the Bardeen, Cooper, Schrieffer theory.

It is also possible to discuss the bulk-nucleation field $H_{c 2}$ for all temperatures, using methods previously developed by one of the authors. ${ }^{2}$ The equation determining $H_{c 2}(T)$ is an implicit one and requires numerical analysis not given here.

Cardona and Rosenblum ${ }^{3}$ have recently reported measurements of $H_{c 3}$ and $H_{c}$ (the thermodynamic critical field) for Pb and $\mathrm{Pb}-\mathrm{Tl}$ alloys, these being strong-coupling materials. In some cases $H_{c 2}$ has also been measured. These authors have interpreted their results as showing that the ratio of $H_{c 3}$ to $H_{c 2}$ is anomalous (1.9 as opposed to 1.7).

Our results are evidently in conflict with this interpretation. However, the conflict may not be one between theory and experiment for the following two reasons. Firstly, in most of the cases studied in Ref. 3, $H_{c 2}$ is a supercooling field not directly measured but inferred semiempirically from $H_{c}$ by methods we have
not been able to understand, but which apparently make use of weak-coupling formulas, the validity of which is not obvious. Secondly, ${ }^{4}$ the surface conditions in the experiments may not have been ideal in that adsorbed gases at the surface may have led to a higher impurity concentration at the surface compared to the bulk material. Since the nucleation fields increase with impurity concentration, an experimental sample of the sort described above would show an $H_{c 3}$ increased relative to $H_{c 2}$. Such an effect, if present, might account for at least some of the discrepancy.
A more direct comparison between theory and experiment could be achieved by working out the prediction of the theory for the slope $\left(\partial H_{c 3} / \partial T\right)_{T_{c}}$ for the experimental materials. However, the residual resistivity enters as a parameter of the theory, and its value for the experimental samples is not reported. A rough calculation carried out in Sec. 5 of this paper shows that for pure lead there is satisfactory agreement between theory and experiment, but more experiments are desirable for a conclusive test.

## 2. THE LINEARIZED SELF-CONSISTENCY EQUATION

We start from the equations of motion for the normal and anomalous electron Green's functions in the phonon model. A useful form for these Green's functions is the matrix

$$
\begin{equation*}
\widehat{G}_{i j}\left(x, x^{\prime}\right)=-i\left\langle T\left[\psi_{i}^{\dagger}(x)\left(\tau_{3} \psi\left(x^{\prime}\right)\right)_{j}\right]\right\rangle \tag{2.1}
\end{equation*}
$$

with

$$
\begin{equation*}
\psi(x)=\binom{\psi_{\imath}(\mathbf{r}, t)}{\psi_{\downarrow}{ }^{\dagger}(\mathbf{r}, t)} \tag{2.2}
\end{equation*}
$$

and $\tau_{3}$ the third Pauli matrix. The four entries in the matrix (2.1) we define as follows:

$$
\widehat{G}=\left(\begin{array}{cc}
G & F  \tag{2.3}\\
F^{\dagger} & G^{\dagger}
\end{array}\right)
$$

The equation of motion is then

$$
\left(\begin{array}{cc}
\zeta_{l}+\mu-\left(2 m^{*}\right)^{-1}\left[i^{-1} \boldsymbol{\nabla}-(e / c) \mathbf{A}(\mathbf{r})\right]^{2}-V(\mathbf{r}) & 0  \tag{2.4}\\
0 & -\zeta_{l}+\mu-\left(2 m^{*}\right)^{-1}\left[i^{-1} \nabla+(e / c) \mathbf{A}(\mathbf{r})\right]^{2}-V(\mathbf{r})
\end{array}\right) \widehat{G}\left(\zeta_{l}, \mathbf{r}, \mathbf{r}^{\prime}\right)
$$

Above $V(\mathbf{r})$ is the scattering potential of the impurities and $\zeta_{l}$ is the usual Fourier-series variable

$$
\begin{equation*}
\zeta_{l}=(2 l+1) \pi i / \beta, \quad 1 / \beta=k_{B} T . \tag{2.5}
\end{equation*}
$$

[^3]In Eq. (2.1) we have accounted for the normal part of the Coulomb self-energy $\Sigma_{\text {el-ol }}$ by using the effective mass

$$
\begin{equation*}
m^{*}=m\left(1+\delta m_{\mathrm{el} 1-\mathrm{el}} / m\right) \tag{2.6}
\end{equation*}
$$

Since we shall only be concerned with variations of physical quantities on a scale large compared to atomic

[^4]dimensions, this would seem to be a good approximation. We also follow Scalapino, Schrieffer, and Wilkins ${ }^{5}$ in treating the Coulomb contribution to the anomalous part of the self-energy by introducing a Coulomb pseudopotential. We have then
$\widehat{\Sigma}\left(\zeta_{l}, \mathbf{r}, \mathbf{r}^{\prime}\right)=-(1 / \beta) \sum_{l^{\prime}} D\left(\zeta_{l}, \zeta_{l^{\prime}}, \mathbf{r}, \mathbf{r}^{\prime}\right) \widehat{G}\left(\zeta_{l^{\prime}} \mathbf{r}, \mathbf{r}^{\prime}\right)$,
where $D$ contains the phonon interaction and the Coulomb pseudopotential. Since the influence of the anomalous part of the electron self-energy, be it posi-tion-dependent or not, on the phonon propagator is extremely small, it can be ignored. The same is true for the pseudopotential, so that $D$ depends only on $\mathbf{r}-\mathbf{r}^{\prime}$. Moreover, since $D$ is essentially zero if $\left|\mathbf{r}-\mathbf{r}^{\prime}\right|$
exceeds a few atomic distances whereas $G$ varies appreciably only over distances $\xi \gg k_{F^{-1}}$, it is a very good approximation to replace the $\mathbf{r}-\mathbf{r}^{\prime}$ dependence of $D$ by a $\delta$ function. We get thus
\[

$$
\begin{align*}
D\left(\zeta_{l}, \zeta_{l^{\prime}}, \mathbf{r}, \mathbf{r}^{\prime}\right) & =\delta^{3}\left(\mathbf{r}-\mathbf{r}^{\prime}\right) \lambda\left(\zeta_{l}, \zeta_{l^{\prime}}\right)  \tag{2.8}\\
\widehat{\boldsymbol{\Sigma}}\left(\zeta_{l}, \mathbf{r}, \mathbf{r}^{\prime}\right) & =\delta^{3}\left(\mathbf{r}-\mathbf{r}^{\prime}\right) \widehat{\boldsymbol{\Sigma}}\left(\zeta_{l}, \mathbf{r}\right) \tag{2.9}
\end{align*}
$$
\]

where
$\hat{\Sigma}\left(\zeta_{l}, \mathbf{r}\right)=\left(\begin{array}{cc}\Sigma & \phi \\ \phi^{\dagger} & \Sigma^{\dagger}\end{array}\right)_{\zeta l, \mathbf{r}}=-\beta^{-1} \sum_{l^{\prime}} \lambda\left(\zeta_{l}, \zeta_{l^{\prime}}\right) \widehat{G}\left(\zeta_{l^{\prime}}, \mathbf{r}, \mathbf{r}\right)$.

