and experiment was about 30%, while for pure niobium the experimental result was higher by a factor of 40 as compared to the theoretical value. One can, therefore, conclude that the experimental evidence on intrinsic type-II superconductors, for samples which show a constant slope in the mixed state, points to larger values of dK/dH than expected from theory and to a steeper variation with temperature.

IV. CONCLUSION

The present study indicates that the mixed-state properties of the thermal conductivity K_m, in a niobium sample of intermediate purity $(l/\xi_0\simeq 1)$, are still in qualitative agreement with the dirty-limit $(l/\xi_0\ll 1)$ theory of Caroli and Cyrot[11] inasmuch as K_m increases linearly as H approaches H_{c2}. This linear behavior extends over an appreciable range of the mixed state. The slope $\partial K_m/\partial H$ varies with temperature much faster than predicted by theory, and this behavior seems characteristic of samples departing from the extreme dirty limit.

The parameter $\kappa_1(t)=H_{c2}(t)/\sqrt{2}H_c(t)$ is found, in agreement with other investigators, to increase with decreasing temperature much faster than expected from theory.

The temperature dependence of the minimum in the mixed state is thought to imply—in addition to the monotonic decrease of K_{gm} with increasing magnetic field—a nonmonotonic variation of K_{es}, viz., a decrease of the electronic conductivity upon entry in the mixed state followed by an increase as H approaches H_{c2}. This is strongly supported by the data of Muto *et al.*[4] The scattering mechanism responsible for this behavior of K_{em}, though it can be conjectured to be scattering by flux lines, merits further investigation.

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Magnetic Properties of Type-II Superconductors in the Two-Band Model

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It has been suggested previously by Wong and Sung that the present discrepancies between theory and experiments on the magnetic properties of some transition metals which are intrinsic type-II superconductors (e.g., Nb) may be caused by the overlapping-band effect of s and d bands. We present here the numerical results of this effect on the magnetic properties. It is shown that the overlapping-band effect in the pure limit can reduce the upper critical field H_{c2} about 30–60% at T close to temperature T_c, and thus enhance the over-all temperature dependence of H_{c2}. The amount of reduction decreases as the superconductors become dirtier. Reasonable parameters which characterize the overlapping-band effect are assumed. We also compute κ_2, which defines the slope of H_{c2} when the external field is slightly less than H_{c2}. It is found that κ_2 becomes smaller in comparison with the present theory as $T\rightarrow T_c$; thus a stronger temperature dependence is also associated with κ_2. The numerical value of this correction in κ_2, however, is very sensitive to the parameters used.

I. INTRODUCTION

The magnetic properties of type-II superconductors close to the upper critical field H_{c2} were first studied by Abrikosov, using the phenomenological Ginzberg-Landau equation[1] near the transition temperature T_c. Later, Gorkov derived Abrikosov's theory in the BCS model throughout the whole temperature range at the "clean" limit (the mean free path l is much larger than the coherence length ξ). Actually, this problem is simpler in the "dirty" limit where it is unnecessary to solve an integral equation for the order parameter (the position-dependent energy gap). This was investigated by Maki and de Gennes,[2] who obtained the temperature dependence of κ_1 and κ_2 (parameters related to H_{c2} and the magnetization for the external field less than H_{c2}) for $l\ll\xi$. Helfand and Werthamer[3] investigated this problem and generalized the treatment given by Gorkov, Maki, and de Gennes to all temperature and purity ranges. Thus, a micro-

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[1] A complete review of the theory of type-II superconductors is given by A. L. Fetter and P. C. Hohenberg, in *Superconductivity*, edited by R. D. Parks (M. Decker, Inc., New York, to be published), Chap. 14.

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scopic theory of H_{c2} and κ_2 close to H_{c2} is well established within the BCS model. A complete numerical calculation was carried out on the basis of the theory of Helfand and Werthamer[3] (HW) by Eilenberger.[4]

Experimentally, however, the theory does not seem to check quantitatively.[5,6] Generally speaking, the theory predicts temperature dependence and purity dependence κ_1 and κ_2 to be less pronounced than experimental data. For instance, if experimental data are fitted to the theory at $T \lesssim T_c$, then H_{c2} is $\sim 50\%$ larger than the theoretical value as $T \to 0$, but this discrepancy is reduced when more impure samples are used. In other words, the experimental data show more remarkable purity and temperature dependence for κ_1 and κ_2 than does the theoretical calculation. Among several attempts which have been advanced to remove this discrepancy by various corrections, Hohenberg and Werthamer[7] have succeeded in showing that the anistropy of the Fermi surface can enhance the temperature dependence of $\kappa_1(T)$ and $\kappa_2(T)$. We will come back to compare the results of this paper with those of HW later.

We notice that most of the pure type-II superconductors, the intrinsic London superconductors, are transition metals (Nb,V) which have complicated electronic structure. It is well known that the transition superconductors do not follow even isotope law. Recently, Garland[8] extended the two-band model given by Suhl, Matthias, and Walker[9] and attributed the deviation to the Coulomb interaction of d electrons. The two-band model, which consists of s and d bands interacting with each other, was used successfully to fit the experimental data[10] of specific heat by Sung and Shen.[11] There is no question that the electronic structure of transition metal is oversimplified by the model where the only adjustable parameters are the effective masses of s and d electrons.

However, the essential feature of the metals with overlapping bands is maintained, namely, the d band dominates the thermodynamical properties, whereas the s band determines the transport properties. It is clear, since H_{c2} and κ_2 are obtained by Maxwell's equation connecting the electric current with the magnetic field, the contribution from the s band can be important. This possibility that might lead to the explanation of the discrepancy in H_{c2} was pointed out by Wong and Sung.[12] We should mention here that a detailed study of equilibrium properties of this model was done by Soda and Wada.[13] H_{c2} and the mixed state close to T_c were investigated by Tilley and Peschel.[14] Recent calculations by Moskalenko[15] and Chow[16] in the model with impurities are not correct.

