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Specific Heat of Superconducting Transition Metals Containing Nonmagnetic Impurities at Low Temperatures*

Richard H. Burkel and W. S. Chow

Department of Physics, University of Cincinnati, Cincinnati, Ohio 45221

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Green's-function theory is used for the calculation of the specific heat of superconducting transition metals containing nonmagnetic impurities at low temperatures, $T \gtrsim 0$. It is found that in this temperature region, the s-band specific heat is lowered by the presence of the nonmagnetic impurities. The logarithm of the s-band specific heat obeys the following relation: $\ln C_s = \ln C_s^{(0)} - \Gamma/k_BT$ for $T \gtrsim 0$, where $C_s^{(0)}$ is the s-band specific heat for a pure two-band superconductor, and Γ is proportional to the density of impurities, the density of states at the d-band Fermi surface, and the strength of the interband impurity scattering. This relation agrees very well with the low-temperature experimental data of Shen, Senozan, and Phillips.

I. INTRODUCTION

It was first proposed by Suhl, Matthias, and Walker (SMW)[1] that at low temperatures, both the s-band and the d-band electrons in transition metals, such as niobium and vanadium, can be in the superconducting phase. This model is known as the two-band model. Recently, the two-band model has received considerable attention, since it does succeed in explaining various physical properties of the superconducting transition metals.[2] On the side of experiments, particularly noteworthy are the specific-heat measurements made by Shen, Senozan, and Phillips[3] in the low-temperature region of the niobium superconductors. They notice that there are two slopes appearing in the logarithm of specific heat versus T^{-1} plot, a larger slope near the transition temperature and a smaller slope in the low-temperature region, $T \gtrsim 0$. Based on the BCS theory and the SMW model, they identify the two slopes as due to the existence of two order parameters in the two-band system, Δ_s and Δ_d, for s band and d band, respectively. The two-slope behavior in the $\ln C$ versus T^{-1} plot is not limited to *pure* niobium crystals. The same behavior is also observed in *impure* niobium crystals, but then the values of the specific heat are generally lowered by the impurities in the temperature region, $10^{-1}T_c > T > 0$. A simple analysis of the data for a *pure* niobium superconductor has been separately given by Sung and Shen.[4] The analysis is simple in the sense that they have only fitted the BCS theory for *pure* one-band superconductors to the data of Shen *et al.* to obtain the values of Δ_s and Δ_d. It should be pointed out that so far no systematic attempt has been made to interpret the specific-heat data of *impure* niobium superconductors, particularly in the most interesting low-temperature region, $10^{-1}T_c > T > 0$.

Recently, a detailed investigation of the thermodynamic properties of two-band superconductors containing nonmagnetic impurities in terms of Green's functions has been made by Chow.[5] It is noted that in the intraband BCS (phonon) coupling limit, the intraband impurity scattering generally does not cause changes in thermodynamic properties of two-band superconductors. This is consistent with the Anderson's theorem for one-band superconductors, containing nonmagnetic impurities. All changes in thermodynamic properties for two-band superconductors containing nonmagnetic impurities in the intraband BCS coupling limit are caused by interband impurity scattering. Thus, the interband impurity scattering in a two-band superconductor plays a similar role of the spin-flipping scattering of the magnetic impurities in one-band superconductors, so far as thermodynamic properties are concerned. It is in this connection that we would expect that the interband impurity scattering must play a decisive role in causing the lowering of the specific heat in the impure niobium superconductors in the low-temperature region. Further, based on the theory already given in Ref. 5, it is natural for us to regard the d-band transition temperature T_{cd} as the transition temperature T_c of the niobium superconductor as a whole, and the s-band transition temperature T_{cs} to be of the order of $10^{-1}T_c$, such that we reach consistency with the niobium specific-heat data.

In Sec. II, we give a brief review of some results obtained in Ref. 5, which are to be applied in the later sections of the present paper. In Sec. III, we first obtain the changes in densities of states for quasiparticles $N_s(\omega)$ and $N_d(\omega)$ for the two bands. As will be shown, only the s-band density of states for quasiparticles $N_s(\omega)$ will be changed significantly by the interband impurity scattering. Following this, we evaluate the change in specific heat due to the interband impurities in the low-temperature region $T \gtrsim 0$. The results are shown to agree very well with the experimental data.