It is convenient to introduce a hybrid normal-state Green's function obeying the equation

$$
\begin{equation*}
\left\{\zeta_{l}+\mu-\left(2 m^{*}\right)^{-1}\left[i^{-1} \boldsymbol{\nabla}-(e / c) \mathbf{A}(\mathbf{r})\right]^{2}-V(\mathbf{r})\right\} G_{\mathrm{ns}}\left(\zeta_{l}, \mathbf{r}, \mathbf{r}^{\prime}\right)=\delta^{3}\left(\mathbf{r}-\mathbf{r}^{\prime}\right)+\Sigma\left(\zeta_{l}, \mathbf{r}\right) G_{\mathrm{ns}}\left(\zeta_{l}, \mathbf{r}, \mathbf{r}^{\prime}\right) \tag{2.11}
\end{equation*}
$$

where $\Sigma$ is given by the upper-left entry of (2.10). Then the first column of the matrix equation of motion (2.4) can be put in the form

$$
\begin{align*}
G\left(\zeta_{l}, \mathbf{r}, \mathbf{r}^{\prime}\right) & =G_{\mathrm{ns}}\left(\zeta_{l}, \mathbf{r}, \mathbf{r}^{\prime}\right)+\int d^{3} r_{0} G_{\mathrm{ns}}\left(\zeta_{l}, \mathbf{r}, \mathbf{r}_{0}\right) \phi\left(\zeta_{l}, \mathbf{r}_{0}\right) F^{\dagger}\left(\zeta_{l}, \mathbf{r}_{0}, \mathbf{r}^{\prime}\right) \\
F^{\dagger}\left(\zeta_{l}, \mathbf{r}, \mathbf{r}^{\prime}\right) & =\int d^{3} \mathbf{r}_{0} G_{\mathrm{ns}}\left(-\zeta_{l}, \mathbf{r}_{0}, \mathbf{r}\right) \phi^{\dagger}\left(\zeta_{l}, \mathbf{r}_{0}\right) G\left(\zeta_{l}, \mathbf{r}_{0}, \mathbf{r}^{\prime}\right) \tag{2.12}
\end{align*}
$$

Now it is a simple matter to linearize in $\phi$. To lowest order in $\phi, G_{\mathrm{ns}}$ must be replaced by $G_{\mathrm{n}}$, the normal-state electron Green's function. Further, in the second equation of (2.12) the last $G$ must also be replaced by $G_{\mathrm{n}}$. Substituting the resulting equation for $F^{\dagger}$ into the self-consistency condition for $\phi^{\dagger}$ one obtains

$$
\begin{align*}
& \phi^{\dagger}\left(\zeta_{l}, \mathbf{r}\right)=-\beta^{-1} \sum_{l^{\prime}} \lambda\left(\zeta_{l}, \zeta_{l^{\prime}}\right) F^{\dagger}\left(\zeta_{l^{\prime}}, \mathbf{r}, \mathbf{r}\right) \\
& \quad=-\beta^{-1} \sum_{l^{\prime}} \lambda\left(\zeta_{l}, \zeta_{l^{\prime}}\right) \int d^{3} r_{0}\left\langle G_{\mathrm{n}}\left(-\zeta_{l^{\prime}}, \mathbf{r}_{0}, \mathbf{r}\right) G_{\mathrm{n}}\left(\zeta_{l^{\prime}}, \mathbf{r}_{0}, \mathbf{r}\right)\right\rangle_{\phi^{\dagger}}\left(\zeta_{l^{\prime}}, \mathbf{r}_{0}\right) \tag{2.13}
\end{align*}
$$

where the brackets denote an average over impurity configurations and we have, in the usual way, neglected the weak correlations between $\phi$ and the product of $G$ 's that are due to the impurities. The similarities between (2.13) and the weak-coupling result are apparent.

If there were no impurities and no magnetic field, $G_{\mathrm{n}}$ would be given by

$$
\begin{align*}
& G_{\mathrm{n}}\left(\zeta_{l}, \mathbf{r}, \mathbf{r}^{\prime}\right) \\
& =\int \frac{d^{3} k}{(2 \pi)^{3}} \exp \left[i \mathbf{k} \cdot\left(\mathbf{r}-\mathbf{r}^{\prime}\right)\right]\left[\zeta_{l} Z_{n}\left(\zeta_{l}\right)-\epsilon(k)\right]^{-1} \tag{2.14}
\end{align*}
$$

where $\epsilon(k)=k^{2} / 2 m^{*}-\mu$ and $Z_{n}\left(\zeta_{l}\right)$ is given, according to the first row and column of (2.10), by

$$
\begin{equation*}
\zeta_{l}\left(1-Z_{n}\left(\zeta_{l}\right)\right)=(\pi N(0) / \beta) \sum_{l^{\prime}} \lambda\left(\zeta_{l}, \zeta_{l^{\prime}}\right) i \operatorname{sgn}\left(\operatorname{Im} \zeta_{l^{\prime}}\right) \tag{2.15}
\end{equation*}
$$

Above $N(0)$ is the density of states (without phonon enhancement) for electrons of one spin at the Fermi surface. The effects of electronic band structure have to be included in $N(0)$.

[^5]The effects of the magnetic field and the impurities can now be included in exactly the same way as for the weak-coupling case, since they influence only the spatial part of the nonlocal kernel in (2.13). Since the details of the calculation are essentially identical to those in Gor'kov's first papers on this subject, ${ }^{6}$ only the briefest sketch of the calculation will be given.
As far as the magnetic field dependence goes, we may use the semiclassical approximation
$G_{\mathrm{n}}\left(\zeta_{l}, \mathbf{r}, \mathbf{r}^{\prime}\right)=\left.G_{\mathrm{n}}\left(\zeta_{l}, \mathbf{r}, \mathbf{r}^{\prime}\right)\right|_{H=0} ^{\prime \prime} \exp \left[\frac{i e}{c} \int_{\mathbf{r}^{\prime}}^{\mathbf{r}} d \mathbf{s} \cdot \mathbf{A}(\mathbf{s})\right]$,
the integral being along the straight-line path. Furthermore, we may use the identity ${ }^{7}$

$$
\begin{align*}
& \exp \left[\frac{2 i e}{c} \int_{\mathbf{r}}^{\mathbf{r} 1} d \mathbf{s} \cdot \mathbf{A}(\mathbf{s})\right] \phi^{\dagger}\left(\zeta_{l}, \mathbf{r}_{1}\right) \\
& \quad=\left.\exp \left[-i\left(\mathbf{r}_{1}-\mathbf{r}\right) \cdot \mathbf{I}^{\dagger}\left(\mathbf{r}_{0}\right)\right] \phi^{\dagger}\left(\zeta_{l}, \mathbf{r}_{0}\right)\right|_{\mathbf{r} 0=\mathbf{r}} \tag{2.17}
\end{align*}
$$

[^6]where $\boldsymbol{\Pi}^{\dagger}$ is the operator
\[

$$
\begin{equation*}
\boldsymbol{\Pi}^{\dagger}\left(\mathbf{r}_{0}\right)=\left(-(1 / i) \boldsymbol{\nabla}_{\mathrm{r}_{0}}-(2 e / c) \mathbf{A}\left(\mathbf{r}_{0}\right)\right) \tag{2.18}
\end{equation*}
$$

\]

