Superconductivity in Transition Metals

Jun KONDO

The Institute for Solid State Physics, University of Tokyo, Azabu, Tokyo

(Received August 18, 1962)

A two-band model of superconductivity is investigated. One band is treated in line with BCS (the cut off the interaction outside the Fermi energy). In the other band the interaction is assumed to be repulsive. The superconducting transition temperature is always raised over that of the single attractive band, when an interaction between the bands are introduced. The increase of the temperature is large when the density of states of the repulsive band at the Fermi surface is large. The isotope effect vanishes when the inter-band interaction is large. This model can account for the superconducting properties of the V_3M series and Nb_5Sn. It is argued that superconducting non-transition metals belong to single-band superconductors, whereas the superconductivity of transition metals is largely due to their overlapping bands, especially in lanthanum.

§ 1. Introduction

Bardeen, Cooper and Schrieffer\(^\text{5}\) describe the superconducting state as a linear combination of normal state configurations in which the one-particle states are occupied in pairs of opposite spin and momentum. The pairing occurs when the interaction between electrons is attractive. In the BCS theory the attractive interaction arises from the electron-phonon interaction, which accounts for the isotope effect of the superconducting transition temperatures of several non-transition elements. On the other hand, from measurements of a number of metals, alloys and compounds, Matthias\(^\text{6}\) argues that the superconductivity of transition metals arises from a mechanism different from the electron-phonon interaction. In particular, a recent measurement has revealed that the isotope effect is absent in Ru\(^\text{6}\) and Os\(^\text{6}\). From this fact it is clear that the BCS theory should be modified in some respects. However, there seems to be no doubt that the superconducting ground state is described by a linear combination of paired states in the transition elements, too. On the other hand, the interaction responsible for the pairing in these metals is quite possibly different from the electron-phonon interaction.

An idea of the new interaction is obtained by deliberating on the superconductivity of typical high-transition-temperature compounds, Nb$_5$Sn and V$_3$Ga. Nb$_5$Sn has been found to show a small isotope effect, only one-fifth of the predicted value.\(^\text{5}\) This compound crystallizes in the $\beta$-W structure and is isomorphous to the V$_3$M series ($M$ = Ga, Si, Ge, Sn, As, Sb, ...). These series have been investigated with regards to their susceptibilities,\(^\text{5}\) Knight shifts and super-
conducting transition temperatures. Moreover the electronic specific heat of \( \text{V}_4\text{Ga} \) has been found to be very large. From these measurements Clogston and Jaccarino have concluded the existence of a very narrow band. They suggested that this band corresponds to \( p \)-orbits of the \( M \) atom, because in the \( \beta \)-\( W \) structure the \( M \) atoms are well separated from each other and the broadening of the level may arise only from the overlapping with the \( V \) atoms. However, this interaction is large enough to quench the spin moments of \( p \)-electrons of the \( M \) atoms. The density of states of this band is quite large, as can be seen from the coefficient of the electronic heat of \( \text{V}_4\text{Ga} \) which is \( 244 \times 10^{-4} \text{ cal/mole-deg}^2 \). Now there is a correlation between the superconducting property and the electronic structure. When this band is half filled so that the density of states at the Fermi level is very large, the compound becomes highly superconducting (e.g. for \( \text{V}_4\text{Ga} \) \( T_c = 16.8 \text{ K} \)), while when it is full, the compound is non-superconducting down to \( 1 \text{ K} \). At first sight this would seem to be consistent with the BCS theory. However, since the density of states is about \( 10^6 \) times as large as that of usual non-transition metals, the superconducting transition temperature might become quite large when the interaction leading to superconductivity is assumed to be of usual magnitude. This is not what is observed. Quite naturally the interaction between electrons in this narrow band is repulsive, being of the order of the intra-atomic Coulomb integral. Thus we must assume that other bands are responsible for the superconductivity. However, if the narrow band takes no parts in superconductivity, we cannot understand the correlation between the superconductivity of the compounds and the existence of the high-density band.

In this paper we shall consider the problem of superconductivity when two bands are overlapping. One band is treated in line with BCS. Thus this band shows a full isotope effect. We shall show that when there exists an interaction between the two bands, the superconducting transition point is always raised over that of the single attractive band, even when the other band is repulsive, and that the increase of the transition point is large when the density of states of the repulsive band is large. (In the following we shall call the superconducting band the \( s \)-band, and the repulsive one the \( d \)-band. These names are only a matter of convenience.)

