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# Specific Heat of Superconductors with Overlapping Bands

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The anomalously small jumps in specific heat, $\Delta C$, of superconducting lanthanum and yttrium compounds are discussed in terms of Suhl, Matthias and Walker's theory of superconductivity in the case of overlapping two bands. It turns out that the law of corresponding states still holds in a generalized sense. The ratio between the jump and the electronic specific heat in the normal phase at the transition temperature, $\Delta C/\gamma T_c$, is a function of four independent quantities, although the theory contains five parameters. The ratio is found to be generally smaller than the BCS result, 1.43, for superconductors with a single conduction band. It is suggested that electron tunneling experiments could determine the two energy gaps at the absolute zero temperature and the ratio between them at the transition temperature, thereby providing sufficient knowledge to estimate the ratio. The experimental results for niobium and molybdenum are discussed. Niobium does not show such a small ratio and is suggested to have rather strong pairing interactions. Molybdenum is a weak coupling superconductor and has a small ratio $\Delta C/\gamma T_c$. In one of the Appendices, a derivation is presented of the electron tunneling characteristics at non-zero temperatures, the time variation in the density matrix being explicitly taken into account.

## § 1. Introduction

Recently, Satoh and Ohtsuka found an anomalous specific heat of superconducting lanthanum and yttrium compounds such as $YSi_{1.90}$, $YGe_{1.62}$, $LaSi_2$, and $LaGe_2$.[1] Their jump in specific heat, $\Delta C$, at the transition temperature $T_c$ was small in comparison with the BCS result.[2] For instance, the ratio between the jump $\Delta C$ and the electronic specific heat at $T_c$ in the normal phase, $\gamma T_c$, is only 0.69 for $LaGe_2$, while the BCS theory gives 1.43. The above authors have concluded that the anomalous specific heat is due to some intrinsic property of the compounds and that since superconductors with isotropic single band tend to give larger jumps as the pairing interactions get stronger,[3] the observed smaller jumps should be related to the presence of a complicated Fermi surface and/or overlapping electronic bands. In the $ThSi_2$ type crystal structure of the above compounds, Si and Ge form a three-dimensional graphite structure. It would be reasonable to assume the existence of a conduction band due to this. On the other hand yttrium and lanthanum would give rise to a $d$ or $f$ band. The latter band might overlap with the former and the Fermi surface would be in the overlapping bands. Thus, it may be worthwhile discussing a model of simple superconductors with two overlapping bands without taking

into account other complications of the Fermi surface such as its anisotropy.

A model with overlapping bands was discussed by Suhl, Matthias and Walker[4] and by Kondo.[5] Suhl, Matthias and Walker generalized the BCS formulation, including interband interactions in a pairing form. The transition temperature was given in terms of five parameters, the cutoff energy in the pairing interactions, the two electronic densities of states in the normal phase, one corresponding to each band, and three interaction strengths, two of which characterize intraband processes and the other interband processes. Since the densities of states are always multiplied by the interaction strengths, there are only five independent parameters in the formalism. It was also pointed out that there are generally two energy gaps and their temperature dependence was indicated. Kondo generalized Suhl, Matthias and Walker's discussion by choosing different cutoff energies for the three processes. Assuming one of the intraband processes and the interband process to be independent of the electron-phonon interactions, he took the corresponding energy cutoffs to be independent of the average phonon frequency and discussed the isotope effect.

In the present work, the simpler model of Suhl, Matthias and Walker is used, since we do not intend to discuss the isotope effect and the theory is not very sensitive to the choice of the cutoffs. The model was applied to explain the specific heat anomaly of pure niobium at low temperatures by Sung and Shen.[6] They were able to fit the experimental data and determine three quantities, the smaller energy gap, the ratio between the two densities of states and the magnitude of the interband interaction.

We shall first investigate the conditions for the energy gap equation to have a solution and derive an expression for the free energy difference between the two phases. The specific heat expression given by Sung and Shen can be obtained from the free energy difference. It is quite remarkable that the law of corresponding states still holds as far as the ratio $\Delta C/\gamma T_c$ is concerned. It is determined if four independent quantities are given in spite of the fact that the formalism contains five parameters. Therefore, one does not have to perform five independent experiments in order to estimate the ratio quantitatively. We would like to suggest electron tunneling experiments to measure the magnitudes of the two gaps at the absolute zero of temperature and the ratio between them at the transition temperature. These three, together with the transition temperature, compose the four quantities. Apart from quantitative estimates, the ratio $\Delta C/\gamma T_c$ is shown to be generally smaller than the BCS value, in qualitative agreement with Satoh and Ohtsuka's experiments. The contribution to the jump $\Delta C$ is determined by the derivative $d\Delta_\lambda^2/dT$ at the transition temperature where $\Delta_\lambda$ is the energy gap in the $\lambda$ band and $T$ denotes the temperature. The band with the larger energy gap gives the main contribution to $\Delta C$, its $d\Delta_\lambda^2/dT|_{T=T_c}$ being large, while the both bands contribute equally to $\gamma T_c$, except for the density of states factor. Thus the ratio $\Delta C/\gamma T_c$ is decreased.

In § 2, a brief derivation of the energy gap equation under the Hartree-Fock-Gorkov approximations[7] is given. Relevant properties of its solutions are investigated. In § 3, the free energy difference between the supperconducting and the normal phases is given in terms of the energy gaps. The expression for the ratio $\Delta C/\gamma T_c$ is written as a function of "observable quantities". In § 4, tunneling experiments are discussed as a possible way of observing the above quantities. This will help us to confirm whether the superconductor is really of overlapping band type. In the last section, the ratio $\Delta C/\gamma T_c$ is discussed for niobium and molybdenum. The former is suggested to be a strong coupling superconductor, while the latter actually possesses a small ratio $\Delta C/\gamma T_c$.

## § 2. Energy gap equation

We shall consider a system of electrons interacting with one another through two-body forces. A Bloch state for an electron is specified by parameters $\boldsymbol{p}$ and $\sigma$, $\boldsymbol{p}$ indicating both the crystal momentum $\boldsymbol{k}$ and the electronic band denoted by $\lambda$. The parameter $\sigma$ gives the spin orientation. The Hamiltonian of the system takes the form

$$H=\sum_{p\sigma}\epsilon_{p\sigma}c_{p\sigma}^{*}c_{p\sigma}+\frac{1}{2}\sum v_{pqp'q'}c_{p\sigma}^{*}c_{q\sigma'}^{*}c_{q'\sigma'}c_{p'\sigma}. \tag{2·1}$$

The operators $c_{p\sigma}$ and $c_{p\sigma}^{*}$ destroy an electron in a Bloch state $(\boldsymbol{p}, \sigma)$, and create an electron in the same state, respectively. $\epsilon_{p\sigma}$ is the kinetic energy of an electron, and $v_{pqp'q'}$ gives the strength of the two-body forces, satisfying the hermiticity condition

$$(v_{pqp'q'})^{*}=v_{p'q'pq},$$

where the asterisk means a complex conjugate quantity.

The energy gap equation can be derived under the Hartree-Fock-Gorkov approximation, the discussion following exactly the same lines as for a system with a single electronic band.[8] We simply replace the crystal momentum suffix $\boldsymbol{k}$ by our $\boldsymbol{p}$. A Bloch state with a parameter $-\boldsymbol{p}$ has the opposite crystal momentum $-\boldsymbol{k}$ in the same band. We shall assume pairing between the electrons in the time-reversed states, neglecting the pairing between the electrons in defferent electronic bands. This is generally a reasonable assumption, since the Fermi momentum varies from band to band.