Retaining terms to second order in $\boldsymbol{\Pi}^{\dagger}$ we encounter the zeroth and second moments of the kernel in (2.13). Performing the average over impurities ${ }^{8}$ we obtain

$$
\begin{align*}
& \int d^{3} r\left\langle G_{\mathrm{n}}\left(-\zeta_{l}, \mathbf{r}_{0}, \mathbf{r}\right) G_{\mathrm{n}}\left(\zeta_{l}, \mathbf{r}_{0}, \mathbf{r}\right)\right\rangle_{H=0} \\
& \quad=\pi N(0) /\left|\zeta_{l} Z_{n}\left(\zeta_{l}\right)\right|,
\end{aligned} \begin{aligned}
& \int d^{3} \boldsymbol{r}\left(\mathbf{r}-\mathbf{r}_{0}\right)^{2}\left\langle G_{\mathrm{n}}\left(-\zeta_{l}, \mathbf{r}_{0}, \mathbf{r}\right) G_{\mathrm{n}}\left(\zeta_{l}, \mathbf{r}_{0}, \mathbf{r}\right)\right\rangle_{H=0}  \tag{2.19}\\
& \quad=\frac{1}{4}\left[\pi N(0) v_{F^{2}}\right]\left[\left|\zeta_{l} Z_{n}\left(\zeta_{l}\right)\right|^{2}\left(\left|\zeta_{l} Z_{n}\left(\zeta_{l}\right)\right|+1 / 2 \tau_{\mathrm{tr}}\right)\right]^{-1}
\end{align*}
$$

Above, $v_{F}=\partial \epsilon(k) /\left.\partial k\right|_{k=k_{F}}$ again does not include the phonon enhancement, and $\tau_{t r}$ is a transport lifetime defined as follows [ $n_{i}$ is the density of impurities]:

$$
\begin{align*}
& \tau_{\operatorname{tr}^{-1}}^{-1}=2 \pi n_{i} N(0) \\
& \times \int_{|\mathrm{k}|=\left|\mathrm{k}^{\prime}\right|=k F} \frac{d \Omega_{\mathrm{k}, \mathrm{k}^{\prime}}}{4 \pi}\left|V\left(k-k^{\prime}\right)\right|^{2}\left(1-\cos \theta_{\mathrm{k}, \mathrm{k}^{\prime}}\right) \tag{2.21}
\end{align*}
$$

Here again the density of states $N(0)$ does not include the phonon correction so that $\tau_{\text {tr }}$ is not the lifetime for the scattering of quasiparticle excitations of the electron-phonon system. Later in this paper it will be interesting to notice that physical quantities can be expressed in terms of properly renormalized parameters.

The above discussion shows that for slow spatial variations the equation for $\phi^{\dagger}$ is reduced to

$$
\begin{equation*}
\phi^{\dagger}\left(\zeta_{l}, \mathbf{r}\right)=\frac{-\pi N(0)}{\beta} \sum_{l^{\prime}} \lambda\left(\zeta_{l}, \zeta_{l^{\prime}}\right)\left[\frac{1}{\left|\zeta_{l^{\prime}} Z_{n}\left(\zeta_{l^{\prime}}\right)\right|}-\frac{\frac{1}{12} v_{F^{2}}\left(\mathbf{\Pi}^{\dagger}(\mathbf{r})\right)^{2}}{\left|\zeta_{l^{\prime}} Z_{n}\left(\zeta_{l^{\prime}}\right)\right|^{2}\left[\left|\zeta_{l^{\prime}} Z\left(\zeta_{l^{\prime}}\right)\right|+1 / 2 \tau_{t \mathbf{r}}\right]}\right] \phi^{\dagger}\left(\zeta_{l^{\prime}}, \mathbf{r}\right) . \tag{2.22}
\end{equation*}
$$

In contrast to the normal Ginsburg-Landau-Gorkov differential equation, this is an integro-differential equation. It is extremely interesting to notice, however, that (2.22) clearly allows a separation of variables. Writing

$$
\begin{equation*}
\phi^{\dagger}\left(\zeta_{l}, \mathbf{r}\right)=\phi\left(\zeta_{l}\right) \psi(\mathbf{r}) \tag{2.23}
\end{equation*}
$$

we get the linearized Ginsburg-Landau equation

$$
\begin{equation*}
((1 / i) \boldsymbol{\nabla}+(2 e / c) \mathbf{A}(\mathbf{r}))^{2} \psi(\mathbf{r})=\alpha(T) \psi(\mathbf{r}) \tag{2.24}
\end{equation*}
$$

The parameter $\alpha$ has to be determined by the condition that

$$
\begin{equation*}
\phi\left(\zeta_{l}\right)=\frac{-\pi N(0)}{\beta} \sum_{l^{\prime}} \lambda\left(\zeta_{l}, \zeta_{l^{\prime}}\right)\left[\frac{1}{\left|\zeta_{l^{\prime}} Z_{n}\left(\zeta_{l^{\prime}}\right)\right|}-\frac{\frac{1}{12} v_{F^{2}}{ }^{2}}{\left|\zeta_{l^{\prime}} Z_{n}\left(\zeta_{l^{\prime}}\right)\right| 2\left[\left|\zeta_{l^{\prime}} Z\left(\zeta_{l^{\prime}}\right)\right|+1 / 2 \tau_{\mathrm{tr}}\right]}\right] \phi\left(\zeta_{l^{\prime}}\right) \tag{2.25}
\end{equation*}
$$

has a nontrivial solution.
Since the strong coupling affects the frequency and not the position dependence of the effective electronelectron interaction, there is no reason for the boundary condition appropriate to (2.23) to differ from the usual one. It then follows as usual ${ }^{1}$ that

$$
\begin{equation*}
H_{c 2}=(c / 2 l) \alpha(T), \quad H_{c 3} / H_{c 2}=1.695 \tag{2.26}
\end{equation*}
$$

The last ratio is thus not affected by the strong coupling.

Equation (2.25), which determines $\alpha(T)$, gives a first impression of intractibility, but we shall see that in its region of validity (near $T_{c}$ ) considerable progress can be made analytically.

## 3. REDUCTION OF $\boldsymbol{H}_{c 2}$ TO QUADRATURES

Since Eq. (2.25) for the frequency-dependent amplitude is only valid near $T_{c}$, we shall solve for $\alpha(T)$ by an expansion about this temperature. We employ the device of comparing (2.25) with the equation for the (position-independent) order parameter of the superfluid phase of the bulk material in the absence of a magnetic field.

As a start it is convenient to consider $\phi, Z_{n}, \zeta_{l}, \lambda$, etc. as functions of $l$ and $T$ instead of $\zeta_{l}$ and $T$. In addition,

[^7]it is convenient to make the kernel of (2.25) more symmetrical. We introduce the functions
\[

$$
\begin{equation*}
X(l, T) \equiv \phi\left(\zeta_{l}\right)\left[\left|\zeta_{l} Z_{n}\left(\zeta_{l}\right)\right|\left(T_{c}-T\right)\right]^{-1 / 2} \tag{3.1}
\end{equation*}
$$

\]

and

$$
\begin{equation*}
W(l, T) \equiv\left|\zeta_{l} Z_{n}\left(\zeta_{l}\right)\right| \tag{3.2}
\end{equation*}
$$

Then (2.25) reads

$$
\begin{align*}
& X(l, T)=\sum_{l^{\prime}} K\left(l, l^{\prime}, T\right) \\
& \times\left\{1-\frac{\frac{1}{12} v_{F}^{2} \alpha(T)}{W\left(l^{\prime}, T\right)\left[W\left(l^{\prime}, T\right)+1 / 2 \tau_{\text {tr }}\right]}\right\} X\left(l^{\prime}, T\right) \tag{3.3}
\end{align*}
$$

where $K$ is the real symmetrical kernel

$$
\begin{align*}
& K\left(l, l^{\prime}, T\right)=-(\pi N(0) / \beta)[W(l, T)]^{-1 / 2} \\
& \times \lambda\left(\zeta_{l}, \zeta_{l^{\prime}}, T\right)\left[W\left(l^{\prime}, T\right)\right]^{-1 / 2} \tag{3.4}
\end{align*}
$$

