Temperature and Purity Dependence of the Superconducting Critical Field, H_{c2}. III. Electron Spin and Spin-Orbit Effects

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A previously obtained solution of the linearized Gor'kov equations for the upper critical magnetic field H_{c2} of a bulk type-II superconductor is extended to include the effects of Pauli spin paramagnetism and spin-orbit impurity scattering. To carry out the calculation, it is necessary to introduce an approximation which assumes that spin-orbit scattering is infrequent in comparison with spin-independent scattering. It is found that spin-orbit scattering counteracts the effects of the spin paramagnetism in limiting the critical field and improves agreement between theory and experiment.

I. INTRODUCTION

IN the preceding article,[1] an exact solution of the linearized Gor'kov equations was given for the bulk upper critical field H_{c2} of a type-II superconductor, as a function of temperature and electron mean free path. A rather simple model of a superconductor was adopted, which assumed that the electrons interact via the weak-coupling BCS model potential and have a spherical Fermi surface. In addition, the effect of the applied magnetic field on the electron spin magnetic moments was neglected.

As was first pointed out by Clogston[2] and by Chandrasekhar,[3] the electron Zeeman energy can make a significant contribution to determining H_{c2} in materials where that field is large (greater than, say, 50 kG). Their argument essentially was that because of the difference in spin susceptibility between superconducting and normal states, the spin paramagnetism lowers the free energy of the normal state relative to the superconducting state and thus lowers the critical field for transition. If there were no other mechanism for the magnetic field to interact with the superconductivity, then the spin paramagnetic effect by itself would lead to a first-order critical field H_p, which at zero temperature would be $H_p(0)=\Delta(0)/2^{1/2}\mu$, where Δ is the BCS energy gap function and μ is the Bohr magneton. For a type-I material, with a complete Meissner effect and an associated thermodynamic critical field H_c, inclusion of the spin paramagnetism would lower the first-order transition to $H_c^*=(H_c^{-2}+H_p^{-2})^{-1/2}$. These situations are illustrated in a schematic free-energy diagram, Fig. 1.

In the case of a type-II material where the magnetic field can penetrate the sample and reduce the gap function, the transition to the normal state is generally of second order. A more precise treatment of the second-order transition field H_{c2}, including the spin paramagnetic and orbital diamagnetic effects together, has been given by Maki[4] in the limit of very short mean free path. This limit is a particularly appropriate one when studying spin effects, since in all materials experimentally investigated to date which possess the necessarily high H_{c2} values, the mean free path is indeed extremely short.

One other process likely to occur in concentrated alloys, and which is known to increase significantly the Pauli spin susceptibility in the superconducting state, is spin-orbit scattering.[5] Furthermore, measurements on such materials tend[6] to yield values for H_{c2} which lie between the theoretical estimates with and without inclusion of the spin paramagnetism. It is thus important to take the two spin effects into account simultaneously in order to obtain theoretical results for H_{c2} which may realistically be compared with experiment.

When the spin paramagnetism is especially strong, the transition to the normal state may be of first, rather than second, order (see Fig. 1). This has been found by Sarma[7] in the special case of a uniform field interacting with the spins only ("exchange field") and no impurity scattering, and by Maki[4] in the dirty limit. However, Fulde and Ferrell[8] have suggested that in such cases the system might instead make a second-order transition to the normal state from an alternative, "depaired" superconducting state in which Cooper pairs all have a single nonvanishing center-of-mass momentum. The transition between the usual and the "depaired" superconducting states would then be of first order. This situation has been studied by Sarma and Saint James[9] for the uniform spin exchange field, with the conclusion that although the Fulde-Ferrell state is indeed possible in the clean limit, for the dirty limit its formation is never favorable and the normal state transition can be first order. Further investigation of the Fulde-Ferrel state is

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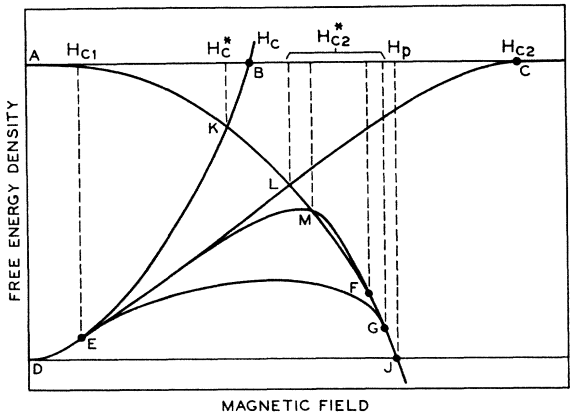

FIG. 1. A schematic plot of free energies of superconducting and normal states versus magnetic field, and associated transitions. Horizontal line AC represents the normal state ignoring the Pauli spin susceptibility, while the parabolic curve AJ represents the normal state with spin paramagnetism. The horizontal line DJ represents the superconducting state assuming it to have no response to the magnetic field. The intersection point J defines the Clogston-Chandrasekhar paramagnetically limited first-order critical field H_p. A type-I superconductor with a Meissner effect is represented by the parabolic curve DB, and the intersection point B gives the traditional thermodynamic critical field H_c. Inclusion of the spin paramagnetism of the normal state lowers the first-order transition to the point K, with associated field H_c^* as defined in the text. A type-II superconductor, with field penetration in the form of vortices above a lower critical field H_{c1} (point E) but no spin, follows schematically the curve DEC. This curve is tangent to the no-spin normal state line at point C, corresponding to a second-order critical field H_{c2}. Inclusion of spin in the normal state but not in the superconductor gives a first-order transition at point L. Also taking account of spin susceptibility in the superconducting state can lead to two possibilities, illustrated by curves DEMF and DEG. The latter is tangent to the normal state (AJ) at point G, and the transition there is second order. Curve DEMF, however, crosses AJ at M before the point of tangency F. In this case, while the transition is first order at M, the superconducting state can exist metastably in fields between M and F, and F represents the point of maximum supercooling.

being carried out by L. W. Gruenberg and L. Gunther.[10] Spin-orbit scattering, on the other hand, since it weakens the degree of spin pairing in the superconductor, may be expected to increase the amount of spin paramagnetism needed to convert the transition from second order to first.

In this paper, we calculate the upper critical field H_{c2}, assuming that the transition is of second order, taking into account both spin paramagnetism and spin-orbit scattering. We derive a formula valid for arbitrary values of the mean free path, but assuming that spin-flip scattering is much less frequent than nonspin-flip scattering, an approximation which certainly is quite realistic physically. We find that spin-orbit scattering reduces the effect of spin paramagnetism in limiting H_{c2}. This is because the spin-orbit interaction destroys spin as a good quantum number, and brings the spin susceptibility of the superconducting state closer[5] to that of the normal state. We compare our calculations in the dirty limit with the data of Strnad and Kim[6] and of Shapira and Neuringer,[6] and find that including spin-orbit scattering improves the agreement between theory and experiment. Finally, we examine the conditions under which the transition might not be of second order[4] and find that a first-order transition is less likely the greater the amount of spin-orbit scattering.

