# CHAPTER III

## THEORY OF TRANSITION METAL SUPERCONDUCTIVITY

### III.1 Suhl-Matthias-Walker Model

Suhl, Matthias, and Walker[12] introduced the two-band model to describe the superconducting state of the transition metals. In most of these metals, the s-band and d-band overlap. Also it has been known that s-d interband scattering contribute to the resistivity of the metal in the normal state.[13] They included an extra phonon-coupling term in the Hamiltonian to account for possible pair formation of electrons from the different bands in addition to the phonon- coupling terms for pairs formation in each individual band.

The Hamiltonian takes the form

$$H = \sum_{k\sigma} \epsilon_{ks} c^{*}_{k\sigma} c_{k\sigma} + \sum_{k\sigma} \epsilon_{kd} d^{*}_{k\sigma} d_{k\sigma} - \sum_{kk'} V_{ss} c^{*}_{k\uparrow} c_{-k\downarrow} c^{*}_{-k'\downarrow} c_{k'\uparrow}$$

$$-V_{dd} \sum_{kk'} d^{*}_{k\uparrow} d_{-k\downarrow} d^{*}_{-k'\downarrow} d_{k'\uparrow}$$

$$-V_{sd} \sum_{kk'} (c^{*}_{k\uparrow} c^{*}_{-k\downarrow} d_{-k'\downarrow} d_{k'\uparrow} + d^{*}_{k\uparrow} d^{*}_{-k\downarrow} c_{-k'\downarrow} c_{k'\uparrow}) , \qquad (3.1)$$

where $\epsilon_{ks}$, $\epsilon_{kd}$ are s- and d-band kinetic energies and $c^{*}$, $c$ and $d^{*}$, $d$ the corresponding creation and annihilation operators. $V_{ss}$, $V_{dd}$, and $V_{sd}$ are the averaged interaction energies resulting from phonon emission and absorption by s-s, d-d, and s-d processes, minus the corresponding shielded Coulomb interaction terms.

We now introduce the following Bogoliubov transformation

$$
\begin{aligned}
c_{k\uparrow} &= \cos(\theta_k/2)\, e_{k\uparrow} + \sin(\theta_k/2) e^{*}_{-k\downarrow}\,, \\
d_{k\uparrow} &= \cos(\varphi_k/2)\, f_{k\uparrow} + \sin(\varphi/2) f^{*}_{-k\downarrow}\,, \\
c_{k\downarrow} &= \cos(\theta_k/2)\, e_{k\downarrow} - \sin(\theta_k/2) e^{*}_{-k\uparrow}\,, \\
d_{k\downarrow} &= \cos(\varphi_k/2)\, f_{k\downarrow} - \sin(\varphi_k/2) f^{*}_{-k\uparrow}\,.
\end{aligned}
$$

By equating to zero the coefficients of $e^{*}_{k}\, e^{*}_{-k}$ and $e_{-k}\, e_{k}$, the parameters $\theta$ and $\varphi$ can be determined by substituting for c and d in Eq.(3.1). Similarly for the f terms. The resulting equations are

$$
\begin{aligned}
\epsilon_{ks} \sin\theta_k - [V_{sd} D + V_{ss} S] \cos\theta_k &= 0\,, \\
\epsilon_{kd} \sin\varphi_k - [V_{dd} D + V_{sd} S] \cos\varphi_k &= 0\,;
\end{aligned}
\tag{3.2}
$$

where

$$
\begin{aligned}
D &= \tfrac{1}{2} \sum_k \sin\varphi_k \left[1 - 2 f_d(E_{kd})\right]\,, \\
S &= \tfrac{1}{2} \sum_k \sin\theta_k \left[1 - 2 f_s(E_{ks})\right]\,,
\end{aligned}
\tag{3.3}
$$

and $f_s(E_{ks})$, $f_d(E_{kd})$, respectively, are the number of quasi-particles deriv-ing from the s and d bands that are excited to energies $E_{ks}$, $E_{kd}$, respectively. These energies are

$$
E_{ks} = (\epsilon_{ks}^2 + A^2)^{1/2}\,, \qquad E_{kd} = (\epsilon_{kd}^2 + B^2)^{1/2}\,,
$$

where

$$
A = V_{sd} D + V_{ss} S\,, \qquad B = V_{dd} D + V_{sd} S.
$$

The self-consistent conditions for Eq.(3.2) and (3.3) give two simultaneous equations for A and B:

$$\begin{aligned} A[1-V_{ss}N_s F(A)] &= BV_{sd}N_d F(B), \\ B[1-V_{dd}N_d F(B)] &= AV_{sd}N_s F(A), \end{aligned} \tag{3.4}$$

where

$$F(A) = \int_0^{\hbar\omega} d\epsilon \tanh\left[\frac{(\epsilon^2+A^2)^{1/2}}{2kT}\right] \Big/ (\epsilon^2+A^2)^{1/2},$$

and where $N_s, N_d$ are the densities of states in the s and d bands near the Fermi level, $\hbar\omega$ is of the order of the maximum available phonon energy.