II. SOME PREVIOUS RESULTS CONCERNING THE s-BAND GREEN'S FUNCTION AND THE d-BAND GREEN'S FUNCTION

The Hamiltonian for a pure two-band superconductor without intrinsic interband BCS (phonon) coupling, i.e., $g_{sd}=0$, can be obtained from Eq. (C 1) in Ref. 5. [Equations from this paper are denoted by the form (C 1), etc.] The interaction Hamiltonian due to impurity scattering is given by Eq. (C 2). The 2×2 matrix Green's functions for the two bands of a two-band superconductor containing nonmagnetic impurities in the intraband BCS coupling limit in the $(\vec{p}, z_\nu)$ space are given by

$$\underline{G}_s(\vec{p}, z_\nu) = \frac{\tilde{z}_{s\nu} + \epsilon_{s\vec{p}}\sigma_3 + \tilde{\Delta}_{s\nu}\sigma_1}{\tilde{z}^2_{s\nu} - \epsilon^2_{s\vec{p}} - \tilde{\Delta}^2_{s\nu}} , \tag{1}$$

$$\underline{G}_d(\vec{p}, z_\nu) = \frac{\tilde{z}_{d\nu} + \epsilon_{d\vec{p}}\sigma_3 + \tilde{\Delta}_{d\nu}\sigma_1}{\tilde{z}^2_{d\nu} - \epsilon^2_{d\vec{p}} - \tilde{\Delta}^2_{d\nu}} , \tag{2}$$

with $z_\nu = i\omega_\nu = i\pi(2\nu+1)T$, ν being any positive or negative integer, and with $\tilde{z}_{s\nu} = i\tilde{\omega}_{s\nu}$, $\tilde{z}_{d\nu} = i\tilde{\omega}_{d\nu}$. σ's are 2×2 Pauli-spin matrices. Various quantities shown here are related to the corresponding quantities for a pure two-band superconductor by the following:

$$\tilde{\omega}_{s\nu} = \omega_\nu + \frac{1}{2\tau_s}\,\frac{\tilde{\omega}_{s\nu}}{(\tilde{\omega}^2_{s\nu} + \tilde{\Delta}^2_{s\nu})^{1/2}} + \frac{1}{2\tau_{sd}}\,\frac{\tilde{\omega}_{d\nu}}{(\tilde{\omega}^2_{d\nu} + \tilde{\Delta}^2_{d\nu})^{1/2}} , \tag{3}$$

$$\tilde{\Delta}_{s\nu} = \Delta_s + \frac{1}{2\tau_s}\,\frac{\tilde{\Delta}_{s\nu}}{(\tilde{\omega}^2_{s\nu} + \tilde{\Delta}^2_{s\nu})^{1/2}} + \frac{1}{2\tau_{sd}}\,\frac{\tilde{\Delta}_{d\nu}}{(\tilde{\omega}^2_{d\nu} + \tilde{\Delta}^2_{d\nu})^{1/2}} , \tag{4}$$

$$\tilde{\omega}_{d\nu} = \omega_\nu + \frac{1}{2\tau_d}\,\frac{\tilde{\omega}_{d\nu}}{(\tilde{\omega}^2_{d\nu} + \tilde{\Delta}^2_{d\nu})^{1/2}} + \frac{1}{2\tau_{ds}}\,\frac{\tilde{\omega}_{s\nu}}{(\tilde{\omega}^2_{s\nu} + \tilde{\Delta}^2_{s\nu})^{1/2}} , \tag{5}$$

$$\tilde{\Delta}_{d\nu} = \Delta_d + \frac{1}{2\tau_d}\,\frac{\tilde{\Delta}_{d\nu}}{(\tilde{\omega}^2_{d\nu} + \tilde{\Delta}^2_{d\nu})^{1/2}} + \frac{1}{2\tau_{ds}}\,\frac{\tilde{\Delta}_{s\nu}}{(\tilde{\omega}^2_{s\nu} + \tilde{\Delta}^2_{s\nu})^{1/2}} , \tag{6}$$

where $\Delta_{s(d)}$ is the order parameter of the $s(d)$ band of a pure two-band superconductor. The τ's are impurity-scattering relaxation times given by the following:

$$1/2\tau_s = \pi n_i N_s(0) \langle |V_s(\vec{p})|^2\rangle_\Omega , \tag{7}$$

$$1/2\tau_d = \pi n_i N_d(0) \langle |V_d(\vec{p})|^2\rangle_\Omega , \tag{8}$$

$$1/2\tau_{sd} = \pi n_i N_d(0) \langle |V_{sd}(\vec{p})|^2\rangle_\Omega , \tag{9}$$

$$1/2\tau_{ds} = \pi n_i N_s(0) \langle |V_{sd}(\vec{p})|^2\rangle_\Omega , \tag{10}$$

where n_i is the impurity density, $N_{s(d)}(0)$ is the density of states for the $s(d)$ band at the Fermi surface, $V_{s(d)}(\vec{p})$ is the Fourier transform of the s- (d-) band intraband impurity-scattering potential due to one impurity, $V_{sd}(\vec{p})$ is that of the interband impurity-scattering potential, and $\langle\cdots\rangle_\Omega$ represents the solid-angle average.

In view of various mistakes made by Sung *et al.*,[6,7] we point out that these equations, Eqs. (1)–(10), are obtained by solving self-consistently the Dyson equations shown in Fig. 1. (For details, see Ref. 5.)

For niobium superconductors, $N_d(0) \gg N_s(0)$. If all of the scattering potentials are assumed to be of the same order in magnitude, we have approximately

$$\tilde{\omega}_{s\nu} \cong \omega_\nu + \frac{1}{2\tau_{sd}}\,\frac{\tilde{\omega}_{d\nu}}{(\tilde{\omega}^2_{d\nu} + \tilde{\Delta}^2_{d\nu})^{1/2}} , \tag{11}$$

$$\tilde{\Delta}_{s\nu} \cong \Delta_s + \frac{1}{2\tau_{sd}}\,\frac{\tilde{\Delta}_{d\nu}}{(\tilde{\omega}^2_{d\nu} + \tilde{\Delta}^2_{d\nu})^{1/2}} , \tag{12}$$

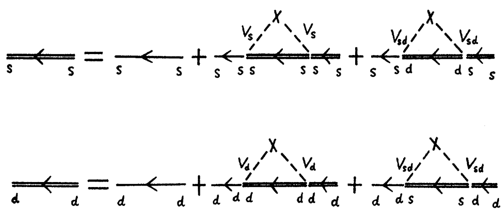

FIG. 1. Dyson equations for the s-band and the d-band Green's functions. The single solid lines are to denote the bare Green's functions, the double solid lines the dressed Green's functions. The dashed lines indicate impurity scattering. The self-energy diagrams are always of second order in impurity-scattering potential. The interband impurity scattering causes the coupling between the two Dyson equations.

$$\tilde{\omega}_{d\nu} \cong \omega_\nu + \frac{1}{2\tau_d} \frac{\tilde{\omega}_{d\nu}}{(\tilde{\omega}_{d\nu}^2 + \tilde{\Delta}_{d\nu}^2)^{1/2}} , \tag{13}$$

$$\tilde{\Delta}_{d\nu} \cong \Delta_d + \frac{1}{2\tau_d} \frac{\tilde{\Delta}_{d\nu}}{(\tilde{\omega}_{d\nu}^2 + \tilde{\Delta}_{d\nu}^2)^{1/2}} . \tag{14}$$

These relations are to be used in Sec. III.

III. SPECIFIC HEAT OF TWO-BAND SUPERCONDUCTORS AT LOW TEMPERATURES

As the lowering of the specific heat due to impurities takes place distinctly in the low-temperature region $T \gtrsim 0$, we shall pay particular attention to the change in s-band specific heat in this temperature region. The reason is the following.

According to the BCS theory for one-band superconductors, as a superconductor passes from its normal phase to its superconducting phase, there is a discontinuous jump in specific heat at T_c; then in the immediate vicinity of T_c, the specific heat decreases linearly with decreasing temperature; and in the low-temperature region $T \gtrsim 0$, it deceases exponentially with decreasing temperature.