In Sec. II which follows, we obtain a gauge-invariant solution of the linearized Gor'kov equations corresponding to H_{c2}, continuing to neglect strong-coupling and Fermi-surface anisotropy effects, but including both spin paramagnetism and spin-orbit scattering. In contrast to the situation when any one of the latter effects is neglected, the integral equation for the impurity vertex cannot be solved rigorously in general. We are able to make analytical progress only after introducing an approximation, which we argue in the Appendix represents the assumption that spin-flip scattering is infrequent in comparison with nonspin-flip scattering. In Sec. III we specialize the implicit algebraic equation for H_{c2} to the experimentally most relevant limit of very short mean free paths. In this limit the possibility of a Fulde-Ferrell state can be rejected,[9] and we analyze the conditions under which the calculated H_{c2} may be a supercooling field, with the actual transition to the normal state being first order. Finally, in Sec. IV we present numerical results for $H_{c2}(T)$, for various values of spin-flip and nonspin-flip scattering times and ratios of spin paramagnetic to orbital diamagnetic strengths, and we compare these with available experimental data.[6]

II. FORMULATION AND SOLUTION

In order to incorporate spin paramagnetism and spin-orbit scattering into the previous calculation[1] of H_{c2}, it is necessary to generalize the formalism in several ways. Firstly, spin indices on the Green's functions must be retained. It proves most convenient to follow as closely as possible the methods of Gor'kov and Rusinov,[11] who define Green's functions which are 2×2 matrices in their spin indices, and who then combine[12] the usual pair of Gor'kov equations for the Green's functions into a single 4×4 matrix equation.[13] We identify all 4×4 quantities by capital script letters, and regard the 4-dimensional space as a direct product of the 2-dimensional spin space with another 2-dimensional space which we may call Nambu space.[12]

Since our subsequent analysis is more convenient in position rather than in momentum space, the generalization to include spin-orbit scattering means that the impurity potential becomes nonlocal in space.

[10] L. W. Gruenberg and L. Gunther (to be published).

[11] L. P. Gor'kov and A. I. Rusinov, Zh. Eksperim. i Teor. Fiz. **46**, 1363 (1964) [English transl.: Soviet Phys.—JETP **19**, 922 (1964)].

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We take as Hamiltonian

$$\mathcal{H}=\int d^3r\,\psi^\dagger(\mathbf{r})[(-1/2m)(\nabla-ie\mathbf{A})^2-\mu\boldsymbol{\sigma}\cdot\mathbf{H}]\psi(r)+\int d^3r d^3r'\,\psi^\dagger(\mathbf{r})V(\mathbf{r},\mathbf{r}')\psi(\mathbf{r}')+\tfrac{1}{2}g\int d^3r\,\psi^\dagger(r)\psi^\dagger(r)\psi(r)\psi(r),$$

where ψ, $\psi^\dagger$ are field operators, $\mathbf{A}$ is the vector potential, g is the BCS model coupling constant, V is the impurity potential specified in more detail in the Appendix, and we adopt units in which $\hbar=c=k_B=1$. The Gor'kov equations can then be written in the form

$$\mathcal{G}_\omega(\mathbf{r},\mathbf{r}')=\mathcal{G}_\omega{}^n(\mathbf{r},\mathbf{r}')+\int d^3r_1\,\mathcal{G}_\omega{}^n(\mathbf{r},\mathbf{r}_1)\mathfrak{D}(\mathbf{r}_1)\mathcal{G}_\omega(\mathbf{r}_1,\mathbf{r}')+\int d^3r_1d^3r_2\,\mathcal{G}_\omega{}^n(\mathbf{r},\mathbf{r}_1)\mathcal{U}(\mathbf{r}_1,\mathbf{r}_2)\mathcal{G}_\omega(\mathbf{r}_2,\mathbf{r}'). \quad (1)$$

Here $\mathcal{G}_\omega$ and $\mathcal{G}_\omega{}^n$ are the superconducting and normal state Green's functions, respectively, where the normal state is defined by the above Hamiltonian with $g=0$; $\mathfrak{D}$ represents the superconducting gap function and is a functional of $\mathcal{G}_\omega$ in a way to be specified shortly; $\mathcal{U}$ is a 4×4 matrix constructed from the spin-dependent impurity potential; and as usual,[14] $\omega=(2\nu+1)\pi T$ with $\nu=$integer. The magnetic field is contained entirely in $\mathcal{G}_\omega{}^n$.

We now average over impurity configurations (denoted by angular brackets), assuming in the standard way[14] that $\mathfrak{D}$ is independent of the averaging process. Then the appropriate diagrammatic sum[11] in the limit of low impurity concentration leads to

$$\langle\mathcal{G}_\omega(\mathbf{r},\mathbf{r}')\rangle=\mathcal{G}_\omega{}^n(\mathbf{r},\mathbf{r}')+\int d^3r_1\,\mathcal{G}_\omega{}^n(\mathbf{r},\mathbf{r}_1)\mathfrak{D}(\mathbf{r}_1)\langle\mathcal{G}_\omega(\mathbf{r}_1,\mathbf{r}')\rangle+\int d^3r_1d^3r_2d^3r_3d^3r_4\,\mathcal{G}_\omega{}^n(\mathbf{r},\mathbf{r}_1)\times\langle\mathcal{U}(\mathbf{r}_1,\mathbf{r}_2)\langle\mathcal{G}_\omega(\mathbf{r}_2,\mathbf{r}_3)\rangle\mathcal{U}(\mathbf{r}_3,\mathbf{r}_4)\rangle\langle\mathcal{G}_\omega(\mathbf{r}_4,\mathbf{r}')\rangle. \quad (2)$$