The interaction responsible for the increase of the transition temperature is such as to transfer a pair in the \( s \)-band to the \( d \)-band, and vice versa, and is expressed by

\[
\sum_{k'k} J(k, k') (a_{k,s}^* a_{k',d} + b_{k,s}^* b_{k',d} + \text{c.c.}),
\]

where \( a^* \) and \( b^* \) are the creation operators of electrons in the \( s \)- and \( d \)-bands, respectively. \( J(k, k') \) is expressed by an exchange-like integral and may be repulsive (positive). However, even when this is repulsive, we can gain an energy from this interaction by taking the following variational function:
2I_β = - \sum_{\alpha} V(\mathbf{k}, \mathbf{k}') I_{\alpha \nu} (1 - 2f_{h\alpha}) / (\epsilon_{h\alpha}^2 + I_{h\alpha}^2)^{1/2} \\
+ \sum_{\alpha} J(\mathbf{k}, \mathbf{k}') K_{\alpha \nu} (1 - 2g_{h\alpha}) / (\epsilon_{h\alpha}^2 + K_{h\alpha}^2)^{1/2}, \quad (4)

2K_h = - \sum_{\alpha} U(\mathbf{k}, \mathbf{k}') K_{\alpha \nu} (1 - 2g_{h\alpha}) / (\epsilon_{h\alpha}^2 + K_{h\alpha}^2)^{1/2} \\
+ \sum_{\alpha} J(\mathbf{k}, \mathbf{k}') I_{\alpha \nu} (1 - 2f_{h\alpha}) / (\epsilon_{h\alpha}^2 + I_{h\alpha}^2)^{1/2}, \quad (5)

where \( f_{h\alpha} \) and \( g_{h\alpha} \) respectively, denote the number of excited quasi-particles with \( k \) in the \( s \)- and \( d \)-bands.

We shall assume that \( V(\mathbf{k}, \mathbf{k}') \) is given by the BCS approximation:

\[
V(\mathbf{k}, \mathbf{k}') = \begin{cases} 
-\nu & |\epsilon_{h\alpha}| < \hbar \omega \\
0 & \text{otherwise}
\end{cases} \quad (6)
\]

On the other hand the wave functions of \( d \)-electrons are presumably contracted near the nucleus so that \( U(\mathbf{k}, \mathbf{k}') \) and \( J(\mathbf{k}, \mathbf{k}') \) may be nearly independent of \( k \) and \( k' \) and are made fairly large so that the electron-phonon interaction will not be sufficient to make them attractive. Then we shall assume that they are constants (denoted by \( U \) and \( J \)). A further approximation is made that the densities of states of both bands are constants, being \( N_s \) and \( N_d \), respectively, for the \( s \)- and \( d \)-band, over the energy ranges of \((-\delta_s, \delta_s)\) and \((-\delta_d, \delta_d)\) and zero outside these ranges. (The Fermi energy is referred to zero.) With these approximations (4) and (5) can be solved by putting

\[
I_{\beta \nu} = \begin{cases} 
I_s & |\epsilon_{h\alpha}| < \hbar \omega \\
I_d & \text{otherwise}
\end{cases} \quad (7)
\]

\[
K_h = K \quad \text{for all } k. \quad (8)
\]

Equations to determine \( I_s, I_d, I, \) and \( K \) are expressed by

\[
2I_s = I_s N_s V \int_{-\delta_s}^{\delta_s} (1 - 2g) (\epsilon^2 + I_s^2)^{-1/2} \, d\epsilon + KN_d \int_{-\delta_d}^{\delta_d} (1 - 2g) (\epsilon^2 + K_s^2)^{-1/2} \, d\epsilon, \quad (9)
\]

\[
2I_d = KN_d U \int_{-\delta_d}^{\delta_d} (1 - 2g) (\epsilon^2 + K_d^2)^{-1/2} \, d\epsilon, \quad (10)
\]

\[
2K = -KN_d U \int_{-\delta_d}^{\delta_d} (1 - 2g) (\epsilon^2 + K_d^2)^{-1/2} \, d\epsilon + I_s N_s V \int_{-\delta_s}^{\delta_s} (1 - 2f) (\epsilon^2 + I_s^2)^{-1/2} \, d\epsilon \\
+ I_d N_d \int_{-\delta_d}^{\delta_d} (1 - 2f) (\epsilon^2 + I_d^2)^{-1/2} \, d\epsilon + I_s N_s \int_{-\delta_s}^{\delta_s} (1 - 2f) (\epsilon^2 + I_s^2)^{-1/2} \, d\epsilon, \quad (11)
\]