The purpose of this paper is to investigate the temperature and purity dependence of H_{c2} and κ_2 in the two-band model. It is found that in the pure limit the model correction gives rise to larger temperature dependence of H_{c2} and κ_2. Roughly speaking, the contribution of the s band is very small except around $T \sim T_c$, where the s band reduces H_{c2} and κ_2 and, consequently, the over-all variation of H_{c2} and κ_2 with respect to temperature is enhanced.

In the Sec. II, the modification due to the two-band model is introduced on the basis of the theory developed in Refs. 1 and 3. In Sec. III, we calculate H_{c2} and κ_2 in the pure limit. In Sec. IV, we carry out the calculation with nonmagnetic impurities, assuming the Born approximation is valid. Finally, we make a detailed comparison with the experimental data.

II. FORMALISM

The Hamiltonian of a superconductor in the two-band model under external vector potential $\mathbf{A}(\mathbf{r})$ is H, where[17]

$$H = H_s + H_d + H_{\text{int}}, \tag{1}$$

$$H_s = -\frac{1}{2m_s}\sum_\sigma \int \psi_{s\sigma}^\dagger(\mathbf{r}t)[\nabla - ie\mathbf{A}(\mathbf{r})]^2 \psi_{s\sigma}(\mathbf{r}t)d\mathbf{r} - J_s \int \psi_{s\uparrow}^\dagger(\mathbf{r}t)\psi_{s\downarrow}^\dagger(\mathbf{r}t)\psi_{s\downarrow}(\mathbf{r}t)\psi_{s\uparrow}(\mathbf{r}t)d\mathbf{r}, \tag{2}$$

$$H_{\text{int}} = -J\int \psi_{s\uparrow}^\dagger(\mathbf{r}t)\psi_{s\downarrow}^\dagger(\mathbf{r}t)\psi_{d\downarrow}(\mathbf{r}t)\psi_{d\uparrow}(\mathbf{r}t)d\mathbf{r} + \text{H.c.}, \tag{3}$$

$\psi_{s\sigma}^\dagger(\mathbf{r}t)[\psi_{s\sigma}(\mathbf{r}t)]$ is the creation (annihilation) operator of s electron of spin σ and $m_{s(d)}$ is the mass of $s(d)$ electron. H_d in Eq. (1) is similarly defined as H_s by changing the subscript s to d. J is the interband coupling constant. J_s and J_d are the usual pairing interaction constants in each band. Since in the following discussion s and d bands appear symmetrically, we sometimes write down only one equation for the s band in order

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[17] We have chosen units such that $\hbar = c = K_B = 1$.

to avoid complicated notations. Furthermore, a subscript $s(d)$ always refers to the quantities in the $s(d)$ band.

The equation of motion for the Green's function $G(\mathbf{rr}',\omega_n)$ and the anomalous Green's function $F(\mathbf{rr}',\omega_n)$ defined by Abrikosov *et al.*[18] remain unchanged in the two-band model:

$$[i\omega_n+(1/2m_s)(\boldsymbol{\nabla}-ie\mathbf{A})^2+\mu_s]G_s(\mathbf{rr}',\omega_n)+\Delta_s(\mathbf{r})F_s^\dagger(\mathbf{rr}',\omega_n)=\delta(\mathbf{r}-\mathbf{r}'), \quad (4a)$$

$$[-i\omega_n+(1/2m_d)(\boldsymbol{\nabla}+ie\mathbf{A})^2+\mu_s]F_s^\dagger(\mathbf{rr}',\omega_n)-\Delta_s^\dagger(\mathbf{r})G_s(\mathbf{rr}',\omega)=0, \quad (4b)$$

where $\Delta_{s(d)}(\mathbf{r})$ is the energy gap whose definition is changed due to the interband interaction H_{int},

$$\Delta_{s(d)}^\dagger(\mathbf{r})=T\sum_n[J_{sd}F_s{}^\dagger{}_{(d)}(\mathbf{rr},\omega_n)+\sum_n JF_d{}^\dagger{}_{(s)}(\mathbf{rr},\omega_n)], \quad (5)$$

where $\mu_{s(d)}$ is the chemical potential and $\omega_n=(2n+1)\pi T$. Equation (5) is the major equation in our calculation which differs from the one-band theory. It can be rewritten as two equations:

$$\left.\begin{aligned} &J_s^{-1}\Delta_s^\dagger(\mathbf{r})-(1-J^2J_s^{-1}J_d^{-1})T\sum_{\omega_n}F_s^\dagger(\mathbf{rr},\omega_n)-JJ_s^{-1}J_d^{-1}\Delta_d^\dagger(\mathbf{r})=0,\\ &J_d^{-1}\Delta_d^\dagger(\mathbf{r})-(1-J^2J_s^{-1}J_d^{-1})T\sum_{\omega_n}F_d^\dagger(\mathbf{rr},\omega_n)-JJ_s^{-1}J_d^{-1}\Delta_d^\dagger(\mathbf{r})=0. \end{aligned}\right\} \quad (6)$$

We may write Eq. (4) as the integral equations

$$G_s(\mathbf{rr}',\omega_n)=g_s(\mathbf{rr}',\omega_n)-\int d^3l G_s(\mathbf{rl},\omega_n)\Delta_s(\mathbf{l})F_s^\dagger(\mathbf{lr}',\omega_n), \quad (7a)$$

$$F_s^\dagger(\mathbf{rr}',\omega_n)=\int d^3l g_s(\mathbf{lr},-\omega_n)\Delta_s^\dagger(\mathbf{l})G_s(\mathbf{lr}',\omega_n). \quad (7b)$$

Here $g_s(\mathbf{rr}',\omega_n)$, which satisfies Eq. (4a) with $\Delta_s=0$, is the Green's function for free electrons. Equations (7a) and (7b) with their corresponding equations for d are the complete set of equations for our discussion.