Now the equation for the order parameter $\phi_{b}\left(\zeta_{l}\right)$ of the bulk superconductor with no magnetic field applied is

$$
\begin{align*}
\phi_{b}\left(\zeta_{l}\right) & =-(\pi N(0) / \beta) \\
& \times \sum_{l^{\prime}} \lambda\left(\zeta_{l}, \zeta_{l^{\prime}}\right) \frac{\phi_{b}\left(\zeta_{l^{\prime}}\right)}{\left[\left|\zeta_{l^{\prime}} Z\left(\zeta_{l^{\prime}}\right)\right|^{2}+\phi_{b^{2}}^{2}\left(\zeta_{l^{\prime}}\right)\right]^{1 / 2}} . \tag{3.5}
\end{align*}
$$

As in (3.1) we define

$$
\begin{equation*}
X_{b}(l, T)=\phi_{b}\left(\zeta_{l}\right)\left[W(l, T)\left(T_{c}-T\right)\right]^{-1 / 2} \tag{3,6}
\end{equation*}
$$

Then, clearly, using quantities defined above,

$$
\begin{align*}
& X_{b}(l, T)=\sum_{l^{\prime}} K\left(l, l^{\prime}, T\right) \\
& \times\left[1+\frac{\left(T_{c}-T\right) X_{b}^{2}\left(l^{\prime}\right)}{W\left(l^{\prime}, T\right)}+\frac{Z^{2}\left(l^{\prime}\right)-Z_{n^{2}}^{2}\left(l^{\prime}\right)}{Z_{n}^{2}\left(l^{\prime}\right)}\right]^{-1 / 2} X_{b}\left(l^{\prime}, T\right) \tag{3.7}
\end{align*}
$$

We note that at $T_{c}$ the function $X_{b}\left(l, T_{c}\right)$ solves (3.3) [and, of course, the linear part of (3.7)] thus showing that $\alpha\left(T_{c}\right)=0$ as it must be.

For temperatures slightly below $T_{c}$ we develop all functions in powers of $\left(T_{c}-T\right)$ :

$$
\begin{align*}
& \alpha(T)=\left(T_{c}-T\right) \alpha^{(1)}+\cdots \\
& X(l, T)=X_{b}\left(l, T_{c}\right)+\left(T_{c}-T\right) X^{(1)}(l)+\cdots, \\
& X_{b}(l, T)=X_{b}\left(l, T_{c}\right)+\left(T_{c}-T\right) X_{b}^{(1)}(l)+\cdots \\
& K\left(l, l^{\prime}, T\right)=K\left(l, l^{\prime}, T_{c}\right)+\left(T_{c}-T\right) K^{(1)}\left(l, l^{\prime}\right)+\cdots, \\
& \left(Z^{2}(l, T)-Z_{n}^{2}(l, T)\right) / Z_{n}^{2}(l, T) \\
& \quad=2\left(T_{c}-T\right) Z^{(1)}(l) / Z_{n}\left(l, T_{c}\right)+\cdots \tag{3.8}
\end{align*}
$$

In the last line above

$$
\begin{equation*}
Z^{(1)}(l) \equiv \lim _{T \rightarrow T_{c}} \frac{Z(l, T)-Z_{n}(l, T)}{T_{c}-T}=\left(\frac{d Z_{n}}{d T}-\frac{d Z_{s}}{d T}\right)_{T=T_{c}} \tag{3.9}
\end{equation*}
$$

It is reasonable to stop the expansions with the first power of $\left(T_{c}-T\right)$ because we have already neglected higher powers of the operator $\Pi^{\dagger}$ which would give rise to higher powers of $\alpha$ in (3.3).

Equating terms linear in $\left(T_{c}-T\right)$, we get from (3.3) and (3.5), respectively:

$$
\begin{equation*}
\sum_{l^{\prime}}\left(\delta_{l l^{\prime}}-K\left(l, l^{\prime}, T_{c}\right)\right) X^{(1)}\left(l^{\prime}\right)=\sum_{l^{\prime}}\left\{K^{(1)}\left(l, l^{\prime}\right)-\frac{K\left(l, l^{\prime}, T_{c}\right) \frac{1}{12} v_{F^{2}} \alpha^{(1)}}{W\left(l^{\prime}, T_{c}\right)\left[W\left(l^{\prime}, T_{c}\right)+1 / 2 \tau_{\mathrm{tr}}\right]}\right\} X_{b}\left(l^{\prime}, T_{c}\right) \tag{3.10}
\end{equation*}
$$

and

$$
\begin{equation*}
\sum_{l^{\prime}}\left(\delta_{l l^{\prime}}-K\left(l, l^{\prime}, T_{c}\right)\right) X_{b}^{(1)}\left(l^{\prime}\right)=\sum_{l^{\prime}}\left\{K^{(1)}\left(l, l^{\prime}\right)-K\left(l, l^{\prime}, T_{c}\right)\left[\frac{X_{b}^{2}\left(l^{\prime}\right)}{2 W\left(l^{\prime}, T_{c}\right)}+\frac{Z^{(1)}\left(l^{\prime}\right)}{Z\left(l, T_{c}\right)}\right]\right\} X_{b}\left(l^{\prime}, T_{c}\right) \tag{3.11}
\end{equation*}
$$

We multiply these equations by $X_{b}\left(l, T_{\mathrm{c}}\right)$ and sum over $l$. Using the symmetry of $K$, the left-hand sides are seen to give zero. The first terms on the right of (3.10)-(3.11) cancel on subtraction, and in the second term we again use

$$
\sum_{l} X_{b}\left(l, T_{c}\right) K\left(l, l^{\prime}, T_{c}\right)=X_{b}\left(l^{\prime}, T_{c}\right)
$$

In this way we finally obtain

$$
\begin{align*}
-\left.(\partial / \partial T) H_{c 2}\right|_{r=T_{c}} & =(c / 2 e) \alpha^{(1)} \\
& =(c / e)\left(I_{1}+I^{\prime}{ }_{1}\right) / I_{2} \tag{3.12}
\end{align*}
$$

where

$$
\begin{align*}
I_{1} & =\frac{2 \pi N(0)}{\beta_{c}} \sum_{l} \frac{Z\left(\zeta_{l}\right)\left[\Delta^{(1)}\left(\zeta_{l}\right)\right]^{4}}{2\left|\zeta_{l}\right|^{3}}  \tag{3.13}\\
I_{1}^{\prime} & =\frac{2 \pi N(0)}{\beta_{c}} \sum_{l} \frac{Z^{(1)}\left(\zeta_{l}\right)\left[\Delta^{(1)}\left(\zeta_{l}\right)\right]^{2}}{\left|\zeta_{l}\right|} \tag{3.14}
\end{align*}
$$

and

$$
\begin{equation*}
I_{2}=\frac{2 \pi N(0)}{\beta_{c}} \frac{1}{6} v_{F^{2}} \sum_{l} \frac{\left[\Delta^{(1)}\left(\zeta_{l}\right)\right]^{2}}{\left|\zeta_{l}\right|^{2}\left[\left|\zeta_{l} Z\left(\zeta_{i}\right)\right|+1 / 2 \tau_{\mathrm{tr}}\right]} . \tag{3.15}
\end{equation*}
$$

Above, all sums are to be evaluated at the critical temperature, i.e.,

$$
\zeta_{l}=\pi k_{B} T_{c}(2 l+1) i
$$

The new symbol in these equations is defined according to

$$
\begin{align*}
{\left[\Delta^{(1)}\left(\zeta_{l}\right)\right]^{2} } & =\lim _{T \rightarrow T_{c}} \frac{\phi_{b}^{2}\left(\zeta_{l}\right)}{\left(T_{c}-T\right) Z^{2}\left(\zeta_{l}\right)} \\
& =\lim _{T \rightarrow T_{c}} \frac{\Delta^{2}\left(\zeta_{l}\right)}{\left(T_{c}-T\right)} \tag{3.16}
\end{align*}
$$

The sums (3.13)-(3.15) may be readily converted into integrals along the positive real-frequency axis. In this form, given below, one has reduced the calculation of $\left(\partial H_{c 2} / \partial T\right)_{T_{o}}$ to integrals over the solutions of the [real-frequency] gap equations. Since these solutions have been obtained numerically for various materials, one can then consider that the problem has been reduced to quadratures. Another approach is to try to express $I_{1}, I_{1}^{\prime}$, and $I_{2}$ in terms of experimentally measurable parameters. This approach is the topic of the next section.