Let us just quote the results of the discussion. Introducing Nambu's matrix notation[9] by

$$\Psi_{p}=\begin{pmatrix} c_{p\uparrow} \\ c_{-p\downarrow}^{*} \end{pmatrix},\quad \Psi_{p}^{+}=(c_{p\uparrow}^{*},\ c_{-p\downarrow}),$$

one defines the thermodynamic Green's function

$$G(\boldsymbol{p}, t_1, t_2)=-\mathrm{Tr}\exp(\beta(\Omega-\mathcal{H}))\,T(\Psi_{p}(t_1)\Psi_{p}^{+}(t_2)).$$

Here, Tr means the trace operation, and $\beta$ is the inverse temperature

$$\beta=1/\kappa T,$$

$\kappa$ being Boltzmann's constant. $\mathcal{H}$ is defined by

$$\mathcal{H}=H-\mu N.$$

$\mu$ is the chemical potential and $N$ the total number of electrons

$$N=\sum_{p\sigma} c_{p\sigma}^{*} c_{p\sigma}.$$

The grand potential $\Omega$ is given by

$$\exp(-\beta\Omega)=\mathrm{Tr}\exp(-\beta\mathcal{H}). \tag{2·2}$$

The symbol $T$ indicates the time ordering operation with the usual sign convention. The wave fields $\Psi_p(t)$ and $\Psi_p^{+}(t)$ are defined to be

$$\Psi_p(t)=\exp(\mathcal{H}t)\Psi_p\exp(-\mathcal{H}t),\quad \Psi_p^{+}(t)=\exp(\mathcal{H}t)\Psi_p^{+}\exp(-\mathcal{H}t).$$

One introduces the Fourier transform of the Green's function by

$$G(\boldsymbol{p}, t_1, t_2)=\frac{1}{\beta}\sum_{n=-\infty}^{\infty}\exp[-iE_n(t_1-t_2)]\cdot G(\boldsymbol{p}, iE_n). \tag{2·3}$$

Here,

$$E_n=(2n+1)\pi/\beta,\ n \text{ being an integer.}$$

Under the Hartree-Fock-Gorkov approximation, $G(\boldsymbol{p}, iE_n)$ is given by

$$G(\boldsymbol{p}, iE_n)=\frac{iE_n+\bar{\epsilon}_p\tau_3+\Delta_{1p}\tau_1+\Delta_{2p}\tau_2}{(iE_n)^2-E_p^{\,2}}. \tag{2·4}$$

Here,

$$\bar{\epsilon}_p=\epsilon_p+\chi_p-\mu,$$
$$E_p^{\,2}=\bar{\epsilon}_p^{\,2}+\Delta_{1p}^2+\Delta_{2p}^2.$$

The $\tau_i$'s are the Pauli spin matrices. The quantities $\chi_p$, $\Delta_{1p}$, and $\Delta_{2p}$ are all real and are determined by the equations

$$\chi_p=\sum_q\left(v_{pqpq}-\frac{1}{2}v_{pqqp}\right)\left\{1-\frac{\bar{\epsilon}_q}{E_q}\tanh\frac{\beta E_q}{2}\right\}, \tag{2·5}$$

$$\Delta_p=-\sum_q V_{pq}\frac{\Delta_q}{2E_q}\tanh\frac{\beta E_q}{2}. \tag{2·6}$$

Here

$$\Delta_p=\Delta_{1p}+i\Delta_{2p},$$
$$V_{pq}=v_{p,-p,q,-q}. \tag{2·7}$$

The first equation, (2·5), gives the Hartree-Fock field in the superconducting

phase and the second one, (2·6), is nothing but the usual BCS equation.

Now we shall introduce simplifying assumptions as in BCS. Since we are concerned only with states close to the Fermi surfaces, so that $|\bar{\epsilon}_{\boldsymbol{p}}|<\omega_0$, where $\omega_0$ is the typical phonon energy, the pairing strength $V_{\boldsymbol{pq}}$ can be replaced by its average value over the crystal momenta. The average depends on the band index $\lambda$ and has three values. Two of them, $V_{ss}$ and $V_{dd}$, give the strengths of the intraband pairings in the $s$ and $d$ bands, respectively. The names of the bands are arbitrarily chosen. The last one, $V_{sd}$, gives the interband pairing strength. Because of the definition of $V_{\boldsymbol{pq}}$, (2·7), $V_{ss}$, $V_{dd}$ and $V_{sd}$ are all real. By a phase transformation of $\Psi_{\boldsymbol{p}}$, one can always take $\Delta_{2\boldsymbol{p}}=0$ and regard the energy gap $\Delta_{\boldsymbol{p}}$ as real.[9] Further, introducing the densities of Bloch states of one spin per unit energy at the respective Fermi surfaces, $N_s$ and $N_d$, we can rewrite the energy gap equation (2·6):

$$\begin{aligned}\Delta_s&=-\eta_s\Delta_s I(\Delta_s,\beta)-\eta_d'\Delta_d I(\Delta_d,\beta),\\ \Delta_d&=-\eta_s'\Delta_s I(\Delta_s,\beta)-\eta_d\Delta_d I(\Delta_d,\beta).\end{aligned}\tag{2·8}$$

The energy gap $\Delta_{\boldsymbol{p}}$ now depends only on the parameter $\lambda$, ($\lambda=s$ or $d$). $\eta_\lambda$ and $\eta_\lambda'$ are defined by

$$\begin{aligned}&\eta_s=V_{ss}N_s,\ \eta_s'=V_{sd}N_s,\\ &\eta_d=V_{dd}N_d,\ \eta_d'=V_{sd}N_d.\end{aligned}\tag{2·9}$$

Finally, $I(\Delta,\beta)$ is

$$I(\Delta_\lambda,\beta)=\int_0^{\omega_0}\frac{d\bar{\epsilon}_{\boldsymbol{p}}}{E_{\boldsymbol{p}}}\tanh\frac{\beta E_{\boldsymbol{p}}}{2}.\tag{2·10}$$

The above equation was first discussed by Suhl, Matthias, and Walker.[4]

In order to obtain the transition temperature $T_c$, one replaces the $I(\Delta_\lambda,\beta)$'s by

$$I(\beta_c)\equiv I(0,\beta_c)=\int_0^{\omega_0}\frac{d\bar{\epsilon}}{\bar{\epsilon}}\tanh\frac{\beta_c\bar{\epsilon}}{2},\ \beta_c=\frac{1}{\kappa T_c},\tag{2·11}$$

and eliminates the remaining $\Delta_\lambda$'s. The quadratic equation for $I(\beta_c)$, thus obtained, has the solutions

$$I(\beta_c)=\frac{1}{2(\eta_s\eta_d-\eta_s'\eta_d')}[-\eta_s-\eta_d\pm\sqrt{(\eta_s-\eta_d)^2+4\eta_s'\eta_d'}].\tag{2·12}$$

Because $I(\beta_c)$ is positive by its definition, (2·11), the right-hand side of (2·12) should be positive. This requirement leads to the conclusions:

(1) when $\eta_s\eta_d>\eta_s'\eta_d'$:

a) if $\eta_s<0$ and $\eta_d<0$, there are two solutions for the transition temperature,

b) if $\eta_s>0$ and $\eta_d>0$, there is no solution for $T_c$.

(2) when $\eta_s'\eta_d'>\eta_s\eta_d$, there is only one transition temperature given by

$$I(\beta_c)=\frac{1}{2(\eta_s\eta_d-\eta_s'\eta_d')}\left[-\eta_s-\eta_d-\sqrt{(\eta_s-\eta_d)^2+4\eta_s'\eta_d'}\right], \tag{2·13}$$

(3) when $\eta_s\eta_d=\eta_s'\eta_d'$:

a) if $\eta_s<0$, there is a transition temperature given by

$$I(\beta_c)=-\frac{1}{\eta_s+\eta_d},$$

b) if $\eta_s>0$, there is no $T_c$.

Here, it is important to note that

$$\eta_s'\eta_d'=V_{sd}^2 N_s N_d\geq 0.$$

In case (1), the effect of the interband interaction $V_{sd}$ is still weak and the criterion for the superconducting transition is given by that for each component band. The two transition temperatures reduce to the transition temperature of each band in the small $V_{sd}$ limit. They can be characterized by the relative phase between $\Delta_d$ and $\Delta_s$ at $T_c$,

$$x_c\equiv\lim_{T\to T_c}\Delta_d/\Delta_s.$$

Using the energy gap equations, (2·8), one finds

$$x_c=-(1+\eta_s I(\beta_c))/\eta_d' I(\beta_c).$$

Substituting the expression for $I(\beta_c)$, (2·12), we have

$$x_c=\frac{1}{2\eta_d'}\left[\eta_d-\eta_s\pm\sqrt{(\eta_s-\eta_d)^2+4\eta_s'\eta_d'}\right]. \tag{2·14}$$

Each of the two signs in (2·14) corresponds to its counterpart in the expression for $I(\beta_c)$, (2·12), respectively. Since the higher transition temperature is given by the negative sign in (2·12), the corresponding $x_c$ has the opposite sign to $\eta_d'$. Thus, we can conclude

$$\text{for higher } T_c,\ \text{sgn } x_c=-\text{sgn } V_{sd},$$

$$\text{for lower } T_c,\ \text{sgn } x_c=\text{sgn } V_{sd}.$$

In case (2)

$$\text{sgn } x_c=-\text{sgn } V_{sd}.$$

There is a similar situation for the solutions of the gap equations (2·8) at the absolute zero of temperature, $\Delta_s^0$ and $\Delta_d^0$. The discussion in Appendix A gives the following conclusions:

(1) When $\eta_s\eta_d > \eta_s'\eta_d'$, and

a) if $\eta_s < 0$ and $\eta_d < 0$, there are two solutions for the energy gaps at zero temperature. Each solution is characterized by the sign of the ratio,

$$x_0 \equiv \Delta_d^0/\Delta_s^0.$$

For the solution with larger $\Delta_\lambda^0$'s,

$$\text{sgn } x_0 = -\text{sgn } V_{sd}, \tag{2·15}$$

for the other solution with smaller $\Delta_\lambda^0$'s,

$$\text{sgn } x_0 = \text{sgn } V_{sd}.$$

b) If $\eta_s > 0$ and $\eta_d > 0$, there is no solution.