In order to find H_{c2}, only linearized Eq. (7b), where G_s is replaced by g_s, is needed. We write

$$g(\mathbf{rr}',\omega_n)=\exp\left[i\int_{r'}^{r}\mathbf{A}(\mathbf{r})dr\right]g^0(\mathbf{rr}',\omega_n),$$

where $g^0(\mathbf{rr}',\omega_n)$ is the normal Green's function of free electrons in the absence of the magnetic field. It is shown[3] that

$$\int dr'g(\mathbf{rr}',\omega_n)g(\mathbf{rr}',-\omega_n)\Delta^\dagger(\mathbf{r}')=\int d\mathbf{r}'g^0(\mathbf{rr}',\omega_n)g^0(\mathbf{rr}',-\omega_n)e^{i(\mathbf{r}-\mathbf{r}')\cdot\boldsymbol{\Pi}(\mathbf{r})}\Delta^\dagger(\mathbf{r}). \quad (8)$$

Here $\boldsymbol{\Pi}(\mathbf{r})=i\nabla-2e\mathbf{A}(\mathbf{r})$ in Eq. (8) is understood as an operator acting on $\Delta^\dagger(\mathbf{r})$.

The linearized (7b) is solved[7] by finding the eigenvalue $E_s(\omega_n{}^s)$ of the eigenequation

$$\int d\mathbf{r}'g_s{}^0(\mathbf{rr}',\omega_n)g_s{}^0(\mathbf{rr}',-\omega_n)e^{i(\mathbf{r}-\mathbf{r}')\cdot\boldsymbol{\Pi}(\mathbf{r})}\Delta_s^\dagger(\mathbf{r})=E_s(\omega_n{}^s)\Delta_s^\dagger(\mathbf{r}). \quad (9)$$

$E_{s(d)}(\omega_n{}^s)$ is determined as a function of temperature through the definition of $2\omega_n{}^s=2\pi(2n+1)T/V_s(eH_{c2})^{1/2}$, where $V_{s(d)}$ is the Fermi velocity of $s(d)$ electrons and we have

$$T\sum_n E(\omega_n{}^s)=N_s\left[\ln\frac{\gamma\omega_D}{\pi T}-\sum_n\frac{1-2\omega_n{}^sF(2\omega_n{}^s)}{(n+\frac{1}{2})}\right], \quad (10)$$

where $\gamma\omega_D=1.78\times$the Debye temperature, $N_{s(d)}$ is the density of the state of the $s(d)$ band, and the function F is given[4] as

$$F(x)=\int_0^\infty dye^{-y^2/2}\tan\left(\frac{y}{x}\right).$$

The extension of the calculation of the magnetization in the one-band model to the two-band model is straightforward, since the contribution of s and d electrons to supercurrent j is additive:

$$\mathbf{j}=\mathbf{j}_s+\mathbf{j}_d, \quad (11)$$

where

$$\mathbf{j}_s(\mathbf{r})=\frac{e}{m_s}\lim[\Pi^*(\mathbf{r})+\Pi(\mathbf{r}')]\times\left(T\sum_n\int d^3ld^3sg_s(\mathbf{r}'\mathbf{s},\omega_n)g(\mathbf{l}\cdot\mathbf{s},-\omega_n)\times g_s(\mathbf{lr},\omega_n)\Delta_s^\dagger(\mathbf{l})\Delta(\mathbf{s})\right), \quad \text{as } r\rightarrow r' \quad (12)$$

$$\equiv(1/4\pi)Z_s(\Pi^2)(\Delta_s^\dagger\Pi\Delta_s+\Pi^*\Delta_s^\dagger\Delta_s),$$

where $Z(\Pi^2)$ is introduced to denote the product of these normal Green's functions acting on Δ in Eq. (12).

The magnetic field in a superconductor $\mathbf{h}(\mathbf{r})$ is related to the energy gaps by Maxwell's equation, curl $\mathbf{h}(\mathbf{r})=4\pi\mathbf{j}(\mathbf{r})$. It is shown[1] that when the energy gaps are small and the nonlocal effect is neglected, $\mathbf{h}(\mathbf{r})$ is directly related to $\Delta_s(\mathbf{r})$ and $\Delta_d(\mathbf{r})$ through

$$\mathbf{h}(\mathbf{r})=H_0-Z_s(H_{c2})|\Delta_s{}^0(\mathbf{r})|^2-Z_d(H_{c2})|\Delta_d{}^0(\mathbf{r})|^2, \quad (13)$$

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[18] A. A. Abrikosov, L. P. Gorkov and I. E. Dryaloshinski, *Methods of Quantum Field Theory in Statistical Physics* (Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963).

where $Z_s(H_{c2})$ is the value of the $Z_s(\Pi^2)$ from Eq. (12) with curl $A=H_{c2}$. $Z_s(H_{c2})$, a function of $E_s=2\pi T/V_s(eH_{c2})^{1/2}$ has been evaluated.[4] $\Delta_s^0(\mathbf{r})$ and $\Delta_d^0(\mathbf{r})$ are the values of $\Delta_s(\mathbf{r})$ and $\Delta_d(\mathbf{r})$ when the external field H_0 is close to H_{c2}.

III. UPPER CRITICAL FIELD AND MAGNETIZATION

The extension of the calculation of H_{c2} is given by Wong and Sung.[12] The equations which determined H_{c2} are the coupled Eq. (6) for s and d which become

$$\begin{aligned}&[J_s^{-1}-(1-J^2J_s^{-1}J_d^{-1})T\sum_n E_s(\omega_n{}^s)]\Delta_s^\dagger(\mathbf{r})\\&\qquad -JJ_s^{-1}J_d^{-1}\Delta_d^\dagger(\mathbf{r})=0,\\&-JJ_s^{-1}J_d^{-1}\Delta_s^\dagger(\mathbf{r})+[J_d^{-1}-(1-J^2J_s^{-1}J_d^{-1})\\&\qquad\times T\sum_n E_d(\omega_n{}^d)]\Delta_d^\dagger(\mathbf{r})=0,\end{aligned}\tag{14}$$

after relations (7b) and (9) are used. The condition that there exists nontrivial solution for $\Delta_s^\dagger$ and $\Delta_d^\dagger$ yields

$$\begin{aligned}&[1-J_s(1-J^2J_s^{-1}J_d^{-1})T\sum_n E_s(\omega_n{}^s)]\\&\quad\times[1-J_d(1-J^2J_s^{-1}J_d^{-1})T\sum_n E_d(\omega_n{}^d)]\\&\qquad=J^2/J_sJ_d.\end{aligned}\tag{15}$$