If we separate $\langle\mathcal{G}_\omega\rangle$ into parts purely diagonal and purely off-diagonal in Nambu space,

$$\langle\mathcal{G}_\omega\rangle=\langle\mathcal{G}_\omega\rangle_{\rm d}+\langle\mathcal{G}_\omega\rangle_{\rm od}, \quad (3)$$

then Eq. (2) can be written in the form,

$$\langle\mathcal{G}_\omega(\mathbf{r},\mathbf{r}')\rangle=\mathfrak{G}_\omega{}^n(\mathbf{r},\mathbf{r}')+\int d^3r_1d^3r_2\,\mathfrak{G}_\omega{}^n(\mathbf{r},\mathbf{r}_1)\mathfrak{D}_\omega(\mathbf{r}_1,\mathbf{r}_2)\langle\mathcal{G}_\omega(\mathbf{r}_2,\mathbf{r}')\rangle, \quad (4)$$

where we introduce new quantities $\mathfrak{G}$ and $\mathfrak{D}$ defined to satisfy

$$\mathfrak{G}_\omega{}^n(\mathbf{r},\mathbf{r}')=\mathcal{G}_\omega{}^n(\mathbf{r},\mathbf{r}')+\int d^3r_1d^3r_2d^3r_3d^3r_4\,\mathcal{G}_\omega{}^n(\mathbf{r},\mathbf{r}_1)\times\langle\mathcal{U}(\mathbf{r}_1,\mathbf{r}_2)\langle\mathcal{G}_\omega(\mathbf{r}_2,\mathbf{r}_3)\rangle_{\rm d}\mathcal{U}(\mathbf{r}_3,\mathbf{r}_4)\rangle\mathfrak{G}_\omega{}^n(\mathbf{r}_4,\mathbf{r}'), \quad (5)$$

and

$$\mathfrak{D}_\omega(\mathbf{r},\mathbf{r}')=\delta^3(\mathbf{r}-\mathbf{r}')\mathfrak{D}(\mathbf{r})+\int d^3r_1d^3r_2\,\langle\mathcal{U}(\mathbf{r},\mathbf{r}_1)\langle\mathcal{G}_\omega(\mathbf{r}_1,\mathbf{r}_2)\rangle_{\rm od}\mathcal{U}(\mathbf{r}_2,\mathbf{r}')\rangle. \quad (6)$$

Although this form is lengthier than Eq. (2), it has the advantage that it facilitates going to the limit of vanishing $\mathfrak{D}$ corresponding to the second-order transition point. We need only iterate Eq. (4) to lowest nonvanishing order in $\mathfrak{D}_\omega$, so that we can substitute into the right-hand sides of Eqs. (5) and (6), respectively,

$$\langle\mathcal{G}_\omega(\mathbf{r}_2,\mathbf{r}_3)\rangle_{\rm d}\to\mathfrak{G}_\omega{}^n(\mathbf{r}_2,\mathbf{r}_3), \quad (7)$$

$$\langle\mathcal{G}_\omega(\mathbf{r}_1,\mathbf{r}_2)\rangle_{\rm od}\to\int d^3r_3d^3r_4\,\mathfrak{G}_\omega{}^n(\mathbf{r}_1,\mathbf{r}_3)\times\mathfrak{D}_\omega(\mathbf{r}_3,\mathbf{r}_4)\mathfrak{G}_\omega{}^n(\mathbf{r}_4,\mathbf{r}_2). \quad (8)$$

The final relation needed is the well-known definition[14] of $\mathfrak{D}$ in terms of the Green's functions, which in the present notation becomes

$$\ln(T_c/T)\mathfrak{D}(\mathbf{r})=T\sum_{\nu=-\infty}^{\infty}\left(\frac{\pi}{|\omega|}\mathfrak{D}(\mathbf{r})-\frac{1}{N(0)}\frac{1}{2}\,\mathrm{tr}\langle\mathcal{G}_\omega(\mathbf{r},\mathbf{r})\rangle_{\rm od}\right), \quad (9)$$

with tr being the trace in spin space. Equations (5)–(9) form a closed set of equations.

In order to account for the formation of superconducting pairs with opposed spins in the absence of a field, we make a unitary transformation with the matrix[11]

$$\mathcal{U}=\begin{pmatrix}1&0\\0&i\sigma_y\end{pmatrix}, \quad (10)$$

where 1 and σ_y are Pauli spin matrices. The transformed 4×4 matrices (for which we elect not to introduce any notation distinguishing them from the untransformed ones) then can be split into Nambu components,

$$\begin{aligned}\langle\mathcal{G}_\omega(\mathbf{r},\mathbf{r}')\rangle&=\begin{pmatrix}G_\omega(\mathbf{r},\mathbf{r}')&-F_\omega(\mathbf{r},\mathbf{r}')\\F_\omega{}^\dagger(\mathbf{r},\mathbf{r}')&\tilde{G}_\omega(\mathbf{r},\mathbf{r}')\end{pmatrix},\\ \mathcal{G}_\omega{}^n(\mathbf{r},\mathbf{r}')&=\begin{pmatrix}G_\omega{}^n(\mathbf{r},\mathbf{r}')&0\\0&\tilde{G}_\omega{}^n(\mathbf{r},\mathbf{r}')\end{pmatrix},\\ \mathfrak{D}(\mathbf{r})&=\begin{pmatrix}0&-\Delta(\mathbf{r})\\\Delta^\dagger(\mathbf{r})&0\end{pmatrix},\\ \mathfrak{D}_\omega(\mathbf{r},\mathbf{r}')&=\begin{pmatrix}0&-\bar{\Delta}_\omega(\mathbf{r},\mathbf{r}')\\\bar{\Delta}_\omega{}^\dagger(\mathbf{r},\mathbf{r}')&0\end{pmatrix},\\ \mathcal{U}(\mathbf{r},\mathbf{r}')&=\begin{pmatrix}V(\mathbf{r},\mathbf{r}')&0\\0&\tilde{V}(\mathbf{r},\mathbf{r}')\end{pmatrix}.\end{aligned} \quad (11)$$

[14] A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Physics* (Prentice-Hall, Englewood Cliffs, New Jersey, 1963).

The quantities with tildes are defined as

$$\tilde{G}_\omega{}^n(\mathbf{r},\mathbf{r}')\equiv G_{-\omega}{}^n(\mathbf{r}',\mathbf{r})\,|_{\sigma\to-\sigma}\,,$$
$$\tilde{V}(\mathbf{r},\mathbf{r}')\equiv V(\mathbf{r}',\mathbf{r})\,|_{\sigma\to-\sigma}\,. \tag{12}$$

After the transformation $\mathfrak{U}$, all 2×2 quantities except for V would be spin-independent in the absence of Zeeman energy. Hence they depend only on the component of spin along the field, $\boldsymbol{\sigma}\cdot\mathbf{H}$, and so commute with each other.