(2) When $\eta_s'\eta_d' > \eta_s\eta_d$, there is only one solution whose $x_0$ has the sign

$$\text{sgn } x_0 = -\text{sgn } V_{sd}. \tag{2·16}$$

(3) When $\eta_s'\eta_d' = \eta_s\eta_d$, and

a) if $\eta_s < 0$, there is a solution whose $x_0$ is given by

$$x_0 = \eta_d/\eta_d'.$$

b) If $\eta_s > 0$, there is no solution.

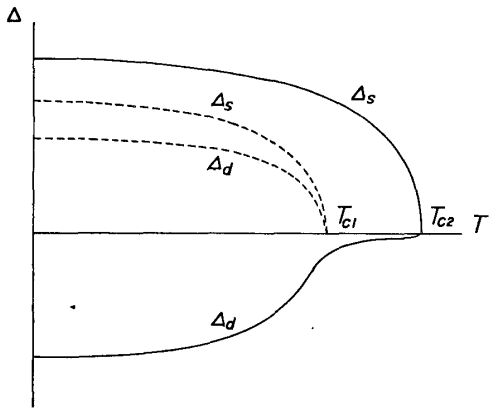


Fig. 1. The two solutions of the energy gap equations in the case (1) a) and $V_{sd} > 0$. The solid curves represent the solution with the larger $\Delta_\lambda^0$*s* and the higher $T_c$, while the dotted curves give the other solution. The solid and dotted curves do not intersect each other.

There is a complete parallelism between the situations at $T=0$ and at $T=T_c$.

These conclusions suggest the temperature dependence of the energy gaps, when there are two solutions. It is illustrated in Fig. 1. The solid curves give $\Delta_\lambda$'s with the larger $\Delta_\lambda^0$'s and the higher $T_c$, while the dotted curves represent $\Delta_\lambda$'s with the smaller $\Delta_\lambda^0$'s and the lower $T_c$. The essential point is that the solid and dotted curves do not cross over, that is, the solution with the larger $\Delta_\lambda^0$'s always has the higher $T_c$. Suppose there were a cross over. Then the sign of the ratio

$$x \equiv \Delta_d/\Delta_s$$

for the solution with the larger $\Delta_\lambda^0$'s would have to change somewhere between $T=0$ and $T=T_c$, $\Delta_d$ vanishing there. This would give rise to a new transition temperature.

The energy gap equation is the condition for the system to have minimum

free energy. When there are two solutions, one of them corresponds to a stable state and the other to a metastable state. The solution with the larger $\Delta_\lambda^0$'s and the higher $T_c$ gives the stable state. Its transition temperature is also given by (2·13). The metastable state solution will not be discussed further.

Finally, we shall explicitly derive the temperature dependence of the energy gaps at temperatures close to $T_c$ in order to calculate the specific heat jump. Eliminating the $\Delta_\lambda$'s outside the $I$'s in the energy gap equations, (2·8), one gets

$$1=-\eta_s I(\Delta_s,\beta)-\eta_d I(\Delta_d,\beta)-(\eta_s\eta_d-\eta_s'\eta_d')I(\Delta_s,\beta)I(\Delta_d,\beta).$$

Substituting the expansion of $I(\Delta,\beta)$ in a power series in $\Delta^2$ at $\beta\sim\beta_c$,[10]

$$I(\Delta,\beta)=I(\beta_c)+\log\frac{\beta}{\beta_c}-\frac{7\zeta(3)}{8}\left(\frac{\beta\Delta}{\pi}\right)^2+O(\beta\Delta)^4, \tag{2·17}$$

we find

$$\begin{aligned}0=&\{\eta_s+\eta_d+2(\eta_s\eta_d-\eta_s'\eta_d')I(\beta_c)\}\log\frac{\beta}{\beta_c}\\&-\frac{7\zeta(3)\beta_c^2}{8\pi^2}[\{\eta_s+(\eta_s\eta_d-\eta_s'\eta_d')I(\beta_c)\}\Delta_s^2\\&\qquad+\{\eta_d+(\eta_s\eta_d-\eta_s'\eta_d')I(\beta_c)\}\Delta_d^2]\\&+O\left(1-\frac{T}{T_c}\right)^2.\end{aligned} \tag{2·18}$$

Here $\zeta(z)$ is the Riemann zeta function and $\zeta(3)=1.2021$. Since

$$\Delta_d^2=x_c^2\Delta_s^2+O\left(1-\frac{T}{T_c}\right)^2,$$

the relation (2·18) gives

$$\Delta_s^2=\frac{8\pi^2}{7\zeta(3)\beta_c^2}\cdot\frac{\eta_s+\eta_d+2I(\beta_c)(\eta_s\eta_d-\eta_s'\eta_d')}{\eta_s+x_c^2\eta_d+(1+x_c^2)I(\beta_c)(\eta_s\eta_d-\eta_s'\eta_d')}\cdot\log\frac{\beta}{\beta_c}+O\left(1-\frac{T}{T_c}\right)^2. \tag{2·19}$$

This expression can be rewritten in terms of observable quantities such as the energy gaps and the transition temperature, instead of the coupling parameters $\eta_\lambda$'s. The energy gap equations (2·8) reduce to

$$\Delta_s^0=-\eta_s\Delta_s^0\log\frac{2\omega_0}{|\Delta_s^0|}-\eta_d'\Delta_d^0\log\frac{2\omega_0}{|\Delta_d^0|},$$

$$1=-(\eta_s+\eta_d'x_c)I(\beta_c),$$

at $T=0$ and $T=T_c$, respectively. Here the weak coupling approximation

$$I(\Delta, \infty) \simeq \log \frac{2\omega_0}{|\Delta|}, \quad \omega_0 \gg |\Delta|$$

is used. $\eta_s$ and $\eta_d'$ turn out to be

$$\eta_s = -\frac{1}{I(\beta_c)} \cdot \frac{x_c \Delta_s^0 I(\beta_c) - \Delta_d^0 \log (2\omega_0/|\Delta_d^0|)}{x_c \Delta_s^0 \log (2\omega_0/|\Delta_s^0|) - \Delta_d^0 \log (2\omega_0/|\Delta_d^0|)},$$

$$\eta_d' = \frac{1}{I(\beta_c)} \cdot \frac{\Delta_s^0 \{I(\beta_c) - \log (2\omega_0/|\Delta_s^0|)\}}{x_c \Delta_s^0 \log (2\omega_0/|\Delta_s^0|) - \Delta_d^0 \log (2\omega_0/|\Delta_d^0|)}. \tag{2·20}$$

Similarly, we obtain

$$\eta_d = \frac{1}{I(\beta_c)} \cdot \frac{\Delta_d^0 I(\beta_c) - x_c \Delta_s^0 \log (2\omega_0/|\Delta_s^0|)}{x_c \Delta_s^0 \log (2\omega_0/|\Delta_s^0|) - \Delta_d^0 \log (2\omega^0/|\Delta_d^0|)},$$

$$\eta_s' = -\frac{1}{I(\beta_c)} \cdot \frac{x_c \Delta_d^0 \{I(\beta_c) - \log (2\omega_0/|\Delta_d^0|)\}}{x_c \Delta_s^0 \log (2\omega_0/|\Delta_s^0|) - \Delta_d^0 \log (2\omega_0/|\Delta_d^0|)}. \tag{2·21}$$

In the weak coupling approximation, one has

$$I(\beta_c) = \int_0^{\omega_0} \frac{d\bar{\epsilon}}{\bar{\epsilon}} \tanh \frac{\beta_c \bar{\epsilon}}{2} = \log (1.14 \beta_c \omega_0), \tag{2·22}$$

according to the BCS estimate. The coupling parameters $\eta_\lambda$'s are thus expressed in terms of $\Delta_\lambda^0$'s, $x_c$, $T_c$ and $\omega_0$. It is quite remarkable that if one substitutes these relations into the expression for $\Delta_s^2$, (2·19), the quantity $\omega_0$ is cancelled out and we have

$$\Delta_s^2 = \frac{8\pi^2}{7\zeta(3)\beta_c^2} \cdot \frac{x_c \bar{\Delta}_s - \bar{\Delta}_d}{x_c^3 \bar{\Delta}_s - \bar{\Delta}_d} \cdot \log \frac{\beta}{\beta_c} + O\left(1 - \frac{T}{T_c}\right)^2. \tag{2·23}$$

Here

$$\bar{\Delta}_\lambda \equiv \Delta_\lambda^0 \log \frac{2|\Delta_\lambda^0|}{3.5 \kappa T_c}.$$

The original energy gap equations, (2·8), contained five independent parameters. Nevertheless, the observable quantity $\Delta_s^2$ depends only on four quantities, the two $\Delta_\lambda^0$'s, $x_c$, and $T_c$. In the BCS theory the gap equation had two parameters, $N(0)V$ and $\omega_0$. But the energy gap depended only on $\beta_c$ at $\beta \sim \beta_c$. It was an example of the "law of corresponding states"[11] which says that the physically observable quantities are universal functions of the reduced temperature $T/T_c$, if they are expressed in reduced units. The present result is a generalization of the law of corresponding states to superconductors with overlapping bands. This reduces the number of experiments which provide the information necessary to estimate $\Delta C/\gamma T_c$.