In a two-band niobium superconductor, the behavior of the specific heat for each individual band shows clearly in the experimental data of Shen *et al.*[3] This is also the reason why in Sec. II we only pay attention to the two-band model in the intraband BCS coupling limit. First, in the temperature region $T_c > T > T_{cs}$, we notice the decrease of d-band specific heat with decreasing temperature. When temperature reaches T_{cs}, the s band provides an increase in specific heat. Since $T_{cs} \cong 10^{-1} T_c$, we expect that in the temperature region $T_{cs} > T > 0$ the s-band specific heat becomes larger than the d-band specific heat. The above qualitative argument should be correct for the pure two-band superconductors and two-band superconductors containing a small amount of nonmagnetic impurities. This is clearly demonstrated by the experimental data of Shen, Senozan, and Phillips.[3]

In the actual calculation of the specific heat, we have to know the densities of states for quasiparticles, $N_s(\omega)$ and $N_d(\omega)$, of the two bands. They can be obtained from the following[8]:

$$N_s(\omega) = -\frac{1}{\pi} \int \frac{d^3p}{(2\pi)^3} \, \mathrm{Im}\, G_s(\vec{p}, z)\big|_{z \to \omega + i\delta} , \tag{15}$$

$$N_d(\omega) = -\frac{1}{\pi} \int \frac{d^3p}{(2\pi)^3} \, \mathrm{Im}\, G_d(\vec{p}, z)\big|_{z \to \omega + i\delta} , \tag{16}$$

where $G_s(\vec{p}, z)$ and $G_d(\vec{p}, z)$ are obtained by analytically continuing the 1-1 components of the 2×2 matrix Green's functions [Eqs. (1) and (2)], to the whole z plane except the real axis on which the singularities of $G_s(\vec{p}, z)$ and $G_d(\vec{p}, z)$ take place. Explicitly, we have

$$G_s(\vec{p}, z) = \frac{\tilde{z}_s + \epsilon_{s\vec{p}}}{\tilde{z}_s^2 - \epsilon_{s\vec{p}}^2 - \tilde{\Delta}_s^2} , \tag{17}$$

$$G_d(\vec{p}, z) = \frac{\tilde{z}_d + \epsilon_{d\vec{p}}}{\tilde{z}_d^2 - \epsilon_{d\vec{p}}^2 - \Delta_d^2} , \tag{18}$$

where

$$\tilde{z}_s = z + \frac{1}{2\tau_{sd}} \frac{\tilde{z}_d}{(\tilde{\Delta}_d^2 - \tilde{z}_d^2)^{1/2}} , \tag{19}$$

$$\tilde{\Delta}_s = \Delta_s + \frac{1}{2\tau_{sd}} \frac{\tilde{\Delta}_d}{(\tilde{\Delta}_d^2 - \tilde{z}_d^2)^{1/2}} , \tag{20}$$

$$\tilde{z}_d = z + \frac{1}{2\tau_d} \frac{\tilde{z}_d}{(\tilde{\Delta}_d^2 - \tilde{z}_d^2)^{1/2}} , \tag{21}$$

$$\tilde{\Delta}_d = \Delta_d + \frac{1}{2\tau_d} \frac{\tilde{\Delta}_d}{(\tilde{\Delta}_d^2 - \tilde{z}_d^2)^{1/2}} . \tag{22}$$

Here, we have used the approximate relations Eqs. (11)–(14).

Upon substituting Eqs. (17) and (18) into Eqs. (15) and (16), we obtain

$$N_s(\omega) = N_s(0) \; \mathrm{Re}\left(\frac{u_s}{(u_s^2 - 1)^{1/2}}\right)_{z \to \omega + i\delta} , \tag{23}$$

$$N_d(\omega) = N_d(0) \; \mathrm{Re}\left(\frac{u_d}{(u_d^2 - 1)^{1/2}}\right)_{z \to \omega + i\delta} , \tag{24}$$

with ω only assuming positive values, and $u_s \equiv \tilde{z}_s / \tilde{\Delta}_s$ and $u_d \equiv \tilde{z}_d / \tilde{\Delta}_d$.