At the superconducting transition temperature \( T_c \), \( I_s, I_d, I, \) and \( K \) vanish and (9), (10) and (11) reduce to
Superconductivity in Transition Metals

\[ I_x = I_x N_x V \log(1.14 \hbar \omega \beta_x) + KN_x J \log(1.14 \Gamma \beta_x) \]

\[ I_x = KN_x J \log(1.14 \Gamma \beta_x) \]  

\[ K = -KN_x U \log(1.14 \Gamma \beta_x) + I_x N_x J \log(1.14 \hbar \omega \beta_x) \]

\[ + I_x N_x J \log(\hbar / \hbar \omega), \]

where \( \beta_x = 1 / kT_c \), \( \delta = (\delta \delta \delta / \delta)^{1/2} \) and \( \Gamma = (\Gamma \Gamma \Gamma / \Gamma)^{1/2} \). Here we have assumed a weak-coupling limit, \( \hbar \omega, \Gamma, \delta \gg kT_c \). The secular equation from the coefficients of \( I_x \), \( I_x \), and \( K \) determines \( \beta_x \). Putting

\[ \log(1.14 \hbar \omega \beta_x) = x, \]

\[ \log(\hbar / \hbar \omega) = b, \]

\[ \log(\Gamma / \hbar \omega) = c, \]

\[ U' = U - N_x J \]

we obtain an equation to determine \( x \):

\[ N_x N_x (U'V + J')x^2 - \{N_x U' - N_x V - N_x N_x (U'V + J') \} x - 1 - N_x U'c = 0. \]

A smaller value of \( x \) means a higher transition temperature.

Firstly we note that when \( N_x \rightarrow 0 \), we have \( x \rightarrow 1 / N_x V \). This is the BCS solution. When \( x \) is expanded in terms of \( N_x \), we have

\[ x = (1 / N_x V) \{1 - (N_x J'/N_x V) (1 + N_x Vc)} \].

Secondly when \( J' \rightarrow 0 \), we also have \( x \rightarrow 1 / N_x V \). Expanded in terms of \( J \), \( x \) becomes

\[ x = \frac{1}{N_x V} \left[ 1 - (J^2 / V) \left\{ U' + \frac{N_x V}{N_x} \right\} \right]^{-1} \].

Thus we see that \( T_c \) increases with \( J \) and \( N_x \).

In the next place we shall make an approximation which may be appropriate to our VIM problem.

(i) \( N_x U' \sim 1 \). This is because \( N_x \) is very large. However \( N_x U' \) does not exceed unity very much, because in that case ferromagnetism might occur.

(ii) \( N_x U' \ll 1 \). This is the usual weak-coupling limit.

(iii) \( N_x J'/U' \ll 1 \). As will be seen later, this is also the condition of the weak-coupling limit.

(iv) \( |c| \ll 1 \). This is because the width of the \( d \)-band is comparable with \( \hbar \omega \).

Under these assumptions we have

\[ x = \frac{1}{N_x [V + (J^2 / U')]}. \]

We note that the same result is obtained when \( N_x U' \sim 1 \), \( N_x V \ll 1 \) and \( c \ll 1 \). An interpolation formula connecting all of these limiting cases is:
In the followings we shall concentrate on (22). Note that (22) is really a weak-coupling solution from (ii) and (iii). Note also that we have made no assumption concerning the ratio $J'/U'V$. When the ratio is infinity, we have $x^{-1} = N_1 J'/U'$. This is the most direct result of assumption (i). If we had set $U' = V = 0$ in (19), we would have $x^{-1} = (N_1 N_2)^{1/2} V$, which is much larger than $N_1 J'/U'$. The Coulomb repulsion prevents $x^{-1}$ from becoming too large.