The transformed Eq. (5), together with (7), is just the equation for the impurity-averaged normal state Green's function, and has been discussed previously in a number of limiting cases: in particular, with neglect of orbital diamagnetism,[11,15] and with neglect of spin-orbit scattering.[4] With all effects taken together, the analysis is not changed in any significant way, and we merely quote the result:

$$\tilde{G}_\omega{}^n(\mathbf{r},\mathbf{r}')\equiv\langle G_\omega{}^n(\mathbf{r},\mathbf{r}')\rangle=-(m/2\pi|\mathbf{r}-\mathbf{r}'|)$$
$$\times\exp\left\{\left[i(p_F v_F-\mu\boldsymbol{\sigma}\cdot\mathbf{H})\,\mathrm{sgn}\omega\right.\right.$$
$$\left.\left.-|\omega|-\frac{1}{2\tau}\right]\frac{|\mathbf{r}-\mathbf{r}'|}{v_F}+ie\int_{\mathbf{r}'}^{\mathbf{r}}\mathbf{A}(\mathbf{s})\cdot d\mathbf{s}\right\}, \tag{13}$$

where $\tau^{-1}=\tau_1^{-1}+\tau_2^{-1}$, and (τ_1,τ_2) are the mean free times for spin-independent and spin-orbit scattering, respectively, defined more precisely in the Appendix.

The remaining equations, (6), (8), and (9), are not completely soluble in full generality, in contrast to the situation when any one of the three effects, orbital diamagnetism, spin paramagnetism, and spin-orbit scattering, is neglected. However, by making an alteration in Eq. (6) we are then able to proceed without further approximation. In the Appendix, it is argued that the alteration corresponds to assuming spin-orbit scattering to be infrequent in comparison with spin-independent scattering, $\tau_1\ll\tau_2$, the argument being based on an analysis of the situation where orbital diamagnetism is omitted. Mathematically, the alteration is to make the replacement inside the angular brackets in Eq. (6),

$$\int d^3r_1 d^3r_2\langle\mathfrak{U}(\mathbf{r},\mathbf{r}_1)\langle\mathcal{G}_\omega(\mathbf{r}_1,\mathbf{r}_2)\rangle_{\mathrm{od}}\mathfrak{U}(\mathbf{r}_2,\mathbf{r}')\rangle$$
$$\to\delta^3(\mathbf{r}-\mathbf{r}')\int d^3r_1\langle\mathfrak{U}(\mathbf{r},\mathbf{r}_1)\langle\mathcal{G}_\omega(\mathbf{r},\mathbf{r})\rangle_{\mathrm{od}}\mathfrak{U}(\mathbf{r}_1,\mathbf{r})\rangle/(\delta^3(0))^2. \tag{14}$$

With this simplification, and the introduction of a kernel $S_\omega(\mathbf{r},\mathbf{r}')$ defined by

$$F_\omega(\mathbf{r},\mathbf{r})=(N(0)/T)\int d^3r'\,S_\omega(\mathbf{r},\mathbf{r}')\Delta(\mathbf{r}'), \tag{15}$$

we can simplify Eqs. (6), (8), (9), (11), and (13) to the set

$$\ln(T_c/T)\Delta(\mathbf{r})=\sum_\nu\int d^3r'\,[|2\nu+1|^{-1}\delta^3(\mathbf{r}-\mathbf{r}')-\tfrac{1}{2}\,\mathrm{tr}S_\omega(\mathbf{r},\mathbf{r}')]\Delta(\mathbf{r}'), \tag{16}$$

$$S_\omega(\mathbf{r},\mathbf{r}')=S_\omega{}^0(\mathbf{r},\mathbf{r}')+\int d^3r_1\,S_\omega{}^0(\mathbf{r},\mathbf{r}_1)[N(0)/T(\delta^3(0))^2]\int d^3r_2\langle V(\mathbf{r}_1,\mathbf{r}_2)S_\omega(\mathbf{r}_1,\mathbf{r}')\tilde{V}(\mathbf{r}_2,\mathbf{r}_1)\rangle, \tag{17}$$

$$S_\omega{}^0(\mathbf{r},\mathbf{r}')=(T/2v_F|\mathbf{r}-\mathbf{r}'|^2)\exp\left[-(2i\mu\boldsymbol{\sigma}\cdot\mathbf{H}\,\mathrm{sgn}\omega+2|\omega|+\tau^{-1})|\mathbf{r}-\mathbf{r}'|/v_F+2ie\int_{\mathbf{r}'}^{\mathbf{r}}\mathbf{A}(\mathbf{s})\cdot d\mathbf{s}\right], \tag{18}$$

which are the generalizations of Eqs. (1)–(5) in Ref. 1.

We now follow Ref. 1 very closely in treating the orbital diamagnetism. We introduce an auxiliary function $\varphi(\mathbf{r})$ defined as an eigenfunction of the kernel $S_\omega{}^0$, with eigenvalue $s_\omega{}^0$:

$$s_\omega{}^0\varphi(\mathbf{r})=\int d^3r'\,S_\omega{}^0(\mathbf{r},\mathbf{r}')\varphi(\mathbf{r}'). \tag{19}$$

If φ is indeed independent of ω and of spin, then φ is also a solution of Eq. (16); upon setting $\Delta(\mathbf{r})=\varphi(\mathbf{r})$, Eq. (16) becomes

$$\ln(T_c/T)=\sum_\nu[|2\nu+1|^{-1}-\tfrac{1}{2}\,\mathrm{tr}s_\omega]. \tag{20}$$

From Eq. (17), s_ω is determined by

$$s_\omega=s_\omega{}^0+s_\omega{}^0[N(0)/T(\delta^3(0))^2]$$
$$\times\int d^3r_1\,\langle V(\mathbf{r},\mathbf{r}_1)s_\omega\tilde{V}(\mathbf{r}_1,\mathbf{r})\rangle. \tag{21}$$

We can carry out the impurity average in Eq. (21), and verify that the right-hand side is independent of $\mathbf{r}$, after we explicitly exhibit the spin dependence of $s_\omega{}^0$ and s_ω. Setting

$$s_\omega=s_\omega{}^{(1)}+s_\omega{}^{(2)}\boldsymbol{\sigma}\cdot\hat{H}\,\mathrm{sgn}\omega,$$
$$s_\omega{}^0=s_\omega{}^{0(1)}+s_\omega{}^{0(2)}\boldsymbol{\sigma}\cdot\hat{H}\,\mathrm{sgn}\omega, \tag{22}$$

then the analysis given in the Appendix shows that Eq.

[15] K. Maki and T. Tsuneto, Progr. Theoret. Phys. (Kyoto) **31**, 945 (1964).