## § 3. Free energy difference and jump in specific heat

In this section, the free energy difference between the superconducting and the normal phases is derived under the Hartree-Fock-Gorkov approximation. The result turns out to be a sum of contributions from the two bands, each having a form given by the BCS theory. The jump in specific heat is then discussed and the ratio $\Delta C/\gamma T_c$ is explicitly given. It turns out to be generally smaller than the BCS value 1.43.

Defining a grand potential $\Omega$ as a function of the volume, temperature and chemical potential, by Eq. (2·2),

$$\exp(-\beta\Omega)=\mathrm{Tr}\ \exp(-\beta\mathcal{H}),$$

one can obtain the difference in the thermodynamical potential (Gibbs' free energy) between the two phases, $\Delta\Phi$, by

$$\Delta\Phi=\Phi_n-\Phi_s=\Omega_n-\Omega_s=\Delta\Omega. \tag{3·1}$$

Here, the suffices $n$ and $s$ specify the normal and superconducting phases, respectively. A brief discussion of the above relation (3·1) is given in Appendix B.

Suppose the two-body interaction $v_{pqp'q'}$ is proportional to a parameter $g$

$$v_{pqp'q'}=gv^0_{pqp'q'}.$$

Then, the grand potential $\Omega$ also depends on the parameter $g$ and one easily finds

$$\frac{\partial\Omega}{\partial g}=\frac{1}{g}\langle H_I\rangle. \tag{3·2}$$

Here, $H_I$ is the second term of the Hamiltonian, (2·1), and the parentheses mean a thermal average:

$$\langle H_I\rangle=\mathrm{Tr}\exp(\beta(\Omega-\mathcal{H}))H_I.$$

Under the Hartree-Fock-Gorkov approximation,[7] this thermal average is transformed to

$$\begin{aligned}\langle H_I\rangle&=\tfrac{1}{2}\sum v_{pqp'q'}\langle c^*_{p\sigma}c^*_{q\sigma'}c_{q'\sigma'}c_{p'\sigma}\rangle\\&=\tfrac{1}{2}\sum v_{pqp'q'}[\langle c^*_{p\sigma}c_{p'\sigma}\rangle\langle c^*_{q\sigma'}c_{q'\sigma'}\rangle-\langle c^*_{p\sigma}c_{q'\sigma'}\rangle\langle c^*_{q'\sigma'}c_{p'\sigma}\rangle\\&\qquad+\langle c^*_{p\sigma}c^*_{q\sigma'}\rangle\langle c_{q'\sigma'}c_{p'\sigma}\rangle]\\&=\sum(2v_{pqpq}-v_{pqqp})n_{p\uparrow}n_{q\uparrow}\\&\quad+\sum V_{pp'}G_{21}(\boldsymbol{p},t,t-0)G_{12}(\boldsymbol{p}',t',t'-0).\end{aligned} \tag{3·3}$$

$n_{p\uparrow}$ is the average number of electrons in a Bloch state $\boldsymbol{p}$ with up spin. In calculating the difference in $\langle H_I\rangle$ between the two phases, we can disregard the first term in the right-hand side of (3·3). $n_{p\uparrow}$ in the superconducting

phase is different from that in the normal phase only at the vicinity of the Fermi surface, $|\bar{\epsilon}_p|<\omega_0$. In this region, the two-body interaction $v$ varies so slowly that the first term in (3·3) depends effectively on the total electron numbers in the region which are independent of the phase.

Substituting the expression for the Green's function, i.e. (2·3) and (2·4) into (3·3), one obtains

$$\begin{aligned}\Delta\langle H_I\rangle &= \langle H_I\rangle_n - \langle H_I\rangle_s \\ &= \sum_p \frac{\Delta_p^2}{2E_p}\tanh\frac{\beta E_p}{2} = \sum_\lambda N_\lambda \Delta_\lambda^2 I(\Delta_\lambda, \beta).\end{aligned} \tag{3·4}$$

In virtue of the energy gap equation (2·8), the integrals $I(\Delta_\lambda, \beta)$ are expressed in terms of $\Delta_\lambda$, $\eta_\lambda$ and $\eta_\lambda'$,

$$\begin{aligned}\Delta_s I(\Delta_s, \beta) &= \frac{\eta_d'\Delta_d - \eta_d\Delta_s}{\eta_s\eta_d - \eta_s'\eta_d'}, \\ \Delta_d I(\Delta_d, \beta) &= \frac{\eta_s'\Delta_s - \eta_s\Delta_d}{\eta_s\eta_d - \eta_s'\eta_d'}.\end{aligned} \tag{3·5}$$

Substituting (3·4) and (3·5) into the equation for $\Delta\Omega$, (3·2), we have

$$\begin{aligned}\Delta\Omega &= \int_0^1 \frac{dg}{g^2(\eta_s^0\eta_d^0 - \eta_s'^0\eta_d'^0)}[N_s\Delta_s(\eta_d'^0\Delta_d - \eta_d^0\Delta_s) + N_d\Delta_d(\eta_s'^0\Delta_s - \eta_s^0\Delta_d)] \\ &= -\int d[\{N_s\Delta_s(\eta_d'^0\Delta_d - \eta_d^0\Delta_s) + N_d\Delta_d(\eta_s'^0\Delta_s - \eta_s^0\Delta_d)\}/g(\eta_s^0\eta_d^0 - \eta_s'^0\eta_d'^0)] \\ &\quad + \int_0^{\Delta_s} d\Delta_s \left\{2N_s(\eta_d'^0\Delta_d - \eta_d^0\Delta_s) + 2N_d(\eta_s'^0\Delta_s - \eta_s^0\Delta_d)\frac{d\Delta_d}{d\Delta_s}\right\} \Big/ g(\eta_s^0\eta_d^0 - \eta_s'^0\eta_d'^0) \\ &= -\int d[\sum N_\lambda\Delta_\lambda^2 I(\Delta\lambda, \beta)] + 2\int_0^{\Delta_s} d\Delta_s \sum_\lambda \Delta_\lambda I(\Delta\lambda, \beta)\frac{d\Delta_\lambda}{d\Delta_s} \\ &= -\sum_\lambda \int_0^{\Delta_\lambda} d\Delta_\lambda N_\lambda\Delta_\lambda^2 \frac{\partial I(\Delta_\lambda, \beta)}{\partial\Delta_\lambda}.\end{aligned} \tag{3·6}$$

Here, the relation

$$N_s\eta_d'^0 = N_sN_dV_{sd}/g = N_d\eta_s'^0$$

is used. Since $\Delta\Omega$ is identical with $\Delta\Phi$, $\Delta\Phi$ turns out to be a direct sum of the contributions from the two bands, each contribution being given by the BCS result. The corresponding result for the specific heat was already used by Sung and Shen in their analysis of the low temperature specific heat of niobium.[6)]

The relation (3·6) is particularly simple in the following two cases. At the absolute zero of temperature, one finds

$$\Delta\Phi=-\sum_{\lambda}\int_{0}^{\Delta_{\lambda}^{0}}d\Delta_{\lambda}^{0}N_{\lambda}\Delta_{\lambda}^{02}\frac{\partial}{\partial\Delta_{\lambda}^{0}}\log\frac{2\omega_{0}}{|\Delta_{\lambda}^{0}|}=\frac{1}{2}\sum_{\lambda}N_{\lambda}\Delta_{\lambda}^{02},\quad T=0,$$

and at temperatures close to $T_c$,

$$\Delta\Phi\simeq\sum_{\lambda}\int_{0}^{\Delta_{\lambda}}d\Delta_{\lambda}N_{\lambda}\Delta_{\lambda}^{2}\frac{\partial}{\partial\Delta_{\lambda}}\left(\frac{7\zeta(3)\beta^{2}\Delta_{\lambda}^{2}}{8\pi^{2}}\right)=\frac{7\zeta(3)\beta^{2}}{16\pi^{2}}\sum_{\lambda}N_{\lambda}\Delta_{\lambda}^{4},\quad T\sim T_{c}.$$

Here, the expansion of $I(\Delta,\beta)$ in terms of $\beta\Delta$, (2·17), is used. Although $\beta_c$ depends on the coupling strength $g$, $I(\beta_c)+\log(\beta/\beta_c)$ does not.