From Eqs. (21) and (22), it is straightforward to show that

$$u_d = z / \Delta_d . \tag{25}$$

This is not surprising at all, since with our approximation [Eqs. (13)–(14)] only intraband impurity scattering is associated with the d band. In the spirit of Anderson's theorem, u_d should be expected to take the same values of a pure superconductor. Physically, this means that since $N_d(0)$ is much larger than $N_s(0)$, the scattering of s electrons into the d band is more favorable than the scattering of d electrons into the s band, and that the d electrons are more likely to be scattered within the d band itself. With Eq. (24), the d-band density of states for quasiparticles is given by the same expression for a pure superconductor with only a d band present:

$$N_d(\omega) = N_d(0)\,\omega/(\omega^2 - \Delta_d^2)^{1/2}\ , \qquad \omega > \Delta_d$$

$$= 0\ , \qquad \omega < \Delta_d. \qquad (26)$$

The expression for u_s is more complicated, since now we must take the interband impurity scattering into account. From Eqs. (19), (20), and (25), we have

$$u_s = \frac{z}{\Delta_s}\ \frac{(1 - z^2/\Delta_d^2)^{1/2} + \Gamma/\Delta_d}{(1 - z^2/\Delta_d^2)^{1/2} + \Gamma/\Delta_s}\ . \qquad (27)$$

For simplicity in notation, we have let $\Gamma \equiv 1/2\tau_{sd}$. Since we are only interested in the temperature region $T_{cs} > T \gtrsim 0$, for reasons to be pointed out later, we have only to know $N_s(\omega)$ accurately in the frequency region $\omega \ll \Delta_d$. From Eq. (23), we obtain

$$N_s(\omega) = N_s(0)\omega/(\omega^2 - \omega_g^2)^{1/2} \qquad \omega_g < \omega \ll \Delta_d$$

$$= 0 \qquad \omega < \omega_g, \quad (28)$$

where

$$\omega_g = \frac{\Delta_s + \Gamma}{1 + \Gamma/\Delta_d}\ . \qquad (29)$$

It is interesting to note that in the absence of impurities ($\Gamma = 0$), ω_g reduces to the order parameter of a superconductor with only an s band present. In view of the familiar form of $N_s(\omega)$, one can regard ω_g as equivalent "energy gap" for the s band in an impure two-band superconductor.

The specific heat for the two-band system can be calculated from the entropy of the system[9]:

$$S = S_s + S_d\ , \qquad (30)$$

$$S_s = 4k_B \int_0^{\omega_D} d\omega\, N_s(\omega)\left(\ln(1 + e^{-\beta\omega}) + \frac{\beta\omega}{e^{\beta\omega} + 1}\right), \qquad (31)$$

$$S_d = 4k_B \int_0^{\omega_D} d\omega\ N_d(\omega)\left(\ln(1 + e^{-\beta\omega}) + \frac{\beta\omega}{e^{\beta\omega} + 1}\right)\ , \qquad (32)$$

where ω_D is the phonon Debye frequency.

As shown in Eq. (26), with our approximation, [Eqs. (13) and (14)] the d-band density of states for quasiparticles is unchanged upon introducing impurities, $N_d(\omega) = N_d^{(0)}(\omega)$ [with superscript (0) to denote quantities for a pure two-band superconductor]. From Eq. (32), we have $S_d = S_d^{(0)}$; that is, the entropy of the d band is also not changed. Thus, the change in entropy of the two-band system in the low-temperature region due to impurities is only associated with the s band. For comparison, we write down the s-band entropy in a pure two-band superconductor:

$$S_s^{(0)} = 4k_B \int_0^{\omega_D} d\omega\, N_s^{(0)}(\omega)\left(\ln(1 + e^{-\beta\omega}) + \frac{\beta\omega}{e^{\beta\omega} + 1}\right), \qquad (33)$$

where

$$N_s^{(0)}(\omega) = N_s(0)\omega/(\omega^2 - \Delta_s^2)^{1/2}\ , \qquad \Delta_s < \omega \ll \Delta_d$$

$$= 0\ , \qquad \omega < \Delta_s\ . \quad (34)$$

In the temperature region $T \ll T_{cs}$ and $T \gtrsim 0$, we have the following approximate relation:

$$\ln(1 + e^{-\beta\omega}) + \beta\omega/(e^{\beta\omega} + 1) \cong e^{-\beta\omega}(1 + \beta\omega)\ . \qquad (35)$$

Since β is large, $e^{-\beta\omega}$ is a rapidly descending function of ω. This explains why, in order to calculate the entropy and the specific heat, in the low-temperature region, we have only to know accurately the expression for $N_s(\omega)$ in the frequency region, $\omega \ll \Delta_d$.