(21) becomes

$$s_\omega = s_\omega{}^0\{1+[\tau^{-1}s_\omega{}^{(1)} + (\tau^{-1}-\tfrac{4}{3}\tau_2{}^{-1})s_\omega{}^{(2)}\boldsymbol{\sigma}\cdot\hat{H}\ \mathrm{sgn}\omega]/2\pi T\}. \quad (23)$$

Using definitions (18) and (22), and evaluating $s_\omega{}^0$ from Eq. (19) in exactly the same manner as the derivation of Eq. (18) in Ref. 1, we obtain the important result that $s_\omega{}^{0(1)}$ and $s_\omega{}^{0(2)}$ are, respectively, the real and imaginary parts of the function

$$I_\omega \equiv [2\pi T/v_F(2eH)^{1/2}]J(\alpha_\omega), \quad (24)$$

where as a generalization of Eqs. (12) and (25) of Ref. 1,

$$J(z)=2\int_0^\infty dw\,\exp(-w^2)\frac{1}{2i}\ln\frac{1+izw}{1-izw}, \quad (25)$$

$$\alpha_\omega = v_F(2eH)^{1/2}(2|\omega|+\tau^{-1}+2i\mu H)^{-1}.$$

It is now a straightforward, but somewhat lengthy, algebraic manipulation to solve Eq. (23), with the result that

$$\tfrac{1}{2}\,\mathrm{tr}s_\omega = s_\omega{}^{(1)} = \{[\mathrm{Re}(I_\omega{}^{-1}-(\tau^{-1}-\tfrac{4}{3}\tau_2{}^{-1})/2\pi T)^{-1}]^{-1} - \tfrac{4}{3}(2\pi T\tau_2)^{-1}\}^{-1}. \quad (26)$$

Equation (20), together with Eqs. (24)–(26), provides the desired implicit relationship between H and T at the second-order transition.

If we allow for the possible existence of a Fulde-Ferrell[8] state, so that we consider the generalization

$$\varphi(\mathbf{r}) \longrightarrow \varphi(\mathbf{r})\,\exp[i(2eH)^{1/2}\eta\hat{H}\cdot\mathbf{r}],$$

then inside the ln of Eq. (25) we make the replacement

$$w \longrightarrow (w^2+\eta^2)^{1/2}.$$

The Fulde-Ferrell state corresponds to finding the maximum value of H_{c2} which solves Eq. (20), as a function of η for fixed T, to be at $\eta\neq 0$. We have shown this not to be the case in the dirty limit, but have not pursued the investigation further for general mean free paths.

III. DIRTY LIMIT

Although the previous section has obtained an implicit formula for $H_{c2}(T)$ valid for arbitrary mean free path (but $\tau_1 \ll \tau_2$), materials with a sufficiently high H_{c2} so that spin effects are significant all have very short mean free paths. (An exception is V_3Si, which is believed to be a high-field superconductor even if ideally pure. It is possible that samples of this material might eventually be made with large enough residual resistance ratio to put the full theory to a test. However, in that case it is likely that at low reduced temperatures our semiclassical approximation for the electron trajectories would break down.) For this reason, we specialize our formula to the dirty limit and only consider this case further.

It now proves convenient to introduce the dimensionless variables,

$$t=T/T_c, \qquad \bar{h}=2eH(v_F{}^2\tau/6\pi T_c), \quad \alpha=3/2mv_F{}^2\tau, \quad \lambda_{so}=1/3\pi T_c\tau_2. \quad (27)$$

The parameter α is identical to that introduced by Maki.[4] In terms of these variables, the dirty limit ($2\pi T\tau \ll 1$) of Eqs. (24)–(26), when substituted into Eq. (20), yields

$$\ln\frac{1}{t} = \sum_{\nu=-\infty}^{\infty}\left\{\frac{1}{|2\nu+1|} - \left[|2\nu+1|+\frac{\bar{h}}{t}+\frac{(\alpha\bar{h}/t)^2}{|2\nu+1|+(\bar{h}+\lambda_{so})/t}\right]^{-1}\right\}. \quad (28)$$

Special cases of Eq. (28) have been used previously by Sarma and Saint James[9] and by Maki[4] in an investigation of the order of the transition. These authors found that for sufficiently large α the transition is actually of first order and that Eq. (28) instead gives the supercooling field. In particular, Maki found for $\lambda_{so}=0$ that t was a double-valued function of $\bar{h}$ when $\alpha>\alpha_c=1$. However, Maki also showed that for fields just below $\bar{h}$ the superconducting state had a lower free energy than the normal state until $\alpha>1.47$. One can conclude that the transition is first order for $\alpha>1.47$ and second order for $\alpha<1$; but when $1<\alpha<1.47$ one seems led to the startling result that the system can undergo a second-order transition from superconducting to normal upon *lowering* the temperature in a fixed field. This strange feature of Maki's model deserves further attention. *Note added in proof.* In accordance with our misgivings, it has been shown recently by Caroli, Cyrot, and de Gennes,[16] and confirmed by Maki,[17] that the calculation of Ref. 4 leading to $\alpha_c=1.47$ is in error. A revised calculation[17] leads to a first-order transition occurring at precisely the point at which the $\bar{h}(t)$ curve becomes re-entrant. This means that our α_c for $\lambda_{so}\neq 0$ computed from the shape of the $\bar{h}(t)$ curve is just the critical value for the transition to become first order. The revised impurity averaging technique of Refs. 16 and 17 now agrees with the earlier, independent work of Tewordt.[18]

On the other hand, we can see from Eq. (28) that a nonvanishing spin-orbit scattering ($\lambda_{so}>0$) tends to reduce the effect of the spin paramagnetic term, and hence could be expected to increase the α_c defined to be the value of α at which t first becomes a double-valued function of $\bar{h}$. We can investigate analytically the dependence of α_c on λ_{so} by observing that α_c is just that value of α for which $(d^2\bar{h}(t)/dt^2)_{t=0}=0$. To take the zero-temperature limit of Eq. (28), it is most convenient to

[16] C. Caroli, M. Cyrot, and P. G. de Gennes, Solid State Commun. (to be published).
[17] K. Maki, Phys. Rev. (to be published).
[18] L. Tewordt, Phys. Rev. **137**, A1745 (1965).

re-express it in terms of digamma functions:

$$\ln\frac{1}{t}=\left(\frac{1}{2}+\frac{i\lambda_{so}}{4\gamma}\right)\psi\left(\frac{1}{2}+\frac{\bar{h}+\frac{1}{2}\lambda_{so}+i\gamma}{2t}\right)+\left(\frac{1}{2}-\frac{i\lambda_{so}}{4\gamma}\right)\psi\left(\frac{1}{2}+\frac{\bar{h}+\frac{1}{2}\lambda_{so}-i\gamma}{2t}\right)-\psi(\tfrac{1}{2}), \quad (29)$$

where $\gamma\equiv[(\alpha\bar{h})^2-(\frac{1}{2}\lambda_{so})^2]^{1/2}$. Using the asymptotic expansion of ψ for large argument, the singular $\ln t$ term can be subtracted from both sides. The remaining equation evaluated at $t=0$ gives

$$2[\psi(\tfrac{1}{2})+\ln 2]=\ln[\bar{h}^2(1+\alpha^2)+\lambda_{so}\bar{h}]-(\lambda_{so}/\gamma)\tan^{-1}[\gamma/(\bar{h}+\tfrac{1}{2}\lambda_{so})]. \quad (30)$$