The transition temperatures are given by the equation

$$[V_{ss}+N_d(V_{sd}^2-V_{ss}V_{dd})F(0)][V_{dd}+N_s(V_{sd}^2-V_{ss}V_{dd})F(0)] = V_{sd}^2,$$

and it is found to be

$$kT_c = 1.14\hbar\omega \exp\left\{-\left[\frac{[V_{sd}^2/N_sN_d+\frac{1}{4}(V_{dd}/N_s-V_{ss}/N_d)^2]^{1/2}}{V_{sd}^2-V_{ss}V_{dd}} - \frac{\frac{1}{2}(V_{dd}/N_s+V_{ss}/N_d)}{V_{sd}^2-V_{ss}V_{dd}}\right]\right\}.$$

They determined that in the intraband limit, the interband scattering ($V_{sd}=0$) being zero, two different transition temperatures resulted, one for each band. But in the interband limit, the intraband scattering ($V_{ss}=V_{dd}=0$) being zero, only one transition temperature occured.

## III.2 Other Possible Mechanisms for Superconductivity in The Transition Metals

As was pointed out in the previous section, there was no justification for assuming a BCS type interaction within each band. Garland[14] has investigated the possible mechanisms which could lead to BCS coupling within each band. He constructed both a two-gap theory of superconductivity applicable to "clean" transition metals and a single-gap theory applicable to "dirty" transition metals. For a clean transition metal, he approximated eigenstates $\psi_n$ of $H_o$ by Bloch states $\Phi_{l,\vec{k},\sigma}$ designated by band index l, wave vector $\vec{k}$, and spin direction $\sigma$. His model implicitly assumes the Fermi surface separable into distinct s-and d-like regions. This resulted in a set of coupled integral equations similar to those of SMW for the gap on the s and d parts of the Fermi surface:

$$\Delta_{l}(\xi) = -\sum_{l'} \int d\xi' \, \mathrm{Re}[\Delta_{l'}(\xi')] K(l,l';\xi,\xi') \tanh \frac{E'_{l'}/2k_BT}{E'_{l'}}.$$

The kernel

$$K(l,l';\xi,\xi') = K_{ph}(l,l';\xi,\xi') + K_c(l,l';\xi,\xi')$$

$$= K_{ph}(l,l';\xi,\xi') + \frac{e^2 k'}{2\pi k \, \partial\xi'/\partial k'} \sum_{\vec{G}} \int_{|\vec{k}+\vec{G}|-k'|}^{|\vec{k}+\vec{G}|+k'} \frac{dq}{q_s}$$

$$\times \left\{ \langle l,\vec{k},\sigma | \rho_{q_s} | l',k',\sigma \rangle \langle l',\vec{k}',\sigma | \rho_{q_c} | l,\vec{k},\sigma \rangle \right\}, \quad (3.5)$$

corresponds to the parameter -N(O)V of the BCS theory;

$$E_{l'} = \left[ \xi'^2 + \Delta_{l'}^2(\xi') \right]^{1/2},$$

is the superconducting quasi-particle energy. $\Delta_\ell(\xi)$ is the l-band gap at energy $\xi$ ; $\xi$ and $\xi'$ are renormalized normal-state energies measured relative to the Fermi level; $\vec{k}$, $\vec{k}'$, and $\vec{q}$ are chosen so that $\vec{k}' = \vec{k}+\vec{q}+\vec{G}$.

The Coulomb contribution $K_c(1,1';\xi,\xi')$ to the kernel may become attractive only for the s-band. The heavy d electrons tend not to follow the motion of the s-electrons during s-s interactions and thus tend to antishield them. As both s and d electrons can follow the motion of the d electrons, the Coulomb interaction between d-electrons is always repulsive.

Thus, the two-gap theory permits three contributions to the superconductivity of the clean transition metals:
(1)the intraband screened Coulomb interaction $V_c(1,1)$, which may be attractive between s-band electrons widely separated in energy,
(2)the intraband interactions $V_{ph}(1,1)$ arising from the virtual exchange of phonons, and
(3)the attractive effective interaction $V(1,1')\Delta_{\ell'}/\Delta_\ell$ arising from the small coupling terms between the s- and d-band gap equations.

For dirty transition metals, on the other hand, he introduced impurity scattering in the crystal Hamiltonian $H_o$ before forming pair states. Following Anderson,[15] we choose paired states

$$\psi_{ns} = \sum_{\ell,\vec{k},\sigma'} b_{\ell\vec{k}\sigma,n\sigma}\,\phi_{\ell\vec{k}\sigma},$$

and $\psi^+_{ns}$ which are linear combinations of all Bloch states within

a small energy range. We take coefficient $b_{l\mathbf{k}\sigma',n\sigma}$ of random phase such that

$$\sum_{\sigma'} \left| b_{l\mathbf{k}\sigma',n\sigma} \right|^2 = \bar{\delta}(\xi_n - \xi_{l\mathbf{k}}) / N(\xi_n) \ ,$$

where $\bar{\delta}(\xi_n - \xi_{l\mathbf{k}})$ is a spread-out delta function of approximate width $2\hbar/\tau$. A single gap $\Delta(\xi)$ result

$$\Delta(\xi) = -\int d\xi' \, \mathrm{Re}[\Delta(\xi')] K(\xi,\xi') \tanh \frac{(E'/2k_BT)}{E'} \ ,$$

where

$$K(\xi,\xi') = \sum_{l} \sum_{l'} [N_l(\xi)/N(\xi)] K(l,l';\xi,\xi') \ , \quad (3.6)$$

where $N_l(\xi)$ is an l-band density of states, and the unimportant spread in energy of $\bar{\delta}$ has been neglected.