Substituting Eq. (35) into Eqs. (31), and (33) and letting $\omega_D \to \infty$, we obtain

$$S_s = (m_s p_{Fs}/\pi^2)(2\pi\omega_g^3\beta)^{1/2}e^{-\beta\omega_g}\ , \qquad (36)$$

$$S_s^{(0)} = (m_s p_{Fs}/\pi^2)(2\pi\Delta_s^3\beta)^{1/2}e^{-\beta\Delta_s}\ . \qquad (37)$$

In the temperature region $T \gtrsim 0$, both Δ_s and ω_g are nearly independent of temperature and approximately equal to the values at $T = 0$: $\Delta_s \cong \Delta_s(0)$ and $\omega_g \cong \omega_g(0)$.

The specific heats for the two cases are

$$C_s = -\beta\frac{\partial S_s}{\partial\beta} = \frac{m_s p_{Fs}}{\pi^2}\ (2\pi\omega_g^5\beta^3)^{1/2}e^{-\beta\omega_g}\ , \qquad (38)$$

$$C_s^{(0)} = -\beta\frac{\partial S_s^{(0)}}{\partial\beta} = \frac{m_s p_{Fs}}{\pi^2}\ (2\pi\Delta_s^5\beta^3)^{1/2}e^{-\beta\Delta_s}\ . \qquad (39)$$

If the impurity density is low enough, we have $\Gamma \ll \Delta_s \ll \Delta_d$ and $\omega_g \cong \Delta_s + \Gamma$. Further, since the temperature dependence of C_s and $C_s^{(0)}$ is mainly associated with the factors $e^{-\beta\omega_g}$ and $e^{-\beta\Delta_s}$, we obtain

$$C_s \cong (m_s p_{Fs}/\pi^2)(2\pi\Delta_s^5\beta^3)^{1/2}e^{-\beta(\Delta_s + \Gamma)} \qquad (40)$$

in the low-temperature region.

From these two equations [(39) and (40)] we reach our final result

$$C_s \cong C_s^{(0)}e^{-\beta\Gamma}\ , \qquad (41)$$

or

$$\ln C_s = \ln C_s^{(0)} - \Gamma/k_B T\ , \qquad (42)$$

with

$$\Gamma = \pi n_i N_d(0)\,\langle\,|V_{sd}(\vec{p})|^2\rangle_\Omega\ . \qquad (43)$$

We notice that the lowering of $\ln C_s$ of an impure two-band superconductor is proportional to the density of impurities, the d-band density of states at the Fermi level, and the interband impurity-scattering strength, represented by $\langle\,|V_{sd}(\vec{p})|^2\rangle_\Omega$. In Fig. 2, we plot the essential features of $\ln C_s$ as a function of T^{-1}, with Γ treated as parameter. In view of the fact that

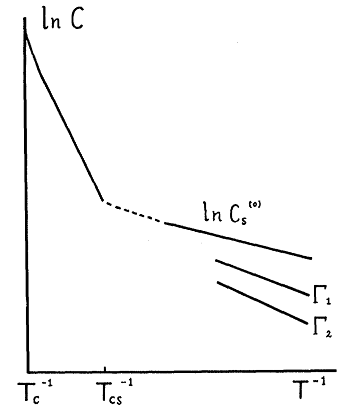

FIG. 2. Essential features of the logarithm of specific heat as a function of temperature, with Γ treated as parameter ($\Gamma_2 > \Gamma_1$).

in the literature only the specific-heat data of one impure niobium superconductor have been reported, and no sufficient information has been supplied on the various quantities such as n_i and $N_d(0)$, we do not intend to make a quantitative comparison between the experimental data and our present theory.[10] Yet, the essential features as plotted do resemble closely those of the experimental data of the impure niobium superconductor given by Shen, Senozan, and Phillips.[3]