When the external field is below H_{c2}, the magnetization inside the superconductor is given by Eq. (12). The absolute of $|\Delta_s^{0\dagger}(\mathbf{r})|^2$ and $|\Delta_d^{0\dagger}(\mathbf{r})|^2$ can be obtained by the Abrikosov second identity as is done in the one-band model.[1] Expanding Eqs. (7a) and (7b) to the third order in $\Delta_{s(d)}$, we obtain

$$\begin{aligned}F_s^\dagger(\mathbf{rr},\omega_n)&=\int d^3l g_s(\mathbf{lr},\omega_n)\Delta^\dagger(\mathbf{l})g_s(\mathbf{lr},-\omega_n),\\&-\int d^3l''d^3l'\int d^3l g_s(\mathbf{lr},\omega_n)\Delta^\dagger(\mathbf{l})g_s(\mathbf{ll}',-\omega_n)\\&\qquad\times\Delta(l')g_s(\mathbf{l}''\mathbf{l}',-\omega_n)\Delta^\dagger(\mathbf{l}''\mathbf{r},\omega_n).\end{aligned}\tag{16}$$

Substitution of Eq. (16) into Eq. (6) yields a set of new eigenequations, which can be written as

$$\begin{aligned}X_s(\Pi^2)|\Delta_s^\dagger(\mathbf{r})\rangle+Y_s(\Pi^2)\Delta_s^\dagger\Delta_s|\Delta_s^\dagger(\mathbf{r})\rangle&\\-JJ_s^{-1}J_d^{-1}|\Delta_d^\dagger(\mathbf{r})\rangle&=0,\end{aligned}\tag{17a}$$

$$\begin{aligned}X_d(\Pi^2)|\Delta_d^\dagger(\mathbf{r})\rangle+Y_d(\Pi^2)\Delta_d^\dagger\Delta_d|\Delta_d^\dagger(\mathbf{r})\rangle&\\-JJ_s^{-1}J_d^{-1}|\Delta_s^\dagger(\mathbf{r})\rangle&=0,\end{aligned}\tag{17b}$$

where $X_s(\Pi^2)$ stands for

$$J_s^{-1}-(1-J^2J_s^{-1}J_d^{-1})\int gg,$$

and $Y_s(\Pi^2)$ represents the product of four Green's functions in Eq. (16). We recall that in this symbolic notation, Eq. (14) becomes

$$\begin{aligned}X_s(H_{c2})|\Delta_s^0(\mathbf{r})\rangle-JJ_s^{-1}J_d^{-1}|\Delta_d^0(\mathbf{r})\rangle&=0,\\X_d(H_{c2})|\Delta_d^0(\mathbf{r})\rangle-JJ_s^{-1}J_d^{-1}|\Delta_d^0(\mathbf{r})\rangle&=0.\end{aligned}\tag{18}$$

When $\langle\Delta_s^0|$ is multiplied to Eq. (17) and the lowest order in the parameter $[h(\mathbf{r})-H_{c2}]$ is taken, Eq. (17a) becomes

$$\begin{aligned}&\langle\Delta_s^0|X_s'(H_{c2})(h(\mathbf{r})-H_{c2})|\Delta_s^0\rangle\\&\qquad+Y_s(H_{c2})\langle\Delta_s^0|(\Delta_s^0)^2|\Delta_s^0\rangle\\&\qquad=JJ_s^{-1}J_d^{-1}(\langle\Delta_d^0|\Delta_s^\dagger\rangle-\langle\Delta_s^0|\Delta_d^\dagger\rangle).\end{aligned}\tag{19}$$

In Eq. (19), we have expanded $X(\Pi^2)$ in the neighborhood of H_{c2} and made use of Eq. (18). Since $\langle\Delta_d^0|\Delta_s\rangle-\langle\Delta_s^0|\Delta_d\rangle\neq0$, the unknown term in the right-hand side of Eq. (19) can only be eliminated by adding its corresponding d equation, and the Abrikosov second identity is obtained as

$$\begin{aligned}&(H_0-H_{c2})(X_s'\langle\Delta_s^{02}\rangle+X_d'\langle\Delta_d^{02}\rangle)+(Z_sX_d'+Z_dX_s')\\&\qquad\times\langle\Delta_s^{02}\Delta_d^{02}\rangle+(Y_s+Z_sX_s')\langle\Delta_s^{04}\rangle\\&\qquad\qquad+(Z_dX_d'+Y_d)\langle\Delta_d^{04}\rangle=0.\end{aligned}\tag{20}$$

The magnetic induction B in the superconductor is given by Eq. (15),

$$B=\langle h(\mathbf{r})\rangle,\tag{21}$$

which can be expressed in terms of the parameter κ_2 defined by

$$B=H_0-[H_{c2}-H_0/(2\kappa_2^2-1)\beta_A],\tag{22}$$

where $\beta=\langle\Delta_d^{04}\rangle/\langle\Delta_d^{04}\rangle^2=1.16$.

In order to evaluate $\langle h(\mathbf{r})\rangle$, we need $\langle\Delta_s^{02}\rangle$ and $\langle\Delta_d^{02}\rangle$, whose ratio is given by Eq. (16). Another needed relation is Eq. (20).

Solving for $\langle\Delta_s^{02}\rangle$ and $\langle\Delta_d^{02}\rangle$ and substituting the values into Eq. (23), we obtain κ_2:

$$2\kappa_2^2=\frac{Y_d}{Z_dX_d'}\frac{1+Y_d^{-1}Y_s\alpha^4}{(1+Z_sZ_d^{-1}\alpha^2)(1+X_s'X_d'^{-1}\alpha^2)},\tag{23}$$

where α is the ratio Δ_s^0/Δ_d^0 which can be obtained from Eq. (18) or (14).

$Y_d/X_d'Z_d$ is the value of $2\kappa_2^2$ without the correction. X_s', Y_s, and Z_s are functions of the variable E_s only, and have been calculated.[4]

IV. LIFETIME AND TRANSPORT TIME IN TWO-BAND MODEL

In this section, we extend the previous calculation to the impure samples. For the reasons to be explained later, we assume that the concentration of impurities is small and the Born approximation is valid. In other words, we always take interaction impurities and electrons only in the lowest order.