Since the analytic continuations $Z\left(\zeta_{l} \rightarrow \omega\right), \Delta\left(\zeta_{l} \rightarrow \omega\right)$ are sufficiently well behaved in the upper and lower half-plane of the complex variable $\omega$, we get, after converting the $\zeta_{l}$ sums to contour integrals in the standard way

$$
\begin{align*}
I_{1}+I_{1}^{\prime} & =-N(0) \int_{0}^{\infty} d \omega \operatorname{Re}\left\{\frac{Z(\omega)\left[\Delta^{(1)}(\omega)\right]^{4}}{\omega^{3}}-\frac{2 Z^{(1)}(\omega)\left[\Delta^{(1)}(\omega)\right]^{2}}{\omega}\right\} \tanh \frac{1}{2}\left(\beta_{c} \omega\right)  \tag{3.17}\\
I_{2} & =-N(0) \frac{1}{3} v_{F_{F}} \int_{0}^{\infty} d \omega \operatorname{Re}\left\{\frac{\left[\Delta^{(1)}(\omega)\right]^{2}}{\omega^{2}\left[\omega Z(\omega)+\left(i / 2 \tau_{\text {tr }}\right)\right]}\right\} \tanh \frac{1}{2}\left(\beta_{c} \omega\right) \tag{3.18}
\end{align*}
$$

Above we have used the well-known ${ }^{9}$ symmetry properties of $Z(\omega)$ and $\Delta(\omega)$. We also note that for finite temperatures $\Sigma(\omega)$ has a nonvanishing imaginary part at $\omega=0$. The quantity $Z(\omega)=1-\Sigma(\omega) / \omega$ therefore has a pole, and $\Delta^{(1)}(\omega)$ vanishes at $\omega=0$. Thus no singularity occurs in the integrands of (3.17) and (3.18). These equations are thus in a form suitable for numerical evaluation, and we hope that they will prove useful for this purpose.

## 4. RELATION OF $H_{\mathrm{c} 2}$ TO OTHER EXPERIMENTAL PARAMETERS

Our formulas (3.12)-(3.15) may also be used to express $\left.(\partial / \partial T) H_{c 2}\right|_{T_{o}}$ quite accurately in terms of other measurable quantities. This possibility is a consequence of the observation that the $\omega$-dependence of $Z$ and $\Delta^{(1)}$ will contribute a rather small correction to the integrals $I_{1}$ and $I_{2}$. Inspecting the tables of $\Delta(\omega)$
and $Z(\omega)^{10}$ for lead, we find that these vary by no more than a few percent in the range $\frac{1}{10} k_{B} T_{c} \leq \omega \leq 4 k_{B} T_{c}$. The variation at small values of $\omega$ comes from the singularity of $Z(\omega)$ mentioned below Eq. (3.18). This variation can be easily taken into account, and the variation for large $\omega$ is unimportant for the problem at hand because of the high power of $\omega$ in the denominator of the integrand.

We introduce

$$
\begin{gather*}
\tilde{Z}(\omega)=Z(\omega)+(\Sigma(0) / \omega)=1-(\Sigma(\omega)-\Sigma(0)) / \omega  \tag{4.1}\\
\tilde{\Delta}^{(1)}(\omega)=\lim _{T \rightarrow T_{c}} \frac{\phi(\omega)}{\left(T_{c}-T\right)^{1 / 2} \widetilde{Z}(\omega)}, \tag{4.2}
\end{gather*}
$$

and

$$
\begin{equation*}
i / 2 \tau_{\mathrm{ph}} \equiv \Sigma(0) / \widetilde{Z}(0), \quad 1 / \tilde{\tau}_{\mathrm{tr}}=1 / \widetilde{Z}(0) \tau_{\mathrm{tr}} \tag{4.3}
\end{equation*}
$$

Using these definitions, the formulas for $I_{1}$ and $I_{2}$ [(3.13) and (3.15)] become

$$
\begin{align*}
I_{1} & =\frac{2 \pi N(0)}{\beta_{c}} \sum_{l=0}^{\infty} \frac{\tilde{Z}\left(\zeta_{l}\right)\left[\tilde{\Delta}^{(1)}\left(\zeta_{l}\right)\right]^{4}}{\left[\left(\pi / \beta_{c}\right)(2 l+1)+\left(|\Sigma(0)| / \tilde{Z}\left(\zeta_{l}\right)\right)\right]^{3}} \\
& =\frac{2 N(0) \beta_{c}^{2}}{\pi^{2}} \widetilde{Z}(0)\left[\tilde{\Delta}^{(1)}(0)\right]^{4} \sum_{l=0}^{\infty} \frac{1}{\left(2 l+1+\beta_{c} / 2 \pi \tau_{\mathrm{ph}}\right)^{3}}+R_{1} .  \tag{4.4}\\
I_{2} & =\frac{2 \pi N(0)}{\beta_{c}} \frac{1}{3} v_{V^{2}} \sum_{l=0}^{\infty} \frac{\left[\tilde{\Delta}^{(1)}\left(\zeta_{l}\right)\right]^{2} / \widetilde{Z}\left(\zeta_{l}\right)}{\left(\left(\pi / \beta_{c}\right)(2 l+1)+\left[\Sigma(0) / \tilde{Z}\left(\zeta_{l}\right)\right]\right)^{2}\left[\left(\pi / \beta_{c}\right)(2 l+1)+\left[\tilde{Z}\left(\zeta_{l}\right)\right]^{-1}\left(|\Sigma(0)|+\left(1 / 2 \tau_{\mathrm{tr}}\right)\right)\right]} \\
& =\frac{2 N(0) \beta_{c}^{2}}{\pi^{2}} \frac{\left[\tilde{\Delta}^{(1)}(0)\right]^{2}}{\tilde{Z}(0)} \frac{1}{3} v_{F}{ }^{2} \sum_{l=0}^{\infty} \frac{1}{\left(2 l+1+\beta_{c} / 2 \pi \tau_{\mathrm{ph}}\right)^{2}\left(2 l+1+\left(\beta_{c} / 2 \pi\right)\left(1 / \tau_{\mathrm{ph}}+1 / \tilde{\tau}_{\mathrm{tr}}\right)\right)}+R_{2} . \tag{4.5}
\end{align*}
$$

The remainders $R_{1}$ and $R_{2}$ can easily be expressed as integrals over real $\omega$. They can be seen to contribute not more than a few percent of the main terms, and they also partially cancel when the ratio $I_{1} / I_{2}$ is taken. The same cancellation occurs for the contribution of $\beta_{c} / 2 \pi \tau_{\mathrm{ph}}$, which is, in any case, of order $0.5 \times 10^{-2}$ in lead and negligible.