IV. CONCLUSION

In conclusion, we point out that the specific heat of a two-band superconductor containing nonmagnetic impurities, as a thermodynamic property, has been shown to be dependent on the interband impurity scattering. It is in this sense that the nonmagnetic impurities in a two-band superconductor play a role similar to that played by the magnetic impurities in an one-band superconductor. Physically, they both have the pair-breaking mechanism in their respective superconductors. Further, in the simple model we have treated, the two Fermi surfaces of the two bands are regarded as spherical, each with its own Fermi momentum and electron effective mass. We have not taken into account other effects, such as band-structure anisotropy and strong phonon-electron interaction. Nevertheless, we still succeed in interpreting the essential features of the specific-heat data for an impure niobium superconductor. Finally, it should be remarked that, at present, more specific-heat experimental data for niobium superconductors with different amounts of impurities and different types of impurities are needed before we can make a quantitative comparison between our theory and experimental results. From these data, one can deduce various important properties, such as the d-band density of states at the Fermi surface for niobium and the strength of interband impurity scattering for particular type of impurity.

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$$(2\tau_{sd})^{-1} = \pi n_i N_d(0)\,\langle V_d(\vec{p})\,V_s(\vec{p})\rangle_\Omega\,, \quad \text{(SW 7)}$$

$$(2\tau_{d\,s})^{-1} = \pi n_i N_s(0)\,\langle V_d(\vec{p})\,V_s(\vec{p})\rangle_\Omega . \quad \text{(SW 13)}$$

They are incorrect because they are not consistent with the interband impurity-scattering self-energy diagrams, as shown in Fig. 1. Their mistake can further be traced back to their perturbation Hamiltonian due to impurity scattering [Eq. (SW 2)] in which terms due to the interband impurity-scattering potential $V_{sd}(\vec{x} - \vec{R}_a)$ are not included. [These terms are correctly shown in Eq. (2) of Ref. 5.] Without these terms, all the results in their paper are meaningless.

[7]C. C. Sung, Phys. Rev. 187, 548 (1969). Equations from this paper will be referred to as (S1), etc. In footnote 19, Sung replaces $\langle V_d(\vec{p})\,V_s(\vec{p})\rangle_\Omega$ in Eqs. (SW 7) and (SW 13) by $\langle V_s(\vec{p})^2\rangle_\Omega$ and $\langle V_d(\vec{p})^2\rangle_\Omega$, respectively. Unfortunately, these replacements again are not consistent with the interband impurity-scattering self-energy diagrams. Even though Eq. (S 24) is correct, his remarks concerning this equation in footnotes 19 and 20 are irrelevant. It is pointed out in AGD [A. A. Abrikosov, L. P. Gorkov, and I. E. Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Physics* (Prentice-Hall, Englewood Cliffs, N. J., 1963), p. 329] that terms linear in $V_s(\vec{x} - \vec{R}_a)$ will only contribute to the ground-state energy of the system, after the impurity-position average is performed, and therefore they are not essential. Only terms of second order in $V_s(\vec{x} - \vec{R}_a)$, related to a same impurity, will contribute essentially to the self-energy. Therefore, after the impurity-position average is performed, Eq. (S 24) becomes

$$\begin{aligned} G_s(\vec{x}, \vec{x}'; \omega_\nu) = {} & G_s^{(0)}(\vec{x}, \vec{x}'; \omega_\nu) \\ & + n_i \int G_s^{(0)}(\vec{x}, \vec{x}''; \omega_\nu)\, V_s(\vec{x}'' - \vec{R}_a)\, G_s(\vec{x}'', \vec{x}'''; \omega_\nu) \\ & \times V_s(\vec{x}''' - \vec{R}_a)\, G_s(\vec{x}''', \vec{x}'; \omega_\nu)\, d^3x''\, d^3x''' \\ & + n_i \int G_s^{(0)}(\vec{x}, \vec{x}''; \omega_\nu)\, V_{sd}(\vec{x}'' - \vec{R}_a)\, G_d(\vec{x}'', \vec{x}'''; \omega_\nu) \\ & \times V_{sd}(\vec{x}''' - \vec{R}_a)\, G_s(\vec{x}''', \vec{x}'; \omega_\nu)\, d^3x''\, d^3x''' , \end{aligned}$$

where n_i is the impurity density. The self-energies are always of second order in impurity-scattering potentials. In terms of diagrams, this equation is shown in Fig. 1. Similar to the self-energy diagrams, vertex corrections are also associated with corresponding terms of second order in the impurity-scattering potential (see p. 332 of AGD). Thus, his arguments in terms of linearity in $V_s(\vec{x} - \vec{R}_a)$ and second order in $V_{sd}(\vec{x} - \vec{R}_a)$ are completely meaningless. Along with this, Sung makes an incorrect assertion in footnote 16 of his paper, a rebuttal against which is published separately [W. S. Chow, Phys. Rev. B (to be published)].