Introducing $u_{s(d)}(\mathbf{r}-\mathbf{r}_a)\psi_{s(d)}^\dagger(\mathbf{r})\psi_{s(d)}(\mathbf{r})$ and $v(\mathbf{r}-\mathbf{r}_a)\times\psi_{s(d)}^\dagger\psi_{d(s)}$ as the scattering potential of the $s(d)$

electron from the $s(d)$ band to the $s(d)$ band and $d(s)$ band, respectively, we may write down the Dyson equation for the Green's function $\tilde{g}^0(\mathbf{r},\mathbf{r}',\omega)$ of free electrons

$$\tilde{g}_s{}^0(\mathbf{r},\mathbf{r}',\omega_n)=g_s{}^0(\mathbf{r},\mathbf{r}',\omega_n)$$
$$+\sum_{\mathbf{a}}\int g_s{}^0(\mathbf{r},\mathbf{r}',\omega_n)u_s(\mathbf{r}''-\mathbf{r}_a)\tilde{g}_s(\mathbf{r}''\mathbf{r}',\omega_n)d^3r''$$
$$+\sum_{a,b}\int g_s{}^0(\mathbf{r},\mathbf{r}'',\omega_n)v(\mathbf{r}''-\mathbf{r}_a)\tilde{g}_d(\mathbf{r}''-\bar{\mathbf{r}})v(\bar{\mathbf{r}}-\mathbf{r}_b)$$
$$\times\tilde{g}_s(\bar{\mathbf{r}},\mathbf{r}',\omega_n)d^3r''d^3\bar{r}, \quad (24)$$

where $\mathbf{r}_a$ and $\mathbf{r}_b$ are locations of impurities.

The lifetime of s electrons and d electrons can be computed easily from the Fourier transform of Eq. (24). After the average is taken over impurities, Eq. (24) becomes

$$\tilde{g}_{s(d)}(p)=g_{s(d)}{}^0(p)+\frac{c}{(2\pi)^3}g_{s(d)}{}^0(p)\int|(u_s(p-p')|^2$$
$$\times g_{s(d)}(p')\tilde{g}_{s(d)}(p)d^3p'+\frac{c}{(2\pi)^3}g_{s(d)}{}^0(p)$$
$$\times\int|v(p-p')|^2g_{d(s)}(p')\tilde{g}_{s(d)}(p)d^3p', \quad (25)$$

where c is the concentration of impurity. We have neglected the terms $\sim u_s$, which does not contribute to the imaginary part of $\tilde{g}(p)$. Equation (25) can be written as

$$\tilde{g}_{s(d)}{}^{-1}(p,\omega_n)=i\omega_n-\frac{p^2}{2m_s-\mu_s}+i\frac{\omega}{|\omega|}\frac{1}{\Gamma_{s(d)}}, \quad (26)$$

where

$$\Gamma_{s(d)}{}^{-1}=\frac{c}{2\pi}\left(N_{s(d)}\int u_s{}^2{}_{(d)}(\theta)d\Omega+N_{d(s)}\int v^2(\theta)d\Omega\right)$$
$$\equiv\Gamma_{1s(d)}{}^{-1}+\Gamma_{2s(d)}{}^{-1}. \quad (27)$$

Various physical quantities can be expressed by the correlation function, the product of two Green's functions. Since the average over the product of two Green's functions is not equal to the product of the two averaged Green's functions, the vertex correction emerges. Finding the vertex correction in the two-band model, in general, is complicated, since the interband scattering makes the s and d vertex functions coupled equations. Fortunately, we are interested only in the case of the small concentration of impurities, and the equations can be decoupled.

In order to carry out the previous calculation of H_{c2} to an impure superconductor, we have to take the average of the kernel $g_s{}^0g_s{}^0$ in Eq. (9) over all impurities. Our result on the basis of Eq. (24) is similar to that which is obtained in Ref. 3, because the contribution from the last terms is of the order of v^4. The product of $g_s{}^0(\mathbf{r},\mathbf{r}',\omega_n)$ and the last term is of the order of v^2, but it is only a self-energy correction to $g_s{}^0(\mathbf{r},\mathbf{r}',\omega_n)$.[19] As a result, the definition of $E_s(\omega_n{}^s)$ in Eq. (9) should be changed to

$$T\sum_n E_s(\omega_n{}^s)=N_s\left(\ln\frac{\gamma\omega_D}{\pi T}\right.$$
$$\left.-\sum_n\frac{1-2\omega_n{}^sF(2\omega_n{}^s)}{(n+\frac{1}{2})[1-(\Gamma_{1s}{}^2V_s{}^2H_{c2})^{-1/2}F(2\omega_n{}^s)]}\right) \quad (28)$$

and

$$2\omega_n{}^s=[2\pi T(2n+1)+\Gamma_s{}^{-1}]/V_s(eH_{c2})^{1/2}. \quad (29)$$

A similar equation holds for $T\sum_n E_d(\omega_n{}^d)$. It should be emphasized again that this result is only valid in the Born approximation and cannot be applied to the dirty limit. We note that the vertex correction is associated with Γ_{1s} and Γ_{1d}, but is independent of Γ_{2s} and Γ_{2d}. If the reasonable assumption is made that $u_s\sim u_d\sim v$, $\Gamma_{1s}\gg\Gamma_{2s}$ and $\Gamma_{1d}\approx\Gamma_d$ as $N_s\ll N_d$, the vertex correction is very small in the s band and Eq. (28) can be written as

$$T\sum_u E_s(\omega_n{}^s)=N_s\left(\ln\frac{\gamma\omega_D}{\pi T}\right.$$
$$\left.-\sum_n[1-2\omega_n{}^sF(2\omega_n{}^s)/n+\tfrac{1}{2}]\right),$$

where $2\omega_n{}^s$ is given by Eq. (29). The summation $\sum_n[1-2\omega_n{}^sF(2\omega_n{}^s)]$, which is essentially the correction due to the s band, decreases as Γ_s increases as a function of impurity concentration. It is interesting to note that if $\Gamma_s\ll\Gamma_{1s}$ would not be taken into account in Eqs. (28) and (29), H_{c2} should have stronger temperature dependence as impurity concentration increases.