The first derivative of the equation at $t=0$ shows that $(d\bar{h}/dt)_{t=0}=0$. Differentiating the equation a second time with respect to t, and also setting $(d^2\bar{h}/dt^2)_{t=0}=0$, leads to the additional relation

$$\alpha=\alpha_c=(\bar{h}+\lambda_{so})/\bar{h}. \quad (31)$$

For $\lambda_{so}=0$, these reduce to $\alpha_c=1$ and $\bar{h}=0.1985$, in agreement with Maki's results.[4] We have solved Eqs. (30) and (31) numerically for $\bar{h}$ and α_c as functions of λ_{so}, which are plotted in Fig. 2. The results are well approximated by the expressions

$$\bar{h}=0.1985[1-(\lambda_{so}/\lambda_{so}{}^c)], \quad \alpha_c=\frac{[1+1.589(\lambda_{so}/\lambda_{so}{}^c)]}{[1-(\lambda_{so}/\lambda_{so}{}^c)]},$$

for $\lambda_{so}\leq\lambda_{so}{}^c=0.5139$. This means that t can still be a double-valued function of $\bar{h}$ for $\lambda_{so}<\lambda_{so}{}^c$, but that the values of α above which this may happen increase with increasing λ_{so}, and the temperature at which it would first occur for given α correspondingly decreases. The order of the transition cannot be established with certainty, however, until one has examined the free energies of both states, a program well beyond the scope of the present work. Finally, for $\lambda_{so}>\lambda_{so}{}^c$, the curve of $\bar{h}$ versus t never becomes re-entrant, no matter how large the value of α. Thus the change in order of transition predicted by Maki is less likely to be observed in practice, since $\lambda_{so}=0.5$ does not seem to be an unusually large value.

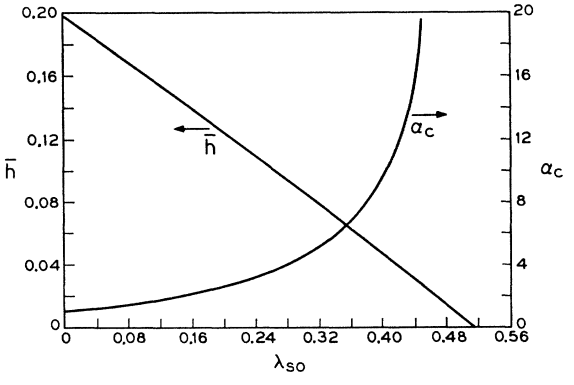

FIG. 2. The value α_c at which the $\bar{h}(t)$ curve becomes re-entrant, as a function of λ_{so}. This is signalled by $(d\bar{h}^2/dt^2)_{t=0}=0$. The corresponding values of $\bar{h}(0)$ are also shown.

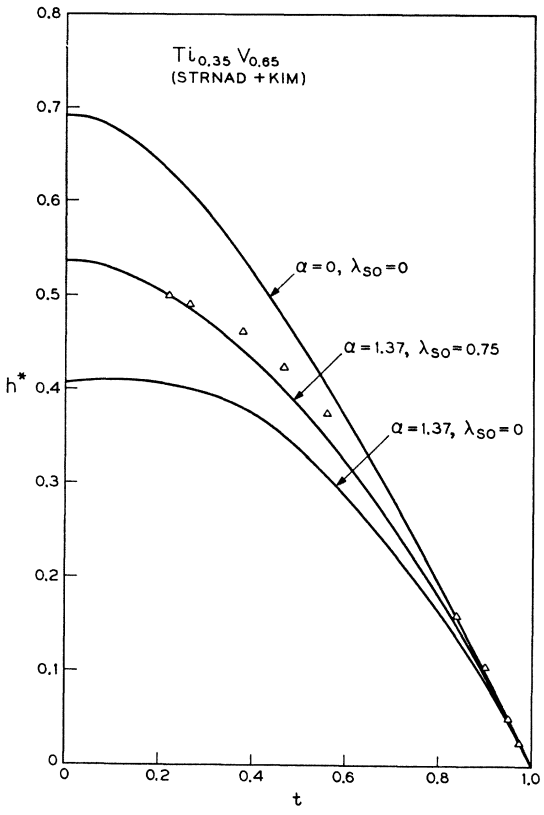

FIG. 3. A plot of $h^*(t)$ for the alloy $Ti_{0.35}V_{0.65}$. The triangles are the data of Strnad and Kim. Theoretical curves shown are for no spin paramagnetic or spin-orbit effects; for spin paramagnetism but no spin orbit; and for spin paramagnetism as well as a best-fit-adjusted spin-orbit parameter.

IV. NUMERICAL RESULTS

We have resorted to numerical methods to solve Eq. (28) for $\bar{h}$ as a function of t, for various values of the parameters α and λ_{so}, which are measures of the spin paramagnetic and spin-orbit effects, respectively. The results of these calculations have been compared with two sets of measurements, those of Strnad and Kim[6] on $Ti_{0.35}V_{0.65}$, and those of Shapira and Neuringer[6] on $Ti_{0.56}Nb_{0.44}$. We have chosen the viewpoint for the comparison that α is not an adjustable parameter, but rather we determine it from additional experimental data using the formula applicable in the dirty limit,

$$\alpha=3e^2\hbar\gamma\rho_n/2m\pi^2k_B{}^2. \quad (32)$$

Here γ is the normal state electronic specific heat coefficient, ρ_n is the normal state dc resistivity, and we have restored previously suppressed factors of $\hbar$ and the Boltzmann constant. In order to apply this formula we have used the data provided by Strnad and Kim[6] for Ti-V, and have been obliged to guess γ for Ti-Nb from other data. This yields $\alpha=1.37\pm10\%$ for Ti-V and $1.22\pm15\%$ for Ti-Nb. On the other hand, we have re-

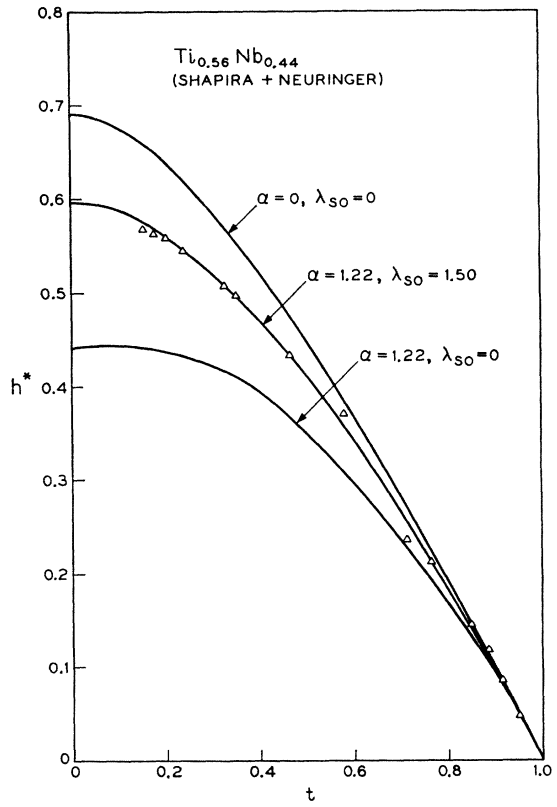

FIG. 4. The same type of plot as Fig. 3, but for the alloy $Ti_{0.56}Nb_{0.44}$ using the data of Shapira and Neuringer.

garded λ_{so} as an adjustable parameter and have chosen that value which seems to give a best fit to the data.