The quantity $\widetilde{Z}(0)=1-((\partial / \partial \omega) \Sigma(\omega))_{\omega=0}$ enters in the above formulas in precisely the correct way to renormalize the various parameters. Thus if we introduce,

$$
\begin{equation*}
v_{F}^{*}=k_{F} / m^{*} \widetilde{Z}(0) \quad \text { and } \quad N^{*}(0)=N(0) \widetilde{Z}(0) \tag{4.6}
\end{equation*}
$$

the quantity $\widetilde{Z}(0)$ disappears from (4.4) and (4.5). Incidentally, $\tilde{\tau}_{\mathrm{tr}}=\widetilde{Z}(0) \tau_{\mathrm{tr}}$ is the renormalized lifetime. ${ }^{11}$

Finally we have to deal with $I_{1}^{\prime}$. It is interesting to notice that the same factor occurs in the calculation of the free-energy difference of normal and super-
conducting states as worked out by Bardeen and Stephen. ${ }^{12}$ From Eq. (13) of this reference we find

$$
\begin{align*}
I_{1}-I_{1}^{\prime} & =4\left[\left(\Omega_{n}-\Omega_{s}\right) /\left(T_{c}-T\right)^{2}\right]_{T \rightarrow T_{c}} \\
& =(2 \pi)^{-1}\left[\partial H_{c}\left(T_{c}\right) / \partial T\right]^{2} \tag{4.7}
\end{align*}
$$

We thus have

$$
\begin{equation*}
I_{1}^{\prime}=I_{1}-(2 \pi)^{-1}\left[\partial H_{c}\left(T_{c}\right) / \partial T\right]^{2} \tag{4.8}
\end{equation*}
$$

which together with Eq. (3.12) yields
$-\frac{\partial}{\partial T} H_{c 2}\left(T_{c}\right)=\frac{e}{c} \frac{2 I_{1}-(1 / 2 \pi)\left[\partial H_{c}\left(T_{c}\right) / \partial T\right]^{2}}{I_{2}}$.
To identify explicitly the effects of strong coupling, we introduce expressions from the Bardeen, Cooper, and Schrieffer theory:

$$
\begin{array}{r}
\left(-(\partial / \partial T) \Delta^{2}\left(T_{c}\right)\right)_{\mathrm{BCS}}=\pi^{2}\left(\frac{7}{8} \zeta(3)\right)^{-1} T_{c} \\
(2 \pi)^{-1}\left(\partial H_{c}\left(T_{c}\right) / \partial T\right)_{\mathrm{BCS}}{ }^{2}=2 \pi^{2}\left(\frac{7}{8} \zeta(3)\right)^{-1} N^{*}(0), \tag{4.11}
\end{array}
$$

[^8]and
\[

$$
\begin{align*}
& \left(-\partial H_{c 2}\left(T_{c}\right) / \partial T\right)_{\mathrm{BCS}}=3 \pi^{2}(c / e)\left(T_{c} / v_{F}^{* 2}\right) \\
& \quad \times\left[\sum_{l=0}^{\infty} \frac{1}{(2 l+1)^{2}\left(2 l+1+1 / 2 \pi T_{c} \tau_{\mathrm{tr}}\right)}\right]^{-1} \tag{4.12}
\end{align*}
$$
\]

Then, using (4.4), (4.5), and (4.9) we get

$$
\begin{equation*}
\left(\frac{H_{c 2, \mathrm{obs}}}{H_{c 2, \mathrm{BCS}}}\right)_{T \rightarrow T_{c}}=\left(2 \frac{\Delta_{\mathrm{obs}}^{2}}{\Delta^{2} \mathrm{BCS}}-\frac{H_{c, \text { obs }}^{2}}{H_{c, \mathrm{BCS}}} \frac{\Delta^{2} \mathrm{BCS}}{\Delta_{\mathrm{obs}}^{2}}\right)_{T \rightarrow T_{c}}, \tag{4.13}
\end{equation*}
$$

where the right-hand side gives the explicit strongcoupling correction.

## 5. COMPARISON WITH EXPERIMENT

We first express our results in terms of quantities susceptible to direct measurement, and also re-introduce factors of $\hbar$ and $k_{B}$, equated to 1 so far.

The relevant measurable quantities are: the coefficient of the linear electronic specific heat $\gamma$; the Fermi wave number $k_{F}=\left(3 \pi^{2} n\right)^{1 / 3}$; the area of the Fermi surface $S$; and the residual conductivity $\sigma$. The relations between the quantities that enter our formulas and these are ${ }^{13}$

$$
\begin{align*}
N^{*}(0) & =\left(\gamma / \gamma_{0}\right)\left(m k_{F} / 2 \pi^{2} \hbar^{2}\right)  \tag{5.1}\\
v_{F}^{*} & =\left(\gamma_{0} S / \gamma S_{0}\right)\left(\hbar k_{F} / m\right)  \tag{5.2}\\
\tilde{\tau}_{\mathrm{tr}} & =\left(3 \pi^{2} m \sigma / k_{F} e^{2}\right)\left(\gamma / \gamma_{0}\right)\left(S_{0} / S\right)^{2} \tag{5.3}
\end{align*}
$$

where we have introduced the free-electron parameters $S_{0}$ and $\gamma_{0}$, corresponding to $S$ and $\gamma$, namely, $S_{0}=4 \pi k_{F}{ }^{2}$ and $\gamma_{0}=\left(2 \pi^{2} k_{B}{ }^{2} / 3\right)\left(m k_{F} / 2 \pi^{2} \hbar^{2}\right), m$ being the freeelectron mass.

Substituting these formulas into Eqs. (4.10)-(4.12), and introducing numerical values for universal constants, we find

$$
\begin{equation*}
-\partial / \partial T\left(\Delta_{\mathrm{BCS}} / k_{B} T_{c}\right)^{2} T_{0}=9.4 / T_{c} \tag{5.4}
\end{equation*}
$$

$$
\begin{aligned}
\left(\partial H_{c}\left(T_{c}\right) / \partial T\right)^{2}{ }_{\mathrm{BCS}} & =\left(4 \pi^{3} / \frac{7}{8} \zeta(3)\right) k_{B}{ }^{2} N^{*}(0) \\
& =0.93 \times 10^{4} k_{F}\left(\gamma / \gamma_{0}\right)\left(\mathrm{Oe} /{ }^{\circ} \mathrm{K}\right)^{2} \AA .
\end{aligned}
$$

$$
\begin{equation*}
\left(-\frac{\partial H_{c 2}\left(T_{c}\right)}{\partial T}\right)_{\mathrm{BCS}}=\frac{3 \pi^{2}}{\frac{7 \zeta}{8} \zeta(3)} \chi^{-1}(\rho)\left(\frac{k_{B}^{2} c}{\hbar e}\right) \frac{T_{c}}{v_{F}^{* 2}} \tag{5.5}
\end{equation*}
$$

$$
=2.36 \chi^{-1}(\rho)\left(T_{c} / k_{F}{ }^{2}\right)\left(\gamma S_{0} / \gamma_{0} S\right)^{2}
$$

$$
\begin{equation*}
\times \mathrm{Oe} /\left({ }^{\circ} \mathrm{K} \AA\right)^{2} \tag{5.6}
\end{equation*}
$$

The symbol $\chi(\rho)$ in this formula denotes the function introduced by Gor'kov ${ }^{6}$

$$
\chi(\rho)=\frac{8}{7 \zeta(3)} \sum_{l=0}^{\infty}[(2 l+1)(2 l+1+\rho)]^{-1}
$$

[^9]where
$\rho=\left(\hbar / 2 \pi k_{B} T_{c} \tilde{\tau}_{\text {tr }}\right)=11.6\left(\frac{k_{F}{ }^{3}}{T_{c} \sigma}\right)\left(\frac{\gamma_{0}}{\gamma}\right)\left(\frac{S}{S_{0}}\right)^{2} \frac{10^{6}}{\Omega \mathrm{~cm}}{ }^{\circ} \mathrm{K} \AA^{3}$.