The jump in specific heat $\Delta C$ is given by

$$\Delta C=C_s-C_n=T_c\frac{\partial^{2}\Delta\Phi}{\partial T^{2}}\bigg|_{T=T_c}=\frac{7\zeta(3)}{8\pi^{2}\kappa^{2}T_c}\sum_{\lambda}N_{\lambda}\left(\frac{d\Delta_{\lambda}^{2}}{dT}\right)_{T=T_c}^{2}$$

$$=\frac{8\pi^{2}\kappa^{2}T_c}{7\zeta(3)}(N_s+x_c^{4}N_d)\left(\frac{x_c\bar{\Delta}_s-\bar{\Delta}_d}{x_c^{3}\bar{\Delta}_s-\bar{\Delta}_d}\right)^{2}.\qquad(3\cdot7)$$

Here, the explicit temperature dependce of $\Delta_{\lambda}^{2}$ at $T\sim T_c$, (2·23), is used. Since the electronic specific heat in the normal phase takes the form

$$C_n=\gamma T=\tfrac{2}{3}\pi^{2}(N_s+N_d)\kappa^{2}T,$$

the ratio between $\Delta C$ and $\gamma T_c$ is

$$\frac{\Delta C}{\gamma T_c}=\frac{12}{7\zeta(3)}\cdot\frac{N_s+x_c^{4}N_d}{N_s+N_d}\cdot\left(\frac{x_c\bar{\Delta}_s-\bar{\Delta}_d}{x_c^{3}\bar{\Delta}_s-\bar{\Delta}_d}\right)^{2}.\qquad(3\cdot8)$$

The ratio $N_d/N_s$ can also be expressed in terms of the observable quantities, since

$$\frac{N_d}{N_s}=\frac{\eta_d'}{\eta_s'}=-\frac{\bar{\Delta}_s}{x_c\bar{\Delta}_d}.$$

Here the definition of $\eta_{\lambda}'$, (2·9), and the expressions for them, (2·20) and (2·21), are used. Substituting this relation into (3·8), one finally obtains

$$\frac{\Delta C}{\gamma T_c}=1.43\frac{x_c(x_c-\bar{x})^{2}}{(x_c\bar{x}-1)(\bar{x}-x_c^{3})},\qquad(3\cdot9)$$

where

$$\bar{x}=\frac{\bar{\Delta}_d}{\bar{\Delta}_s}=\frac{\Delta_d^{0}}{\Delta_s^{0}}\cdot\frac{\log(2|\Delta_d^{0}|/3.5\kappa T_c)}{\log(2|\Delta_s^{0}|/3.5\kappa T_c)},\qquad(3\cdot10)$$

and

$$x_c=\lim_{T\to T_c}\Delta_d/\Delta_s.$$

The ratio $\Delta C/\gamma T_c$ thus turns out to be different from the BCS value 1.43 by the factor in (3·9).

In order to see that this factor is generally less than unity, we shall first show that one of the energy gaps, $2|\Delta_\lambda^0|$, is generally larger than $3.5\,\kappa T_c$, while the other is smaller. In the simple BCS case, the energy gap at zero temperature, $2|\Delta^0|$ is equal to $3.5\,\kappa T_c$. Therefore, $3.5\,\kappa T_c$ would give a sort of average of the gaps in our case. Then it is reasonable to expect that one of the gaps would be larger than the average, and the other smaller. This can be proved if it is shown that

$$\log\frac{2|\Delta_s^0|}{3.5\kappa T_c}\cdot\log\frac{2|\Delta_d^0|}{3.5\kappa T_c}=\left\{I(\beta_c)-\log\frac{2\omega_0}{|\Delta_s^0|}\right\}\cdot\left\{I(\beta_c)-\log\frac{2\omega_0}{|\Delta_d^0|}\right\}\leq 0. \qquad (3\cdot 11)$$

Here, the expression for $I(\beta_c)$, (2·22), is used. The second expression in (3·11) can be rewritten in terms of the coupling parameters, $\eta_\lambda$ and $\eta_\lambda'$, and $x_0$,

$$\begin{aligned}\log\frac{2|\Delta_s^0|}{3.5\kappa T_c}\cdot\log\frac{2|\Delta_d^0|}{3.5\kappa T_c}=\frac{1}{2(\eta_s\eta_d-\eta_s'\eta_d')^2}\Big[&4\eta_s'\eta_d'\\&-\eta_d'x_0\{\eta_s-\eta_d-\sqrt{(\eta_s-\eta_d)^2+4\eta_s'\eta_d'}\}\\&-\frac{\eta_s'}{x_0}\{\eta_d-\eta_s-\sqrt{(\eta_s-\eta_d)^2+4\eta_s'\eta_d'}\}\Big].\end{aligned}$$

Here the expressions for $I(\beta_c)$, (2·13), and for $\log(2\omega_0/|\Delta_\lambda^0|)$, (A·1), are used. The above expression is not positive, if

$$\eta_d'x_0\{\eta_s-\eta_d-\sqrt{(\eta_s-\eta_d)^2+4\eta_s'\eta_d'}\}+\frac{\eta'_s}{x_0}\{\eta_d-\eta_s-\sqrt{(\eta_s-\eta_d)^2+4\eta_s'\eta_d'}\}\geq 4\eta_s'\eta_d'.$$

Neither side of this inequality is negative, since $\eta_s'\eta_d'\geq 0$ and sgn $x_0=-$sgn $V_{sd}$, (2·15) and (2·16). Therefore, we can square the two sides and calculate the difference. This turns out to be

$$\left\{\left(\eta_d'x_0+\frac{\eta_s'}{x_0}\right)(\eta_s-\eta_d)-\left(\eta_d'x_0-\frac{\eta_s'}{x_0}\right)\sqrt{(\eta_s-\eta_d)^2+4\eta_s'\eta_d'}\right\}^2.$$

Since the sign of $x_c$ is the same as that of $x_0$, as discussed in § 2, the definition of $\bar{x}$, (3·10), gives

$$\bar{x}=-a^2x_c,$$

with a positive constant $a^2$. Substituting this relation into the expression for $\Delta C/\gamma T_c$, (3·9), one finds

$$\frac{\Delta C}{\gamma T_c}=1.43\,\frac{(1+a^2)^2x_c^2}{(1+a^2x_c^2)(a^2+x_c^2)},$$

which is smaller than 1.43, since

$$(1+a^2x_c^2)(a^2+x_c^2)-(1+a^2)^2x_c^2=a^2(1-x_c^2)^2\geq 0.$$

The ratio, (3·9), reduces to the BCS value only if $x_c=1$ or $\bar{x}=0$.

The reduction in the ratio $\Delta C/\gamma T_c$ could be understood if one considers the case of weak interband interactions $V_{sd}$. The jump in specific heat depends on the derivative of $\Delta_\lambda^2$ at $T_c$, (3·7). If there is no interband interaction, $V_{sd}=0$, one of the gaps vanishes at $T_{c1}$, and the other at $T_{c2}$. A small $V_{sd}$ lets the first gap linger on to $T_{c2}$, as illustrated in Fig. 1. The derivative $d\Delta_\lambda^2/dT$ of that gap at $T_{c2}$ becomes small. Therefore, the jump $\Delta C$ is of the same order of magnitude as that of the single band case. On the other hand, $\gamma T_c$ is increased owing to the increase of the electronic density of states. The ratio $\Delta C/\gamma T_c$ is thus reduced.

To estimate $\Delta C/\gamma T_c$ numerically, the four quantities $\Delta_s^0$, $\Delta_d^0$, $x_c$ and $T_c$ have to be known. Since $T_c$ is already known, one has to observe the energy gaps. We would like to suggest electron tunneling experiments as one of the possibilities to find them. In the next section, the tunneling characteristics of superconductors with overlapping bands will be discussed.

## § 4. Tunneling characteristics of superconductors with overlapping bands

It is worth while emphasizing here that electron tunneling experiments will give a direct check that a superconductor has overlapping bands in Suhl, Matthias and Walker's sense. Since there are two energy gaps in their model, the tunneling characteristics should exhibit a corresponding structure.