The quantity we choose to plot is not $\bar{h}$, but rather

$$h^* \equiv \frac{\bar{h}}{(-d\bar{h}/dt)_{t=1}} = (\pi^2/4)\bar{h}, \tag{33}$$

which is the same reduced magnetic field employed in Ref. 1. We have calculated

$$h^* = H_{c2}/(-dH_{c2}/dt)_{t=1}$$

from the experimental H_{c2} data by visually constructing the tangent at $t=1$, with an estimated error of $\pm 5\%$. *Note added in proof.* Knowledge of the tangent provides an alternative way of estimating α from superconducting data, rather than from the normal state via Eq. (32). The Maki formula $\alpha = H_{c2}(T=0, \alpha=0)/2^{1/2}H_p(T=0)$ can be rearranged into the convenient form $\alpha = (5.2758 \times 10^{-5})(-dH_{c2}/dT)_{T=T_c}$ where the tangent is in units of gauss per °K. It is a test of the applicability of our model for the superconductor that these two determinations of α should agree. The comparison between theory and experiment is given in Figs. 3 and 4. We find that $\lambda_{so}=0.75$ gives a best fit to the Ti-V data, but that the agreement is by no means perfect. On the other hand, the choice $\lambda_{so}=1.5$ gives quite a good account of the Ti-Nb data. These values for λ_{so} seem to be reasonable physically, since they correspond to a spin-flip scattering time longer than the nonspin-flip scattering time by roughly a factor of 100.

In our judgment, the agreement must be considered good under the circumstances, but not yet a definitive test of the theory. Further quantitative comparison between theory and experiment must await more careful measurements. In particular, γ and ρ_n need to be measured accurately, in order to determine α with greater precision; the slope of $H_{c2}(t)$ at $t=1$ is also needed in order to normalize the data meaningfully. Measurements at very low reduced temperatures would be desirable, since theory predicts that the most interesting structure occurs there. With precise data, and especially very low-t data, it should be possible to determine λ_{so} with considerable sensitivity. Even more significantly, it may be possible to demonstrate conclusively the presence of spin-orbit effect by showing that a fit cannot be achieved merely by numerically adjusting α and fixing $\lambda_{so}=0$. However, even with the present data such a fit requires a value of $\alpha \approx \frac{3}{4}$, which is far outside the limits of accuracy.

ACKNOWLEDGMENTS

We wish to thank Dr. L. Gruenberg for an informative conversation concerning the Fulde-Ferrell state and its relevance to the present calculation. We also are indebted to Y. B. Kim, Y. Shapira, and L. J. Neuringer for discussions and communication of data prior to publication.

APPENDIX

In the analysis of Sec. II, an approximation was introduced which we claimed corresponded to the assumption $\tau \ll \tau_2$. This approximation can be investigated in full detail and the claim justified for the special case where the orbital diamagnetism is ignored. Comparison can also be made with the less complete treatments of this case by Gor'kov and Rusinov[11] and by Maki and Tsuneto.[15]

With orbital interactions absent, the normal state Green's function $\tilde{G}_\omega{}^n(\mathbf{r},\mathbf{r}')$ becomes a function of $\mathbf{r}-\mathbf{r}'$ only. A consistent Ansatz then is that $\bar{\Delta}_\omega(\mathbf{r},\mathbf{r}')$ and $F_\omega(\mathbf{r},\mathbf{r}')$ are also functions of $\mathbf{r}-\mathbf{r}'$ only, and that $\Delta(\mathbf{r})$ is independent of $\mathbf{r}$. Removing the Nambu matrix structure, Eqs. (6), (8), and (9), transformed with (10), become

$$\bar{\Delta}_\omega(\mathbf{r}-\mathbf{r}') = \delta^3(\mathbf{r}-\mathbf{r}')\Delta + \int d^3r_1 d^3r_2 \langle V(\mathbf{r},\mathbf{r}_1) F_\omega(\mathbf{r}_1-\mathbf{r}_2) \tilde{V}(\mathbf{r}_2,\mathbf{r}')\rangle, \tag{A1}$$

$$F_\omega(\mathbf{r}-\mathbf{r}') = \int d^3r_1 d^3r_2\, \tilde{G}_\omega{}^n(\mathbf{r}-\mathbf{r}_1) \times \bar{\Delta}_\omega(\mathbf{r}_1-\mathbf{r}_2)[\tilde{G}_{-\omega}{}^n(\mathbf{r}'-\mathbf{r}_2)]_{\sigma\to-\sigma}, \tag{A2}$$

$$\ln(T_c/T) = T\sum_\nu [(\pi/|\omega|) - \tfrac{1}{2}\,\mathrm{tr}(F_\omega(0)/N(0)\Delta)]. \tag{A3}$$

Because of the translational invariance, it is now most convenient to work in momentum space. The Fourier

transform of the impurity potential is taken to be

$$V(\mathbf{r},\mathbf{r}')=\sum_i(2\pi)^{-6}\int d^3p d^3q\,\exp[i\mathbf{p}\cdot(\tfrac{1}{2}(\mathbf{r}+\mathbf{r}')-\mathbf{R}_i) +i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')](u_1+iu_2\hat{p}\times\hat{q}\cdot\boldsymbol{\sigma}), \quad \text{(A4)}$$

where u_1 and u_2 are constants, $\hat{p}$ and $\hat{q}$ are unit vectors evaluated on the Fermi surface, and the $\mathbf{R}_i$ are the positions of the impurities, each an independent random variable. After Fourier transformation and averaging over impurity configurations, the form of the potential (A4) allows Eqs. (A1)–(A3) to be expressed simply in terms of the quantity

$$S_\omega(\hat{p})\equiv\int_{-\infty}^{\infty}d\epsilon\, TF_\omega(\mathbf{p})/\Delta, \quad \text{(A5)}$$