Equation (24) can also be used to obtain the transport life time in the Born approximation. Since our equations are almost identical to those in Ref. 18 except for minor modification, we just write down the transport life time of s and d electrons, $\Gamma_{s(d)}{}^t$,[20]

$$[\Gamma_{s(d)}{}^t]^{-1}=\frac{c}{(2\pi)^3}\left(N_{s(d)}\int(1-\cos\theta)u_{s(d)}{}^2(\theta)d\Omega\right.$$
$$\left.+N_{d(s)}\int v^2(\theta)d\Omega\right). \quad (30)$$

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[19] The vertex correction due to the interband scattering does not exist in the Born approximation because there are no linear terms of v in Eq. (24). This explains why no vertex correction is taken into consideration in C. C. Sung and V. Wong, J. Phys. Chem. Solids **28**, 1933 (1967) [$\bar{V}_s{}^2$ and $\bar{V}_d{}^2$ should replace $\bar{V}_s\bar{V}_d$ of Eqs. (7) and (13) in the conventional notation of V_s and V_d].

[20] This is a well-known result used in the transport theory of transition metals. See, e.g., H. Jones, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956). We recall that $\int\cos\theta v^2(\theta)d\Omega$ is the vertex correction. Since there is no vertex correction due to the interband scattering according to Eq. (24), $\int\cos\theta v^2(\theta)d\Omega$ does not appear.

Since it is reasonable to assume that the integrals in Eq. (30) are of the same order of magnitude $\Gamma_s{}^t \sim \Gamma_d{}^t$ the transport properties are dominated by the s band. The electric current and heat current are inversely proportional to the mass of particles and the lighter particles always dominate the transport properties. In other words, the mean free path of s electrons is larger than that of d electrons. This conclusion is important to analyze the data later where most thermodynamical properties are dominated by the d band whose deduced parameters cannot be used to determine the mean free path. Instead, a free-electron model (s band) should be more suitable.

In the comparison of the calculation of one-band theory and experimental data, a parameter $\rho = (2\pi T_c \Gamma)^{-1}$, where Γ is the lifetime of the electrons, is introduced to denote the purity dependence. In our case, ρ is defined as $(2\pi T_c \Gamma_d)^{-1}$, which dominates $H_{c2}(0)$ in the dirty samples, but it is noted that $\Gamma_d \approx \Gamma_s{}^t$ if we assume $v \sim u_s \sim u_d$.

V. RESULTS

A. Parameters in the Model

It is important to review the parameters involved in the two-band model so that the corrections due to the two bands are clear. First, we discuss the ratio m_d/m_s, where m_s is taken to be the free-electron mass. The normal specific heat c_V of Nb is dominated by the d-band contribution. Using[21]

$$c_V = 3.26 \times 10^{-5} V^{2/3} n_d{}^{1/3} T (m_d/m) \text{ cal/mole deg}, \qquad (31)$$

where V is the molar volume, n_d the number of d electrons per atom, we obtain $m_d/m \approx 10$.

m_d can be derived from experimental data of H_{c2}, which, at zero temperatures, is given by

$$H_{c2}(0) = (1/eV_d{}^2)(13.3/2)\Delta_d{}^2(0), \qquad (32)$$

where V_d, inferred from experimental data of H_{c2} is about 2.0×10^5 m/sec. If we take the Fermi velocity of the free-electron model as $V_s = 1.25 \times 10^6$ m/sec, and assume the Fermi momenta of the s and d band to be about the same, then $m_d/m \approx 8$. Since the values m_d/m obtained from Eqs. (31) and (32) are reasonably close, we believe it reasonable to use $V_s/V_d \approx 10 - 8$.

Since most equilibrium properties are determined by d electrons, $J_d N_d$ can be obtained from the BCS theory[22] as

$$J_d N_d \approx 0.3. \qquad (33)$$

We are not aware of any ways of determining $J^2/J_s J_d$ and $J_s N_s$ directly, but some rough estimate of these numbers can be obtained by fitting the experimental data and theoretical values of specific heat. First of all, $J^2/J_s J_d$ is very small $\sim 10^{-3}$, and $J_s N_s$ is related to the energy gap $\Delta_s(0)$ at zero temperature, through

$$\Delta_s(0) \cong \omega_D \exp\left[-\left(1 - \frac{\Delta_d(0)}{\Delta_s(0)} \frac{J}{J_d} \right) \Big/ J_s N_s \right], \qquad (34)$$

if we assume the same Debye temperature for both bands. We will choose

$$J^2/J_s J_d = 0.6 \times 10^{-2}, \quad J_s N_s = 0.15. \qquad (35)$$

These numerical values are used in the following discussion, but it must be emphasized that the correction to H_{c2} is practically determined by $J^2/J_s J_d$ and that other parameters are not very important. When nonmagnetic impurities are present, we introduce one parameter $\rho = (2\pi T \Gamma_d)^{-1}$, and let $\Gamma_s = \Gamma_{1d} = \Gamma_d$, and $\Gamma_{1s} \cong 0$.

B. Results in the Pure Limit

Since $J^2/J_s J_d$ is very small, Eq. (15) can be written as[23]

$$\begin{aligned}
\ln T/T_c + \sum_n & \frac{(1-2\omega_n{}^d) F(2\omega_n{}^d)}{(n+\frac{1}{2})[1-(\Gamma_{1d}{}^2 V_d{}^2 e H_{c2})^{-1/2} F(2\omega_n{}^d)]} \\
&= -\frac{N_d J_d N_s J_s}{J_d N_d - J_s N_s} \frac{J^2}{J_s J_d} \left(\ln \frac{T}{T_c} \right. \\
&\quad \left. + \sum_n \frac{(1-2\omega_n{}^s) F(2\omega_n{}^s)}{(n+\frac{1}{2})[1-(\Gamma_{1s}{}^2 V_s{}^2 e H_{c2})^{-1/2} F(2\omega_n{}^s)]} \right) \\
&\quad \times \left[J_d N_d - J_s N_s + J_s N_s J_d N_d \left(\ln \frac{T}{T_c} \right. \right. \\
&\quad \left. \left. + \sum_n \frac{(1-2\omega_n{}^s) F(2\omega_n{}^s)}{(n+\frac{1}{2})[1-(\Gamma_{1s}{}^2 V_s{}^2 e H_{c2})^{-1/2} F(2\omega_n{}^s)]} \right) \right]^{-1}.
\end{aligned} \qquad (36)$$