The discussion of the characteristics follows exactly that for the superconductors with a single band. Suppose the tunneling Hamiltonian takes the form[12]

$$H_T=\sum_{\boldsymbol{pp}'\sigma}\{T_{\boldsymbol{pp}'}\,c^{r*}_{\boldsymbol{p}'\sigma}\,c^{l}_{\boldsymbol{p}\sigma}+\text{h.c.}\}. \tag{4·1}$$

Here, $T_{\boldsymbol{pp}'}$ is the matrix element for an electron in a Bloch state $\boldsymbol{p}$ to tunnel through the junction from left to right into a Bloch state $\boldsymbol{p}'$. The superscripts $l$ and $r$ refer to the left and right metals, respectively. Since the electrons at the Fermi surfaces contribute to the tunneling, $T_{\boldsymbol{pp}'}$ can be replaced by its value on the Fermi surfaces. Suppose the left metal has two overlapping bands, while the right one has a single band. Then, $T_{\boldsymbol{pp}'}$ has two typical values

$$T_\lambda=T_{k_F{}^l\lambda\,;\,k_F{}^r},\ (\lambda=s \text{ or } d),$$

where $k_{F\lambda}^l$ and $k_F{}^r$ are the Fermi momenta of the left and right metals, respectively.

The expression for the tunneling currents given by Scalapino, Schrieffer and Wilkins[13] is rederived in Appendix C as a result of the time variation of the density matrix. The formulation may have further applications. If a potential difference $V$ is applied across the junction ($V>0$, if the potential is higher at the right

metal), the tunneling current from right to left, $I(V)$, is given by

$$I(V)=-\frac{4\pi e}{\hbar}\sum_{\lambda}|T_{\lambda}|^2N_{\lambda}{}^{l}N^{r}\int_{-\infty}^{\infty}d\omega\,\mathrm{Re}\left(\frac{|\omega|}{\sqrt{\omega^2-|\Delta_{\lambda}|^2}}\right)\left(\frac{1}{1+e^{\beta\omega}}-\frac{1}{1+e^{\beta(\omega-eV)}}\right). \tag{4·2}$$

Here, the right metal is supposed to be in the normal phase and $e$ is the absolute value of the electronic charge.

$dI/dV$ is easily calculated and one immediately finds that the contribution to the $\omega$ integral comes mainly from the region $eV-\kappa T\leq\omega\leq eV+\kappa T$, thereby giving rise to the possibility of observing the energy gaps $\Delta_{\lambda}$'s. At the absolute zero of temperature, the ratio of $dI/dV$ between the superconducting and the normal phases is given by

$$\left(\frac{dI}{dV}\right)_{0s}\Big/\left(\frac{dI}{dV}\right)_{0n}=\frac{|T_s|^2N_s{}^{l}(|eV|/\sqrt{(eV)^2-|\Delta_s{}^{0}|^2})+|T_d|^2N_d{}^{l}(|eV|/\sqrt{(eV)^2-|\Delta_d{}^{0}|^2})}{|T_s|^2N_s{}^{l}+|T_d|^2N_d{}^{l}}.$$

The $dI/dV$ curve thus gives $\Delta_s{}^{0}$ and $\Delta_d{}^{0}$, which determine the ratio $\bar{x}$ defined by (3·10). The other ratio $x_c$ could also be determined by tunneling experiments at temperatures close to $T_c$. Then we would be able to estimate the ratio $\Delta C/\gamma T_c$ according to (3·9) and immediately know if the small specific heat jumps are really due to the overlapping of the electronic bands.

Finally, let us note possible difficulties in observing the tunneling characteristics. First, if one of the $|T_{\lambda}|^2N_{\lambda}{}^{l}$'s is quite small in comparison with the other, it might be difficult to observe both $\Delta_{\lambda}$'s. Secondly, when one of the gaps is too small compared to the other, the relevant structures in the $dI/dV$ curve might be overlooked. According to Sung and Shen's analysis,[6] niobium might belong to this case. Finally, if the two gaps, $\Delta_s$ and $\Delta_d$ are quite close each other, the structure would be masked by the anisotropy effect, reducing the $dI/dV$ curve to that of a single band superconductor.

## § 5. Discussion

We have discussed the Suhl-Matthias-Walker model for superconductors with overlapping bands and shown that the ratio between the jump in specific heat, $\Delta C$, and the electronic specific heat at the transition temperature, $\gamma T_c$, is generally smaller than the BCS value 1.43. In order to know the ratio quantitatively, the parameters in the model have to be given. It has been suggested that we observe the tunneling characteristics at low temperatures and at temperatures close to $T_c$. These two experiments would be enough to provide the information necessary to estimate $\Delta C/\gamma T_c$, since the system still satisfies a generalized "law of corresponding states". Moreover, tunneling experiments would give a direct check to see if the system is really a superconductor with overlapping bands.

Let us next consider the cases of two transition elements, niobium and molybdenum, for which the observed values of $\Delta C/\gamma T_c$ are available. Leupold

and Boorse measured the ratio for niobium, which presumably has overlapping $5s$ and $4d$ bands, and found[14]

$$\frac{\Delta C}{\gamma T_c}=1.87.$$

The result was larger than the BCS value. We believe that this large value is due to strong coupling effects. When the electron-phonon interactions become strong, the ratio is enhanced, as in lead and mercury.

The strength of the interactions is indicated by the ratio of $T_c$ and the Debye temperature $\theta$. According to Leupold and Boorse,

$$T_c=9.195^\circ\,\mathrm{K},\ \theta=275^\circ\,\mathrm{K},\ \text{for niobium,}$$

thereby giving

$$T_c/\theta=0.033.$$

Lead has the ratio 0.07 and aluminum, 0.002. This clearly indicates that niobium has a rather strong electron-phonon coupling and may not be understood by the simple weak-coupling theory presented in this paper. Actually, Leupold and Boorse observed an anomaly in the temperature dependence of the critical field, which is typical of strong coupling superconductors.

Meanwhile, a specific heat anomaly at low temperatures ($T<0.2T_c$) was found by Shen, Senozan and Phillips.[15] Sung and Shen analyzed the anomaly using the Suhl, Matthias, and Walker's model. They were able to select a set of parameters which could reproduce the experimental data for pure specimens. This may mean that the strong coupling effect is not so dominant at low temperatures. The characteristic phenomenon in the strong coupling superconductors is the strong damping of quasiparticle excitations. The damping rate, however, becomes less appreciable at low temperatures.

According to Sung and Shen, one of the two gaps, $\Delta_s$, is quite small,

$$\Delta_s{}^0\simeq 0.16\kappa T_c.$$

This may be the reason why many tunneling experiments on niobium have overlooked two-band effects.

Rorer, Onn and Meyer measured the transition and the Debye temperatures of molybdenum,[16]

$$T_c\simeq 0.92^\circ\,\mathrm{K},\ \theta=461+10^\circ\,\mathrm{K},\ \text{for molybdenum,}$$

thereby giving the ratio

$$T_c/\theta=0.002.$$

The pairing interactions are presumably as weak as aluminum. In fact, the ratio $\Delta C/\gamma T_c$ was found to be

$$\frac{\Delta C}{\gamma T_c}=1.29\pm0.15,$$

which is smaller than the BCS value.

In this paper we have discussed only the anomaly in the specific heat jump. Suhl, Matthias and Walker's model has also been applied to other phenomena such as accoustic attenuation, nuclear spin relaxation and electromagnetic absorption. The results of these discussions will be published in separate papers.

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## Appendix A

*The energy gap equations at the absolute zero of temperature*

In this Appendix, we shall discuss the energy gap equations, (2·8) at the absolute zero of temperature and derive the results given in § 2.

At $T=0$, the integral $I(\Delta_\lambda, \beta)$, defined by (2·10), takes the form

$$I(\Delta_\lambda^0, \infty)=\int_0^{\omega_0}\frac{d\bar{\epsilon}_p}{E_p}=\log\frac{[\omega_0+\sqrt{\omega_0^2+|\Delta_\lambda^0|^2}]}{|\Delta_\lambda^0|},$$

which reduces to

$$I(\Delta_\lambda^0, \infty)=\log\frac{2\omega_0}{|\Delta_\lambda^0|},$$

in the weak coupling limit. $I(\Delta_\lambda, \beta)$ is always positive by definition. It can also be rewritten as

$$\begin{aligned}I(\Delta_s^0, \infty)&=\frac{\eta_d-\eta_d' x_0}{\eta_s'\eta_d'-\eta_s\eta_d}\equiv f(x_0)>0,\\ I(\Delta_d^0, \infty)&=\frac{\eta_s-(\eta_s'/x_0)}{\eta_s'\eta_d'-\eta_s\eta_d}\equiv g(x_0)>0.\end{aligned}\qquad(\text{A}\cdot1)$$

Here one of the $I(\Delta_\lambda^0, \infty)$ is eliminated in the energy gap equations. The $I$'s should be always positive as functions of $x_0$. The absolute magnitudes of the energy gaps are given by