[8]S. Skalski, O. Betboder-Matibet, and P. R. Weiss, Phys. Rev. 136, A1500 (1964).

[9]V. Ambegaokar, in *Superconductivity*, edited by R. D. Parks (M. Dekkar, New York, 1969).

[10]I. M. Tang, Phys. Rev. B 2, 1299 (1970). Tang's paper involves a serious error. His Eqs. (4.3) and (4.4) are valid only when temperature is very close to T_c (or T_{cd}). His conclusion, Eq. (4.16), that the change in specific heat due to impurity scattering is *negative*, is not correct in this temperature region. Leupold and Boorse [H. A. Leupold and H. A. Boorse, Phys. Rev. 134, A1322 (1964)] noticed that, at $T \lesssim T_c$, the niobium specific-heat data exhibit a small upward deviation from the specific-heat values predicted by the BCS theory for pure one-band superconductors; that is to say, the change in specific heat due to impurity scattering should be *positive* in this temperature region. The correct theory concerning the specific heat in this temperature region is given by Chow [W. S. Chow, J. Phys. F (to be published)].

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Electronic Structure of the Intermediate State in Type-I Superconductors

Reiner Kümmel*
Institut für Theoretische Physik der Universität Frankfurt am Main, Germany
and
Departamento de Fiscia, Universidad del Valle, Cali, Colombia
(Received 12 August 1970)

The quasiparticle wave functions and the energy-eigenvalue equations of the intermediate state in extreme type-I superconductors are calculated for the full range of the excitation spectrum. A WKBJ method of solving the Bogoliubov equations at any temperature below T_c is used. The periodicity of the pair potential leads to Bloch-type wave functions and a band structure of the energy spectrum for fixed momenta parallel to the phase boundaries. The magnetic field has an effect on the quasiparticle energies only by its influence on the structural and thermodynamic properties of the system. The width of the normal regions, and an effective variation length summing up the space dependence of the pair potential, are the variational parameters of the theory. From the general eigenvalue equations explicit energy spectra are obtained for simplified models of the pair potential.

I. INTRODUCTION

The excitation spectrum of a sequence of superconducting and normal or nearly normal regions has been discussed in a number of recent investigations.

Bound states with quantized energy levels have been found (a) in the isolated normal regions of the intermediate state of type-I superconductors,[1] (b) in the core of a single vortex line in the mixed state of type-II superconductors,[2–4] and (c) in the normal regions of normal-superconducting contacts.[5,6] The spectrum of these states with energies less than the maximum value Δ of the pair potential determines the low-temperature properties of the respective samples.

For the mixed state of type-II superconductors, the scattering states with $E > \Delta$ have also been analyzed,[3] and the periodic structure of the intermediate state has been considered by van Gelder, who, using a Kronig model of a periodic steplike pair potential, obtained a band structure of the energy spectrum in the one-dimensional case.[7]

Common to all these investigations is the use of the Bogoliubov equations,[8] the Schrödinger-like equations for electrons and holes, coupled by the pair potential $\Delta(\vec{r})$ of the superconductor. Whereas often it has been found necessary to assume simple forms such as step functions for the pair potential, or to limit the discussion to rather low temperatures where only the lowest-lying bound states are important, we intend to look into the periodic intermediate-state structure using the WKBJ approximation of solving the Bogoliubov equations, developed in Ref. 3. This allows us to treat the full energy spectrum at any temperature below T_c without introducing a simplified pair potential.

In Ref. 3 the problem of self-consistency of the pair potential $\Delta(\vec{r})$ and of the local magnetic field $\vec{h}(\vec{r})$ of a vortex line has been dealt with by using