§ 3. Isotope effect

From (15) we have

$$kT_c = 1.14 \hbar \omega e^{-2}.$$  \hspace{1cm} (24)

We note that $x$ depends on $\hbar \omega$ through $b$ and $c$, (16) and (17). Then differentiating (24) with respect to $\omega$, we have

$$\frac{\Delta T_c}{T_c} = \frac{\Delta x}{x} = \frac{1}{\omega} \left( 1 + \frac{\partial x}{\partial b} + \frac{\partial x}{\partial c} \right).$$  \hspace{1cm} (25)

The factor

$$\alpha = 1 + \frac{\partial x}{\partial b} + \frac{\partial x}{\partial c}.$$  \hspace{1cm} (26)

measures the effectiveness of the isotope effect. In the BCS theory it is unity, because the interaction does not depend on $\omega$. When $x$ is given by (22), this depends on $b$ through $U'$. Then we have

$$\alpha = 1 - \left[ 1 + \frac{U'V}{J'} \right]^{-2}.$$  \hspace{1cm} (27)

In the limit of $V < J'/U'$, we have $\alpha \to 0$, i.e., we have no isotope effect. In this extreme limit $kT_c$ is expressed by

$$kT_c = 1.14 \hbar \omega \exp \left( -U'/N_1 J' \right) = 1.14 \hbar \omega \exp \left( - (U - N_1 J' b) / N_1 J' \right)$$

$$= 1.14 \hbar \omega \exp \left( - U / N_1 J' \right).$$  \hspace{1cm} (28)

Thus in this limit superconductivity is caused solely by the interband interaction. We may interpret the result (28) as follows: Consider a process in which a pair in the $s$-band is virtually excited and becomes a pair in the $d$-band and then returns to the $s$-band. This second order process always acts as an attraction in the $s$-band, regardless of the sign of $J$. The effective interaction is quite naturally expressed by $J'/U$.

We can now understand the superconducting properties of the $V_1M$ series, if we assume that $N_1 V$ is very small and $N_1 J'/U'$ is of a usual magnitude, $\sim 0.3$. 
When the $d$-band is full, we have $kT_e=1.14 \ h \ \omega \ \exp \left( -1/N_e V \right)$, which is very small. When the $d$-band is half filled and its density of states is very large, assumption (i) is satisfied and (22) is applied. Then $T_e$ becomes high. In this case we see from (27) that the isotope effect is very small. This has in fact been observed in Nb$_3$Sn. Assuming tentatively $\theta_D=300^\circ \ K$ for Nb$_3$Sn, and by use of $T_e=18.1^\circ \ K$ and $\alpha=1/5$, we obtain $N_e V=0.036$ and $N_e J'/U'=0.304$. Assuming tentatively $b=6$, we have $N_e J'/U'=1/9.3$. Since $N_e V$ is very small, $T_e$ will be $\sim 10^{-10} \ K$, when the $d$-band is full.

§ 4. Empty $d$-band

When the $d$-band is empty but very close to the Fermi level, we can also expect enhancement of superconductivity. We shall assume that the edges of the band are located at $\Gamma_1$ and $\Gamma_2$ above the Fermi level, both being larger than $kT_e$, and that the density of states is constant ($N_e)$ over this range. Then the relevant integral which should take place in (9), (10) and (11) at the transition temperature is expressed by

$$\int_{\Gamma_1}^{\Gamma_2} (1-2q)/c \ \delta e \approx \log \left( \frac{F_2}{F_1} \right) = a. \quad (29)$$

A calculation similar to the previous sections shows that

$$x=\frac{1}{N_e \left[ V + J^* \left( U' + (1/N_e a) \right)^{-1} \right]}. \quad (30)$$

When the band-width, $F_2-F_1$, is much smaller than $F_1$, we have

$$N_e a \approx Z/F_1, \quad (31)$$

where $Z$ is the total number of electrons per atom which can be accommodated in the band. Then we have

$$x=\frac{1}{N_e \left[ V + J^* \left( U' + (F_1/Z) \right)^{-1} \right]}. \quad (32)$$

When the band becomes broader, $T_e$ is lower than that given by this equation. Thus we see that the interband interaction enhances superconductivity when a sharp and dense empty band lies near the Fermi level.

Now it is quite possible that this situation is encountered in lanthanum. This shows a marked increase of the magnetic susceptibility$^{13}$ and the Knight shift$^{12}$ with decreasing temperature. Besides, its electronic heat is large.$^{13}$ From these facts, the $f$-bands of lanthanum are supposedly very close to or overlapping the Fermi level. Then it is quite naturally understood by introducing the interband interaction that lanthanum has a high superconducting transition temperature ($\sim 5^\circ \ K$), whereas scandium and yttrium are not superconducting.
References

4) See reference 2).