*) After this work was finished, Dr. A. J. Leggett informed us of a paper by Yu Luh and Gu Ben-Yuan, who discussed Suhl, Matthias and Walker's model in a special case where the three pairing strengths $V_{\lambda\lambda'}$ are only slightly different one from another.[18] They obtained a reduction in $\Delta C/\gamma T_c$ in this case.

$$|\Delta_s^0| = \frac{\omega_0}{\sinh f(x_0)}, \quad |\Delta_d^0| = \frac{\omega_0}{\sinh g(x_0)}, \tag{A·2}$$

where the parameter $x_0$ is determined by

$$\sinh f(x_0) = |x_0| \sinh g(x_0). \tag{A·3}$$

Introducing the notation

$$\tilde{\xi}_\lambda = \eta_\lambda / (\eta_s' \eta_d' - \eta_s \eta_d), \quad \tilde{\xi}_\lambda' = \eta_\lambda' / (\eta_s' \eta_d' - \eta_s \eta_d),$$

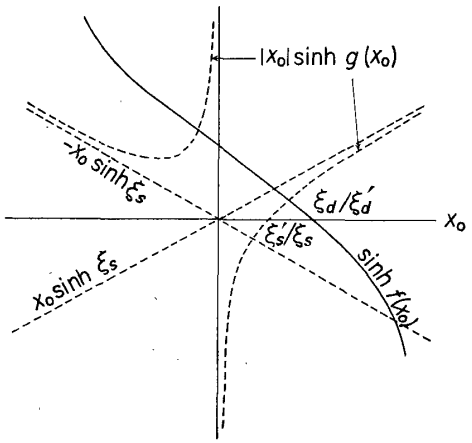


Fig. 2. The two functions in the equation (A.3) when all $\tilde{\xi}_\lambda$ and $\tilde{\xi}_\lambda'$ are positive. The solid curve gives $\sinh f(x_0)$ and the dotted ones represent $|x_0| \sinh g(x_0)$. There is always one intersection at $x_0<0$. The other one at $x_0>0$ appears on the upper half plane if $\tilde{\xi}_d/\tilde{\xi}_d' > \tilde{\xi}_s'/\tilde{\xi}_s$.

one can draw the curves of the functions on the two sides of Eq. (A·3). $\sinh f(x_0)$ is represented by a solid curve in Fig. 2 in the case that $\tilde{\xi}_d>0$ and $\tilde{\xi}_d'>0$. It increases *exponentially* when $x_0$ approaches negative infinity. The curve intersects the $x_0$ axis at $x_0=\tilde{\xi}_d/\tilde{\xi}_d'$. The two dotted curves give $|x_0|\sinh g(x_0)$ when $\tilde{\xi}_s$ and $\tilde{\xi}_s'>0$. The function tends to $|x_0|\sinh \tilde{\xi}_s$ at $x_0 \to \pm\infty$, that is, it increases *linearly*. The intersection with the $x_0$ axis is $x_0=\tilde{\xi}_s'/\tilde{\xi}_s$. Now it is evident that we always have one root for Eq. (A·3) at $x_0<0$, because of the difference in the asymptotic behavior of the two functions. Moreover, if $\tilde{\xi}_d/\tilde{\xi}_d'$ is larger than $\tilde{\xi}_s'/\tilde{\xi}_s$, one has another root at $x_0>0$; this root gives a larger value for $|\Delta_s^0|$ as can be seen from Fig. 2 and (A·2). Since there is symmetry between the $s$ and $d$ bands, the latter root also gives a larger value for $|\Delta_d^0|$ than the former. A similar discussion can be applied for the various cases with respect to the signs of $\tilde{\xi}_\lambda$ and $\tilde{\xi}_\lambda'$. The intersections between the solid and dotted curves on the upper half plane are relevant, since $f(x_0)$ and $g(x_0)$ should be positive, (A·1). Then one easily obtains the results:

(1) When $\tilde{\xi}_s'$ and $\tilde{\xi}_d'>0$, and

$$\tilde{\xi}_s>0, \begin{cases} \tilde{\xi}_d/\tilde{\xi}_d' > \tilde{\xi}_s'/\tilde{\xi}_s, & \text{then there are two roots, of which the one with } x_0>0 \text{ gives the larger gaps,} \\ \tilde{\xi}_s'/\tilde{\xi}_s > \tilde{\xi}_d/\tilde{\xi}_d', & \text{there is one negative root,} \end{cases}$$

$$\tilde{\xi}_s<0, \begin{cases} \tilde{\xi}_d/\tilde{\xi}_d' > \tilde{\xi}_s'/\tilde{\xi}_s, & \text{one negative root,} \\ \tilde{\xi}_s'/\tilde{\xi}_s > \tilde{\xi}_d/\tilde{\xi}_d', & \text{no root.} \end{cases}$$

(2) When $\tilde{\xi}_s'$ and $\tilde{\xi}_d'<0$, and

$$\xi_s>0,\begin{cases}\xi_s'/\xi_s>\xi_d/\xi_d', & \text{two roots, of which the negative one gives the larger gaps,}\\ \xi_d/\xi_d'>\xi_s'/\xi_s, & \text{one positive root,}\end{cases}$$

$$\xi_s<0,\begin{cases}\xi_s'/\xi_s>\xi_d/\xi_d', & \text{one positive root,}\\ \xi_d/\xi_d'>\xi_s'/\xi_s, & \text{no root.}\end{cases}$$

The above results exhaust all cases since $\xi_s'\xi_d'$ is always positive. Now it is straightforward to derive the final conclusions given in § 2.

## Appendix B

### *Difference in thermodynamic functions between the normal and the superconducting phases*

For the sake of completeness, we shall here show that the difference in the grand potential between the normal and superconducting phases is identical with that in the thermodynamical potential (Gibbs' free energy), although this fact has been used extensively.[17]

The grand potential $\Omega$ is evaluated from the equation

$$\exp(-\beta\Omega)=\mathrm{Tr}\exp(-\beta\mathcal{H})$$

as a function of the volume $V$, the temperature $T$, and the chemical potential $\mu$. It takes the form

$$\Omega_\alpha=-Vp_\alpha(\mu, T)$$

in the phase $\alpha$. $\alpha$ stands for the suffixes $n$ and $s$. $p_\alpha$ is the pressure

$$p=p_\alpha(\mu, T),$$

which gives the chemical potential in the $\alpha$ phase, $\mu_\alpha$, as a function of pressure and temperature. According to the Gibbs-Duhem relation, the total number of electrons $N$ is given by

$$N=V\left.\frac{\partial p_\alpha}{\partial\mu}\right|_T. \tag{B·1}$$

The difference in the thermodynamical potential $\Phi$ can be written as

$$\Delta\Phi=\Phi_n-\Phi_s=N\{\mu_n(T, p)-\mu_s(T, p)\}.$$

The difference in the grand potential $\Omega$ takes the form

$$\Delta\Omega=\Omega_n-\Omega_s=-V\{p_n(\mu, T)-p_s(\mu, T)\}.$$

Taking $\mu=\mu_s$ and $V=V_s$, one obtains

$$\begin{aligned}\Delta\Omega&=-V_s\{p_n(\mu_n-\Delta\mu, T)-p\}\\&=V_s\left\{\left.\frac{\partial p_n}{\partial\mu_n}\right|_T\Delta\mu-\frac{1}{2}\left.\frac{\partial^2 p_n}{\partial\mu_n^2}\right|_T(\Delta\mu)^2+\cdots\right\}.\end{aligned} \tag{B·2}$$

The second term in the parentheses is smaller than the first by a factor $\Delta\mu/\mu_n$. $\partial p_n/\partial\mu_n|_T$ gives the density of the system, by the relation (B·1); this is proportional to $k_F^3$, $k_F$ being the Fermi momentum. $\partial^2 p_n/\partial\mu_n^2|_T$ is proportional to $3k_F m$. Here, $m$ is the effective mass of the electrons. Therefore, the ratio between the second and the first terms turns out to be

$$\frac{3m}{2k_F^2}\Delta\mu \approx \frac{3\Delta\mu}{4\mu_n}.$$

The volume in the superconducting phase $V_s$ can be replaced by $V_n$, if one again neglects small corrections of the order of $\Delta\mu/\mu_n$. The expression for $\Delta\Omega$, (B·2), then gives

$$\Delta\Omega \simeq V_n \frac{\partial p_n}{\partial\mu_n}\bigg|_T \Delta\mu = N\Delta\mu = \Delta\Phi.$$

## Appendix C

*Tunneling characteristics at non-zero temperatures*

In this Appendix we would like to present a general discussion in order to obtain the tunneling characteristics at non-zero temperatures. Although the discussion will simply reproduce the known results, it might provide the basis for more general analyses and for further applications to other problems.