These formulas should prove useful for other applications.

The only application of our results we shall make here, in view of the somewhat unclear experimental situation described in the Introduction, is to pure lead. The relevant experimental data for Eqs. (5.5)-(5.6) are $k_{F}=1.57 \AA^{-1} ;\left(S / S_{0}\right)=0.7$ (Ref. 14) $;\left(\gamma / \gamma_{0}\right)=2.05$ (Ref. 15) ; $T_{c}=7.2^{\circ} \mathrm{K}$. Using these data we obtain

$$
\begin{equation*}
\left(-\partial H_{c 2}\left(T_{c}\right) / \partial T\right)_{\mathrm{BCS}}=56 \chi^{-1}(\rho) \mathrm{Oe} /{ }^{\circ} \mathrm{K} \tag{5.8}
\end{equation*}
$$

and

$$
\begin{equation*}
\left(-\partial H_{c}\left(T_{c}\right) / \partial T\right)_{\mathrm{BCS}}=173 \mathrm{Oe} /{ }^{\circ} \mathrm{K} \tag{5.9}
\end{equation*}
$$

For the other quantities in the enhancement factor, Eq. (4.13) we use the experimental result $\left(\partial H_{c} / \partial T\right)_{T_{c}}=$ $235\left(\mathrm{Oe} /{ }^{\circ} \mathrm{K}\right),{ }^{15}$ and the fact that for lead $\Delta(T) / \Delta(0)$ versus $T / T_{c}$ follows the BCS curve very closely ${ }^{16}$ to get ${ }^{17}$

$$
\begin{aligned}
&\left(\Delta_{\mathrm{obs}}^{2} / \Delta^{2}{ }_{\mathrm{BCS}}\right)_{T \rightarrow T_{\mathrm{c}}}=\left(\Delta_{\mathrm{obs}}^{2} / \Delta^{2} \mathrm{BCS}\right)_{T \rightarrow 0} \\
&=\left(\Delta_{\mathrm{obs}}(0) / 1.76 k_{B} T_{c}\right)^{2}=1.52
\end{aligned}
$$

With the above values and the result (5.9), we obtain for the factor on the right of (4.13)

$$
\begin{equation*}
\left[2 \frac{\Delta^{2}{ }_{\mathrm{obs}}}{\Delta^{2}{ }_{\mathrm{BCS}}}-\frac{H_{c, \mathrm{obs}}^{2}}{H_{c, \mathrm{BCS}}^{2}} \frac{\Delta^{2} \mathrm{BCS}^{2}}{\Delta_{\mathrm{obs}}}\right]=1.8 \tag{5.10}
\end{equation*}
$$

We thus have the prediction from (4.13) and (2.26).

$$
\begin{align*}
\left(-\partial H_{c 3} / \partial T\right)_{T_{c}} & =1.7 \times 1.8 \times 56 \chi^{-1}(\rho) \mathrm{Oe} /{ }^{\circ} \mathrm{K} \\
& =170 \chi^{-1}(\rho) \mathrm{Oe} /{ }^{\circ} \mathrm{K} . \tag{5.11}
\end{align*}
$$

Cardona and Rosenblum ${ }^{3}$ reported that for pure lead $\left(H_{c 3} / H_{c}\right)_{r_{c}}=0.88$. Using the experimental value for $H_{c}$ given below Eq. (5.9) we find

$$
\begin{equation*}
\left(-\partial H_{c 3} / \partial T\right)_{T_{c}, \exp }=206 \mathrm{Oe} /{ }^{\circ} \mathrm{K} \tag{5.12}
\end{equation*}
$$

For the bulk of the experimental material one would certainly expect $\chi(\rho)=1$ to be an excellent approximation. This would then suggest a $20 \%$ discrepancy between theory and experiment, which would be disturbing since we have reduced our results, with small errors, to a consistency check between experiments with no free parameters whatsoever.

[^10]One source of the discrepancy may be the assumption of isotropy inherent in the relation between the parameters of the theory and empirical quantities (5.1)-(5.3). Different averages of the Fermi velocity over the Fermi surface occur in the formal expressions for the conductivity $\sigma$ and the density of states $N^{*}(0)$. Equating these average velocities may have led to error of perhaps $10 \% .^{14}$

Another way out of the difficulty is to assume that the value of 1.9 for $H_{c 3} / H_{c 2}$ quoted by Cardona and Rosenblum reflects a concentration gradient of impurities in their sample so that

$$
\begin{equation*}
\chi^{-1}(\rho)_{\text {surface }} / \chi^{-1}(\rho)_{\text {bulk }}=1.9 / 1.7 \tag{5.13}
\end{equation*}
$$

If we take $\chi(\rho)_{\text {bulk }}$ to be 1 and substitute (5.13) into (5.11) we get $\left(\partial H_{c 3} / \partial T\right)_{T_{c}, \text { theory }}=190 \mathrm{Oe} /{ }^{\circ} \mathrm{K}$, leaving an $8 \%$ discrepancy which is as small as one could reasonably expect, particularly in view of the remarks in the preceding paragraph. However, this interpretation is speculative and can be criticized because the thickness of the surface sheath ${ }^{1}$ is roughly $3 \times(\hbar c / e H)^{1 / 2}$ which becomes large near $T_{c}\left(\sim 10^{4} \AA\right.$ for $\left.H \sim 10^{2} \mathrm{Oe}\right)$. It may not be reasonable to assume that the surface imperfections extend to such a depth.

It is, of course, also possible that we have taken the experimental numbers too seriously above, and that some of the error is experimental.

Our conclusion, therefore, is that the theory of $\left(\partial H_{c 3} / \partial T\right)_{T_{c}}$ is in good, though not perfect, agreement with existing experiments, but that more of the latter are clearly desirable. As a last remark it is interesting to notice that without the explicit strong-coupling correction (5.10), theory and experiment would be in serious disagreement.
[Note added in proof: After submitting this paper for publication we became aware of related work by N . Menyhàrd [Nuovo Cimento, 44, 213 (1966); Acta Phys. Hung. 21, 277 (1966)]. In this work the Gins-burg-Landau equations, including the nonlinear term, for strong-coupling superconductors are derived. The separation into a differential equation in space and an integral equation in frequency is pointed out, but no specific applications are made. We are grateful to Mrs. Szépfalusy for bringing this work to our attention, and apologize for not having been aware of it.

An unpublished report by E. D. Yorke and A. Bardasis has also recently reached us. This work has much the same aim and approach as ours, and reaches much the same conclusions by the use, however, of numerical methods.

Dr. B. Rosenblum has informed us that we have taken too seriously what was intended to be a tentative suggestion that the measured ratio 1.9 might have something to do with strong coupling.]