Although Eq. (36) is numerically complicated to solve for H_{c2}, a general picture of the two-band-model correction due to the right-hand side in Eq. (36) is easy to assess. Since $\sum_n (1-2\omega_n{}^s) F(2\omega_n{}^s)$ is considerably larger than $\ln T/T_c$, the right-hand side is about 10^{-2}. Thus, the correction to the solution of H_{c2} by neglecting the modification is not important for $t \equiv T/T_c \ll 1$, whereas at $t \gtrsim 0.8$ the correction will substantially *reduce* H_{c2}. In other words, the slope of H_{c2} at $t \approx 1$ is extremely sensitive to the correction term. The limit is

$$\left(\frac{dH_{c2}}{dt} \right)_{t=1} \Big/ \left(\frac{dH_{c2}}{dt} \right)_{t=1}^{\text{HW}} \cong \left(1 + \frac{J^2 N_s N_d V_s{}^2}{(J_d N_d - J_s N_s{}^2 V_d{}^2)} \right)^{-1}.$$

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[21] J. G. Daunt, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (Wiley-Interscience, Inc., New York, 1955), Vol. I.

[22] If the electron-phonon interaction is taken into account, all the parameters $J_d N_d$, $J^2/J_s J_d$, and $J_s N_s$ may be changed substantially. Since we use them as parameters here, our results are not affected by this change.

[23] The expression of T_c in the two-band model is used to obtain Eq. (36).

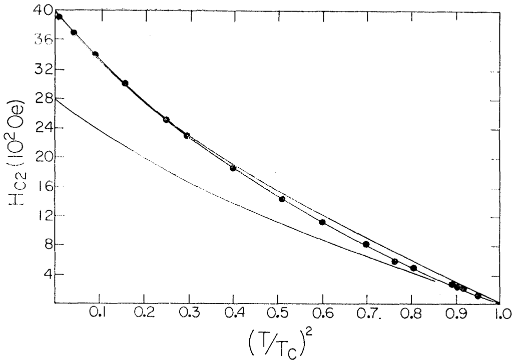

FIG. 1. Temperature dependence of H_{c2} for pure sample. The lower and upper curves are computed from the HW theory by fitting the theory of the slope of $H_{c2}(T_c)$ and $H_{c2}(0)$, respectively. The middle curve is obtained from the present work. The dots are some data taken from Ref. 5.

We want to remark here that although H_{c2} and κ_2 are determined by d electrons for most of the temperature region, they are strongly influenced by s electrons near T_c. Hence, the statement[12] that the s electron dominates H_{c2} is correct only near T_c.

Our results are plotted in Fig. 1. The lower curve is obtained from the HW theory which is made to fit the slope of H_{c2} at $t=1$, as is done in many experimental papers, while the upper curve fits H_{c2} at $t=0$. The middle curve is our numerical result which is obtained by taking the s-band correction into the upper curve.

Since the correction of the theory of Hohenberg and Werthamer[7] raises the value of H_{c2} as $t \to 0$, their theory can certainly fit the experimental data also.

A word is in order to compare the HW theory and our model. The two-band model used in this paper consists of two isotropic bands. The anisotropy of the energy gap and the Fermi surface of "each" band is neglected. In terms of a very general model, where both anisotropy of the Fermi surface and energy gap are considered, our model is mathematically equivalent to a specific choice of anisotropy. However, our choice that $N_s(0) \ll N_d(0)$, $J^2/J_sJ_d \ll 1$, inferred from experimental information, implies that the anisotropy is not small, and the approximation used in Ref. 7 and by Gorkov *et al.* is not applicable. Because of the large density of the state of the d band, the measured anisotropy of the energy gap and the Fermi surface should be referred to the d band. Thus, if we include the small anisotropy of the d band, as is done in Ref. 7, in this paper, this work would be considered as a study of the effect of the s band in addition to what is accomplished in Ref. 7. Although to include the d-band anisotropy makes the model more realistic and can be done in a straightforward manner, there are too many parameters involved and comparison of the experimental data will be meaningless.

The question as to which correction is more important, the s electron or the anisotropy of the Fermi surface, still remains, but it can be tested at $1 > t \geqslant 0.95$, where Eq. (36) predicts the slope of H_{c2} to vary substantially,[24] i.e., $H_{c2}{}^{\mathrm{HW}}(0.95)/H_{c2}(0.95)=1.3$ and $H_{c2}{}^{\mathrm{HW}}(1)/H_{c2}(1)=1.5$. In the following discussion, we take the slope of dH_{c2}/dt from $t=0.95$. Since we can never determine the absolute value of $H_{c2}(0)$, the measurement of H_{c2} at $t \to 1$ is the only way to distinguish the difference between the HW theory and our work.

Since Y_s/Y_d is smaller than Z_s/Z_d by a factor $V_s{}^2/V_d{}^2$,[25]

$$\kappa_2/\kappa_2{}^{\mathrm{HW}} \cong (1+\alpha^2 Z_s/Z_d)^{-2}$$
$$\equiv 1+(N_s/N_d)(V_s{}^2/V_d{}^2)(J/J_d)^2 S(V_s/V_d)^{-2},$$

where $S(V_s/V_d)$ is a function sensitive to the choice of the parameter V_s/V_d. If we use the parameters in this section, $N_sV_s{}^2J^2/N_dV_d{}^2J_d{}^2S(V_s/V_d)$ is about 0.1 at $t \cong 0.9$. Thus the correction to κ_2 and H_{c2} is qualitatively similar. This result also checks with experimental evidence,[6] although the uncertainty of data makes any quantitative comparison impossible. Since $\kappa_2/\kappa_2{}^{\mathrm{HW}}$ is too sensitive to the choice of V_s/V_d, and the function S can be easily computed from Ref. 4, we do not plot it.