Suppose a potential difference $V$ is applied across the junction. $V$ is taken to be positive when the right metal has a higher potential. The total Hamiltonian takes the form

$$H = H_l + H_r - eVN_r + H_T.$$

Here, $H_l$ and $H_r$ are the Hamiltonians of the left and right metals, respectively, each having a form like (2·1). $N_r$ is the total number of the electrons in the right metal and the electronic charge is denoted by $-e$, $e$ being positive. The tunneling Hamiltonian $H_T$ takes the form given in (4·1). We shall measure energies relatively to the Fermi surface by introducing

$$\mathcal{H}_l = H_l - \mu N_l,$$
$$\mathcal{H}_r = H_r - \mu N_r.$$

The chemical potential $\mu$ has the same value in the two metals.

The statistical average of a dynamical quantity $A$ at time $t$ is given by

$$\langle A\rangle_t = \mathrm{Tr}(A\rho(t)), \tag{C·1}$$

where $\rho(t)$ is the density matrix, which satisfies the equation

$$i\hbar\frac{d\rho}{dt} = H\rho - \rho H.$$

Since $\rho(t)$ can be written as

$$\rho(t)=\exp\left(-\frac{iHt}{\hbar}\right)\rho(0)\exp\left(\frac{iHt}{\hbar}\right),$$

the statistical average, (C·1), takes the form

$$\langle A\rangle_t=\mathrm{Tr}(\rho(0)A(t)). \tag{C·2}$$

Here, $A(t)$ is a Heisenberg operator

$$A(t)=\exp\left(\frac{iHt}{\hbar}\right)A\ \exp\left(-\frac{iHt}{\hbar}\right).$$

In actual tunneling experiments, the junction is first manufactured and then a potential difference is applied. In the theoretical discussion, we reverse the order, first applying a potential difference between two separate pieces of metals and bringing them together to a contact across an insulating film at time $t=0$. Since the total system is in thermal equilibrium at $t\leq 0$, the density matrix takes the form

$$\rho(0)=\exp\{\beta(\Omega-\mathcal{H}_l-\mathcal{H}_r)\} \tag{C·3}$$

at $t=0$. Here,

$$\Omega=\Omega_l+\Omega_r,$$

$$\exp\{-\beta\Omega_l\}=\mathrm{Tr}\ \exp\{-\beta\mathcal{H}_l\},\ \text{etc.}$$

At $t=0$, the tunneling Hamiltonian $H_T$ begins to operate so that the system is no longer in equilibrium and relaxation takes place to a new equilibrium, currents passing across the junction. Ordinarily, the experiments are carried out at constant temperature. There might be heat exchanges between the system and its environment to keep the temperature constant. If the entropy variation due to the heat exchanges is small in comparison with the intrinsic entropy increase associated with the relaxation, the process could effectively be regarded as adiabatic, and the formulation in this Appendix could be applied. If the process gave rise to appreciable Joule heat, the present discussion could not apply.

Before going into the calculations, one has to make one more remark. Strictly speaking, the currents associated with the relaxation are not identical with those observed in the experiments. The observed currents are stationary and never vanish. However, when the system is sufficiently large, the above two currents should be practically the same since the potential difference is kept approximately constant, even though a small amount of relaxation current tunnels through the junction.

Now let us consider a Heisenberg operator $N_l(t)$, the total number of

electrons in the left metal. This can be written as

$$N_l(t) = \exp\{i\mathcal{H}t/\hbar\} N_l \exp\{-i\mathcal{H}t/\hbar\} = U^*(t) N_l U(t),$$

where

$$\mathcal{H} = H - \mu(N_l + N_r),$$

$$U(t) = \exp\{i(\mathcal{H}_l + \mathcal{H}_r - eVN_r)t/\hbar\} \exp\{-i\mathcal{H}t/\hbar\},$$

and $U^*(t)$ is the Hermitian conjugate of $U(t)$. The operator $U(t)$ satisfies the equation

$$i\hbar \frac{dU}{dt} = H_T(t) U(t).$$

Here, $H_T(t)$ is defined by

$$H_T(t) = \exp\{i(\mathcal{H}_l + \mathcal{H}_r - eVN_r)t/\hbar\} H_T \exp\{-i(\mathcal{H}_l + \mathcal{H}_r - eVN_r)t/\hbar\}.$$

$U(t)$ is obtained in a power series in $H_T$:

$$U(t) = 1 + \frac{1}{i\hbar}\int_0^t H_T(t_1)\, dt_1 + \frac{1}{(i\hbar)^2}\int_0^t\int_0^{t_1} H_T(t_1) H_T(t_2)\, dt_2 dt_1 + \cdots.$$

$N_l(t)$ is given by

$$N_l(t) = N_l - \frac{1}{i\hbar}\int_0^t [H_T(t_1), N_l]\, dt_1$$

$$+ \frac{N_l}{(i\hbar)^2}\int_0^t\int_0^{t_1} H_T(t_1) H_T(t_2)\, dt_2 dt_1 + \frac{1}{(i\hbar)^2}\int_0^t\int_0^{t_1} H_T(t_2) H_T(t_1)\, dt_2 dt_1 N_l$$

$$- \frac{1}{(i\hbar)^2}\int_0^t H_T(t_1)\, dt_1 N_l \int_0^t H_T(t_2)\, dt_2,$$

up to the second order in $H_T$.

Introducing the eigenstates $|n\rangle$ and the corresponding eigenvalues $E_n$ of the Hamiltonians $\mathcal{H}_l$ and $\mathcal{H}_r$ by

$$\mathcal{H}_l |n_l\rangle = E_n^{\,l} |n_l\rangle,$$

$$\mathcal{H}_r |n_r\rangle = E_n^{\,r} |n_r\rangle,$$

one can write a matrix element of the tunneling Hamiltonian:

$$\langle n_l' n_r' | H_T(t) | n_l n_r \rangle = \exp(iE_{n'n}t/\hbar) \cdot \langle n_l' n_r' | H_T | n_l n_r \rangle,$$

where

$$E_{n'n} = E_{n'}^{l} + E_{n'}^{r} - eVN_{n'}^{r} - E_n^{\,l} - E_n^{\,r} + eVN_n^{\,r}.$$

Making use of this time dependence and the relation

$$\frac{\sin^2(E_{n'n}t/2\hbar)}{E_{n'n}^2}\to\frac{\pi t}{2\hbar}\delta(E_{n'n}),\ \text{as}\ t\to\infty,$$

we obtain the diagonal matrix elements of $N_l(t)$:

$$\langle n_l n_r|N_l(t)|n_l n_r\rangle=N_n{}^l+\frac{2\pi t}{\hbar}\sum_{n_l'n_r'}(N_{n'}^l-N_n{}^l)\delta(E_{n'n})|\langle n_l'n_r'|H_T|n_l n_r\rangle|^2. \quad (C\cdot4)$$

The average tunneling current from the right to the left at a potential difference $V$ is

$$I(V)=-e\lim_{t\to\infty}\frac{1}{t}[\langle N_l\rangle_t-\langle N_l\rangle_0].$$

Substituting (C·4) into the definition of the statistical average, (C·2), and using the expression for $\rho(0)$, (C·3), one finds

$$\begin{aligned}I(V)=&\frac{2\pi e}{\hbar}\sum_{\substack{n_l n_r\\ n_l'n_r'}}\exp[\beta(\Omega-E_n{}^l-E_n{}^r)]\cdot\\ &\times|\sum_{pp'\sigma}T_{pp'}\langle n_l'n_r'|c_{p'\sigma}^{r*}c_{p\sigma}^{l}|n_l n_r\rangle|^2\delta(E_{r'}^l+E_{n'}^r-E_n{}^l-E_n{}^r-eV)\\ &-|\sum_{pp'\sigma}T_{pp'}^*\langle n_l'n_r'|c_{p\sigma}^{l*}c_{p'\sigma}^{r}|n_l n_r\rangle|^2\delta(E_{n'}^l+E_{r'}^r-E_n{}^l-E_n{}^r+eV)].\end{aligned}$$

In this way, we have recovered the expression which Scalapino, Schrieffer and Wilkins derived by explicitly calculating the transition probabilities.[13] The discussion hereafter follows theirs exactly, and the tunnelling current between two superconductors, one with overlapping bands and the other with a single band, takes the form

$$I(V)=\frac{4\pi e}{\hbar}\int_{-\infty}^{\infty}d\omega\sum_\lambda|T_\lambda|^2N_\lambda{}^l(\omega)N^r(\omega-eV)\left[\frac{1}{1+e^{\beta(\omega-eV)}}-\frac{1}{1+e^{\beta\omega}}\right],$$

where

$$N_\lambda{}^{l,r}(\omega)=N_\lambda{}^{l,r}\,\mathrm{Re}\frac{|\omega|}{\sqrt{\omega^2-|\Delta_\lambda{}^{l,r}|^2}}.$$

The above expression reduces to (4·2) when the right metal is normal.

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