## APPENDIX: THE BULK NUCLEATION FIELD FOR ALL TEMPERATURES

In Sec. 2 we have seen that the procedure which leads to an expression for $F^{\dagger}$ is essentially independent of the strong-coupling assumption; one simply had to replace $\zeta_{l}$ and $\Delta(r)$ in the weak-coupling expression by $\zeta_{l} Z\left(\zeta_{l}\right)$ and $\phi\left(\zeta_{l}, r\right)$, respectively, to get the strongcoupling expression.
This principle may be applied to derive an equation for $H_{c 2}$ at arbitrary temperatures. In doing this, we apply step by step the methods developed in a recent paper by one of the authors, ${ }^{2}$ arriving at

$$
\begin{equation*}
F^{\dagger}\left(\zeta_{l}, \mathbf{r}_{0}, \mathbf{r}\right)=\pi N(0)\left(1+\frac{\eta_{l} f\left(\eta_{l}\right)-1}{D\left(\eta_{l}\right)}\right) \frac{\phi\left(\zeta_{l}\right) \psi(\mathbf{r})}{\left|\zeta_{l} Z\left(\zeta_{l}\right)\right|} \tag{A1}
\end{equation*}
$$

for the term of $F^{\dagger}$ which is linear in $\phi$. The new symbols in this formula mean

$$
\begin{align*}
\eta_{l} & =\frac{2\left|\zeta_{l} Z\left(\zeta_{l}\right)\right|+1 / \tau}{v_{F}\left[(e / c) H_{c 2}(T)\right]^{1 / 2}}  \tag{A2}\\
\tau^{-1} & =2 \pi n_{i} N(0) \int_{|\mathbf{k}|=\left|\mathbf{k}^{\prime}\right|=k_{F}} \frac{d \Omega_{\mathrm{kk}^{\prime}}}{4 \pi}\left|V\left(k-k^{\prime}\right)\right|^{2} \tag{A3}
\end{align*}
$$

and the functions $f$ and $D$ are those defined and discussed in Ref. 2. As in Sec. 2, the assumption was made that $\phi^{\dagger}\left(\zeta_{l}, \mathbf{r}\right)$ separates [Eq. (2.23)] and that $\psi(\mathbf{r})$ is an eigenfunction of Eq. (2.24) with $\alpha(T)=(2 e / c) H_{c 2}$ ( $T$ ), where $H_{c 2}(T)$ still has to be determined.
Using Eq. (A1), we get the self-consistency condition

$$
\begin{align*}
\phi\left(\zeta_{l}\right) \psi(\mathbf{r})=- & \frac{\pi N(0)}{\beta} \sum_{l^{\prime}} \lambda\left(\zeta_{l}, \zeta_{l^{\prime}}\right) \\
& \times\left(1+\frac{\eta_{l^{\prime}} f\left(\eta_{l^{\prime}}\right)-1}{D\left(\eta_{l^{\prime}}\right)}\right) \frac{\phi\left(\zeta_{l}\right) \psi(\mathbf{r})}{\left|\zeta_{l} Z\left(\zeta_{l}\right)\right|} \tag{A4}
\end{align*}
$$

The position-dependent function $\psi(\mathbf{r})$ cancels out of Eq. (A4), proving the correctness of the assumption (2.23) for the general case. If we were to assume $\lambda$ constant (and to employ the well-known procedure for removing the consequent divergence of the sum) $\phi\left(\zeta_{l}\right)$ would be constant and also cancel out. We would then be left with an algebraic equation, identical to Eq. (4.7) of Ref. (2), which contains $H_{c 2}(T)$ rather implicitly and has the meaning that $H_{c 2}(T)$ is to be so determined as to satisfy this equation.

Equation (A4) is now an even more implicit equation for $H_{c 2}(T)$, since, for any given temperature $T, H_{c 2}$ has to be chosen so as to allow the homogeneous integral equation to have a nonzero solution $\phi\left(\zeta_{l}\right)$. We have chosen not to undertake the large numerical effort required to solve this equation, but have thought it worthwhile to make the formula known.


[^0]:    ${ }^{26}$ M. Doidge, Phil. Trans. Roy. Soc. London 248, 553 (1956).
    ${ }^{27}$ J. Bardeen and J. R. Schreiffer, Progr. Low Temp. Phys. 3, 170 (1961).

[^1]:    ${ }^{28} \mathrm{M}$. Tinkham (unpublished).

[^2]:    * Supported in part by the Office of Naval Research under Contract No. NONR-401 (38), Technical Report No. 17.
    $\dagger$ On leave of absence from the Institut für Theoretische Physik der Universität Göttingen, Germany.

[^3]:    ${ }^{1}$ D. Saint-James and P. G. de Gennes, Phys. Letters 1, 306 (1963).
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    ${ }^{3}$ M. Cardona and B. Rosenblum, Phys. Letters 8, 308 (1964); B. Rosenblum and M. Cardona, ibid. 9, 220 (1964); 13, 33 (1964).

[^4]:    ${ }^{4}$ One of the authors (G. E.) thanks Professor Cardona for a discussion of this point.

[^5]:    ${ }^{5}$ D. J. Scalapino, J. R. Schrieffer, and J. W. Wilkins, Phys. Rev. 148, 263 (1966).

[^6]:    ${ }^{6}$ L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. 36, 1918 (1959); 37, 1407 (1959) [English transls.: Soviet Phys.-JE'TP 9, 1364 (1959) ; 10, 998 (1960)].
    ${ }^{7}$ For a proof see N. R. Werthamer, Superconductivity, edited by R, Parks (M. Dekker, New York, to be published).

[^7]:    ${ }^{8}$ See Ref. 6 and also, e.g., A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaloshinski, Methods of Quantum Field Theory in Statistical Physics (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

[^8]:    ${ }^{9}$ See, e.g., V. Ambegaokar and L. Tewordt, Phys. Rev. 134, A805 (1964), Appendix A.
    ${ }^{10}$ J. W. F. Woo, thesis, Cornell University, 1966 (unpublished). The functions tabulated there were kindly provided by J. C. Swihart.
    ${ }^{11}$ Referring to Eq. (2.21) we see that $\tilde{\tau}_{\text {tr }}$ is not obtained from $\tau_{\text {tr }}$ by simply correcting the density of states. This correction gives a $\widetilde{Z}$ in the numerator of (2.21). However, to get the renormalized lifetime one must also remember that $V\left(k-k^{\prime}\right)$ in (2.21) is a matrix element between electrons and not quasiparticles. Renormalizing each of the four wave functions in the matrix element squared by the probability that a quasiparticle is contained in a bare state, namely, ( $\tilde{Z})^{-1 / 2}$, we get a net factor of $\widetilde{Z}$ in the denominator of (2.21). This small but amusing point is also discussed in J. S. Langer, Phys. Rev. 124, 1003 (1961), Eq. (3.17), and V. Ambegaokar in Astrophysics and the Many-Body Problem (W. A. Benjamin, Inc., New York, 1963 ), p. 398. In these references the renormalization constant is defined in the conventional manner of field theory, namely, as $(\widetilde{Z})^{-1}$.
    ${ }^{12}$ J. Bardeen and M. J. Stephen, Phys. Rev. 136, A1485 (1964).

[^9]:    ${ }^{13}$ These relations are perhaps most self-evident in the form $\gamma=\left(2 \pi^{2} / 3\right) k_{B}^{2} N^{*}(0) ; \quad \sigma=\left(2 e^{2} / 3\right) N^{*}(0)\left(v_{F}^{*}\right)^{2} \tilde{\tau}_{\mathrm{tr}} ; \quad$ and $N^{*}(0)=$ $S /(2 \pi)^{3} \hbar v_{F}{ }^{*}$.

[^10]:    ${ }^{14}$ N. Ashcroft (private communication).
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