C. Effect of Nonmagnetic Impurities

To apply the model to the very dirty samples which consist of the transition superconducting metal and another superconducting material perhaps is not meaningful. For instance, Nb+xTi used in Ref. 6

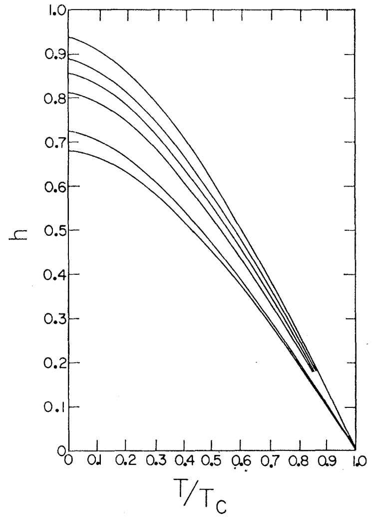

FIG. 2. Temperature and impurity concentration dependence of $h(t)=H_{c2}(t)/(dH_{c2}/dt)_{t=1}$ as a function of $\rho=(2\pi T\Gamma_d)^{-1}$. From the top to the bottom, $\rho=0$, 0.2, 0.5, and 1.0. The next two curves are from the HW theory with parameters $\rho=0$ and ∞, respectively.

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[24] T. Ohtsuka and N. Takano, J. Phys. Soc. Japan **23**, 983 (1967); and S. Williamson, Phys. Letters **28A**, 665 (1969) have measured the value of $H_{c2}(T)$ at $T \to T_c$.

[25] The relation $X_{s(d)}{}'=Z_{s(d)}$ of Ref. 4 is used.

changes the value of the normal specific hear more than 10% when $x > 5\%$, and it is clear that correction due to the presence of Ti is more important than that of the s electron. The so-called dirty limit calculation[15,16] is of pedestrian interest only, in our opinion, unless one can compute the properties of the superconducting alloys. Our discussion here thus can be applied to superconductors with small concentration of impurities.

It is pointed out[3] that the quantity $h(t) = H_{c2}(t)/dH_{c2}/dt|_{t=1}$ is more suitable in comparing theory with experiment. In Fig. 2, we plot the results which show that h has a larger purity dependence than predicted for the HW theory. This, of course, is a consequence that the correction term in Eq. (34) becomes smaller as impurities are introduced. The experimental data in Ref. 6 show that $h(0) = 0.7$ at the pure limit consistent with the HW theory, but $h(0)$ has larger purity dependence. We notice that the crucial number $dH_{c2}/dt|_{t=1}$ is 6.1 kOe and 4.8 kOe in Refs. 6 and 5, respectively, despite small difference in ρ. Consequently, an accurate comparison is not possible. The confusion is caused, we believe, by the difficulty in reading the number $(dH_{c2}/dt)_{t=1}$ from the experimental data.

The only available experimental work to measure $h(t)$ carefully is given by Ohtsuka and Takano,[24] who show $h(0)$ is about 20% larger than the HW theory at the pure limit. In Fig. 2, the choice of the parameter J^2/J_sJ_d assumes the discrepancy is about 30% from reading the data in Ref. 5. There are only two or three experimental points available from Ref. 6 and the new reference consistent with the prediction of larger ρ dependence of $h(0)$ derived from this paper. No detailed comparison between theory and experiment is made for another reason, namely, ρ cited in the experimental data of $H_{c2}(1)$ may remarkably differ from the ρ determined from the lifetime, the theoretical value. Again, we wish to emphasize that whether or not (dH_{c2}/dt) $(t \lesssim 1)$ is, indeed, very sensitive to the purity, especially at the small value of ρ, is decisive proof of the correction due to s electrons. On the basis of the data available so far, we cannot come to any definite conclusion, although we are able to obtain a stronger impurity dependence of $h(t)$, indicated in Fig. 2.

Since our result changes substantially when t approaches one, and the value $\kappa_1(1)$ is not certain, we plot $\kappa_1(0.1)/\kappa(0.95)$ in Fig. 3 to show the strong purity dependence in our model, but it does not contain more information than Fig. 2. Although the calculated curve in Fig. 3 and the corresponding experimental curve in Ref. 6 are similar, a quantitative comparison is meaningless.

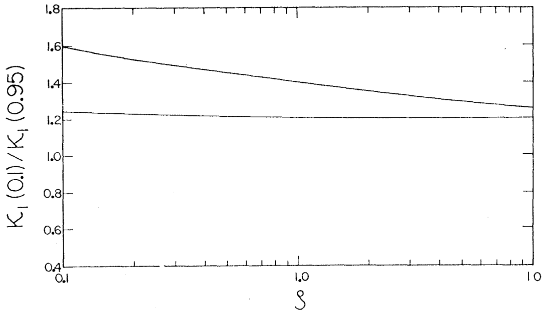

FIG. 3. The purity dependence of $\kappa_1(0.1)/\kappa_1(0.95)$. The upper curve is from this calculation and the lower curve is taken from Ref. 4. (The assumption is made that the transport time and life time are equal.) We write $\kappa_1(0.95)$ instead of $\kappa_1(1)$ to emphasize the important difference between these two quantities.

In conclusion, we make the following remarks pertinent to the experimental data:

(1) Since the resistivity and $H_{c2}(0)$ are determined by s electrons and d electrons, respectively, it is not surprising that the values of ρ from the experimental data of these quantities differ. Furthermore, since $H_{c2}(1)$ is strongly influenced by s electrons, no single value of ρ should be used to fit the data of $H_{c2}(1)$ as a function of ρ.

(2) Properties of superconducting alloys (two kinds of superconducting materials) are very complicated. It is difficult to analyze the data of H_{c2} and κ_2 of superconducting alloys in terms of the purity dependence.

(3) Whether or not the two-band effect is important depends on the experimental data of H_{c2} at $t \lesssim 1$ to prove the assertion in Sec. V B. The purpose of comparing the experimental data with this work is to point out that the present discrepancy is not necessarily at $T \rightarrow 0$. If both anisotropy of the d band and the effect of the s band are taken into account, as should be done, the discrepancy may not appear as serious as is cited in numerous experimental papers.