where ϵ is the kinetic energy measured from the Fermi surface. We find

$$\ln(T_c/T)=\sum_\nu\left[|2\nu+1|^{-1}-\tfrac{1}{2}\mathrm{tr}\int d\hat{p}\,S_\omega(\hat{p})\right], \quad \text{(A6)}$$

$$S_\omega(\hat{p})=S_\omega{}^0\Big[1+(nN(0)/T)\int d\hat{p}'\,(u_1+iu_2\hat{p}\times\hat{p}'\cdot\boldsymbol{\sigma}) \times S_\omega(\hat{p}')(u_1-iu_2\hat{p}\times\hat{p}'\cdot\boldsymbol{\sigma})\Big], \quad \text{(A7)}$$

where n is the impurity concentration, and

$$S_\omega{}^0=T\int_{-\infty}^{\infty}d\epsilon\,\bar{G}_\omega{}^n(\mathbf{p})[\bar{G}_{-\omega}{}^n(-\mathbf{p})]_{\sigma\to-\sigma} =2\pi T/(2|\omega|+\tau^{-1}+2i\mu\boldsymbol{\sigma}\cdot\mathbf{H}\,\mathrm{sgn}\omega). \quad \text{(A8)}$$

Exhibiting the spin dependence of S_ω explicitly in the same way as in Eq. (22),

$$S_\omega(\hat{p})=S_\omega{}^{(1)}(\hat{p})+S_\omega{}^{(2)}(\hat{p})\boldsymbol{\sigma}\cdot\hat{H}\,\mathrm{sgn}\omega, \quad \text{(A9)}$$

the spin products on the right of Eq. (A7) can be simplified:

$$S_\omega(\hat{p})=S_\omega{}^0\Big\{1+\int d\hat{p}'\,[(\tau_1{}^{-1}+\tfrac{3}{2}|\hat{p}\times\hat{p}'|^2\tau_2{}^{-1})S_\omega{}^{(1)}(\hat{p}') +(\tau_1{}^{-1}+\tfrac{1}{2}[1-3(\hat{p}'\cdot\hat{H})^2 +(\hat{p}\cdot\hat{H})^2(-3+5(\hat{p}'\cdot\hat{H})^2)]\tau_2{}^{-1}) \times S_\omega{}^{(2)}(\hat{p}')\boldsymbol{\sigma}\cdot\hat{H}\,\mathrm{sgn}\omega]/2\pi T\Big\}. \quad \text{(A10)}$$

The scattering times are defined as

$$\tau_1{}^{-1}\equiv 2\pi nN(0)u_1{}^2, \quad \tau_2{}^{-1}\equiv\tfrac{2}{3}2\pi nN(0)u_2{}^2. \quad \text{(A11)}$$

Inspection of the right-hand side of Eq. (A10) reveals that it depends on $\hat{p}$ only through a term linear in $(\hat{p}\cdot\hat{H})^2$. Hence the solution has the general form

$$S_\omega(\hat{p})=[S_\omega{}^{(11)}+S_\omega{}^{(12)}(\hat{p}\cdot\hat{H})^2] +[S_\omega{}^{(21)}+S_\omega{}^{(22)}(\hat{p}\cdot\hat{H})^2]\boldsymbol{\sigma}\cdot\hat{H}\,\mathrm{sgn}\omega, \quad \text{(A12)}$$

where the $S_\omega{}^{(ij)}$ are four constants to be determined. By substituting Eq. (A12) into Eq. (A10), the latter can be reduced to a set of four linear algebraic equations in the coefficients $S_\omega{}^{(ij)}$, whose solution is straightforward. However, since the equations are lengthy, and their manipulation is a good deal lengthier, we merely quote the final result. Equation (A6) for the transition point becomes

$$\ln(T_c/T)=\pi T\sum_\nu\left\{\frac{1}{|\omega|}-\left[|\omega|+\frac{(\mu H)^2}{|\omega|+\frac{2}{3}\tau_2{}^{-1}Z}\right]^{-1}\right\}, \quad \text{(A13)}$$

where

$$Z\equiv\frac{1-\frac{4}{5}\gamma_2[1+\frac{1}{5}\gamma_2(1+(\mu H/\tilde{\omega})^2)]/(1+\frac{1}{5}\gamma_2)}{1-\frac{1}{3}\gamma_2[1+\frac{1}{5}\gamma_2(1+(\mu H/\tilde{\omega})^2)]/(1+\frac{1}{5}\gamma_2)}, \quad \text{(A14)}$$

and

$$\gamma_2\equiv\frac{\tilde{\omega}/2\tau_2}{|\tilde{\omega}|^2+(\mu H)^2}, \quad \tilde{\omega}\equiv|\omega|+\frac{1}{2\tau}. \quad \text{(A15)}$$

Since $\mu H\ll\tilde{\omega}$, we find that $Z-1\lesssim 0(\tau/\tau_2)$.

On the other hand, the alteration to Eq. (6) made in Sec. II corresponds in the present notation to replacing Eq. (A7) by

$$S_\omega(\hat{p})=S_\omega{}^0\Big[1+(nN(0)/T)\int d\hat{p}'d\hat{p}'' \times(u_1+iu_2\hat{p}\times\hat{p}'\cdot\boldsymbol{\sigma})S_\omega(\hat{p}'')(u_1-iu_2\hat{p}\times\hat{p}'\cdot\boldsymbol{\sigma})\Big] =S_\omega{}^0\Big\{1+\int d\hat{p}'\,[\tau^{-1}S_\omega{}^{(1)}(\hat{p}') +(\tau_1{}^{-1}-\tfrac{1}{3}(\hat{p}\cdot\hat{H})^2\tau_2{}^{-1}) \times S_\omega{}^{(2)}(\hat{p}')\boldsymbol{\sigma}\cdot\hat{H}\,\mathrm{sgn}\omega]/2\pi T\Big\}. \quad \text{(A16)}$$

The solution of this equation is quite a bit easier than for Eq. (A10), and, upon substituting the result for $S_\omega(\hat{p})$ into Eq. (A6), we now find

$$\ln(T_c/T)=\pi T\sum_\nu\left\{\frac{1}{|\omega|}-\left[|\omega|+\frac{(\mu H)^2}{|\omega|+\frac{2}{3}\tau_2{}^{-1}}\right]^{-1}\right\}, \quad \text{(A17)}$$

which is identical to Eq. (A13) but with $Z\to 1$. This confirms our claim that the alteration we introduced represents an approximation valid in the limit $\tau\ll\tau_2$.

Maki and Tsuneto[15] have previously obtained Eq. (A16), but in no way indicate that it is only an approximate result. Gor'kov and Rusinov,[11] on the other hand, who were only considering the limit $T_c-T\ll T_c$, obtained the first term of an expansion of (A17) in powers of $(\mu H)^2$, but did acknowledge that they had assumed $\tau\ll\tau_2$.