Thus, in the dirty transition metals the superconducting quasi-particles have both s-and d-like character. As the ratio $N_s(0)/N_d(0) \ll 1$, the quasi-particles are primarily d-like and their superconductivity arises primarily from d-d interactions. Garland found numerically that the largest possible attractive Coulomb contribution to the superconductivity of any dirty transition metal element is an order of magnitude smaller than the attractive contribution arising from the virtual exchange of phonons.

His numerical calculations of the interactions $V_c(s,s)$ and $V(s,\alpha)$ permit an investigation of the expected differences between the clean and dirty transition metal superconductors. The kernel

$K_c(s,s;\xi,\xi')$ was found to be large and negative for energy transfers $|\xi-\xi'|$ between one and two eV in any transition metal having a narrow ($\ll$ 1 eV) peak in the density of states near the Fermi level and a small s-band Fermi wave number ($k_F^s/k \lesssim \frac{1}{2}$). The interaction V(s,d) was found to be very small $\left[|N_s(0)N_d(0)V^2(s,d)|^{1/2} \lesssim .05\right]$. Both interactions were found to be approximately independent of the details of the model chosen for the band structure. However, the interaction $V_c(s,s)$ was found to be very strongly dependent upon the parameters $E_d$, $n_s$, and $g_d$. Thus, the lack of good band-structure calculations precludes any theoretical determination of the existence or nonexistence of a large negative kernel $K_c(s,s;\xi,\xi')$ in a real material.

The existence of such a large negative kernel $K_c(s,s;\xi,\xi')$ in a clean transition metal would imply (1) a transition temperature $T_c$ much higher than in the dirty state, coupled with a free-energy difference $G_N-G_S$ and critical field $H_c$ only slightly larger, (2) a nearly vanishing isotope effect, and (3) a relative insensitivity of $T_c$ to change in N(0).

In the absence of such an attractive interaction, the increase in $T_c$ upon purification will be little more than that in a nontransition metal. However, the clean state will be experimentally distinguishable from the dirty state by the presence of at least two partially decoupled energy gaps which are anisotropic. As a result anomalies in $H_c(T)$ and $C_v(T)$ will appear. If one assumes a large interband interaction V(s,d), contrary to the above calcula-

tions, one obtains a further anomaly in the $\Delta_\ell(T)$ and $H_c(T)$ curves, which continue to rise rapidly as $T/T_c$ approaches zero. Thus, Garland conclude that all present theories of superconductivity which neglect the mixing of s and d states by impurity scattering contradict observed experimental results. This is not surprising, since only tantalum, and perhaps molybdenum, have ever been purified sufficiently to approach the clean state.

III.3 Theory for the Electron-Phonon Coupling Constant

Mc-Millan [16] has shown that the superconducting transition temperature $T_c$ is related in a simple manner to the electron-phonon coupling constant $\lambda \approx m^*/m - 1$. His generalized equation for $T_c$ is given by

$$T_c = \frac{\langle \omega^2 \rangle^{1/2}}{1.20} \exp\left\{ - \frac{1 + \lambda + \mu_{spin}}{0.96\lambda - (\mu^* + \mu_{spin})(1 + 0.6\lambda)} \right\} . \qquad (3.7)$$

Here, $\mu^*$ is the Coulomb psudopotential, $\mu_{spin}$ the effective electron-spin excitation coupling constant, and $\langle \omega^2 \rangle^{1/2}$ gives the weighted root mean square phonon frequency. The principal problem in the calculation of $T_c$ for d-and f-band metals is the determination of $\lambda$. Bennemann and Garland [17] have shown that $\lambda$ can be expressed in terms of measurable normal-state quantities and the atomic parameter $\eta_0$ as

$$\lambda = \frac{\eta_0}{M \langle \omega^2 \rangle \Omega^{4/3}} \frac{N(0)}{\left[1 + (0.6 N(0) + 0.7 \overline{N_d(E)}) \left( \frac{\Omega}{15 A^{\circ 3}} \right)^{-1/3} \right]^2} . \qquad (3.8)$$

Here, $\eta_0$ is an atomic parameter which varies smoothly and pre-

dictably as a function of position in the periodic table, $\Omega$ is the atomic volume, $\overline{N_d(E)}$ is the average d-band density of states, M is the mass of the unit cell.

The transition temperature $T_c$ could be calculated by assuming for $\eta_0(Z)$ a smooth curve which has the general shown in Fig.(3.1), and which is approximately determined by fitting to two $\eta_0$ values obtained by using Eq.(3.7) and Eq.(3.8) from the experimental $T_c$ values for two metals within the same transition metal series.

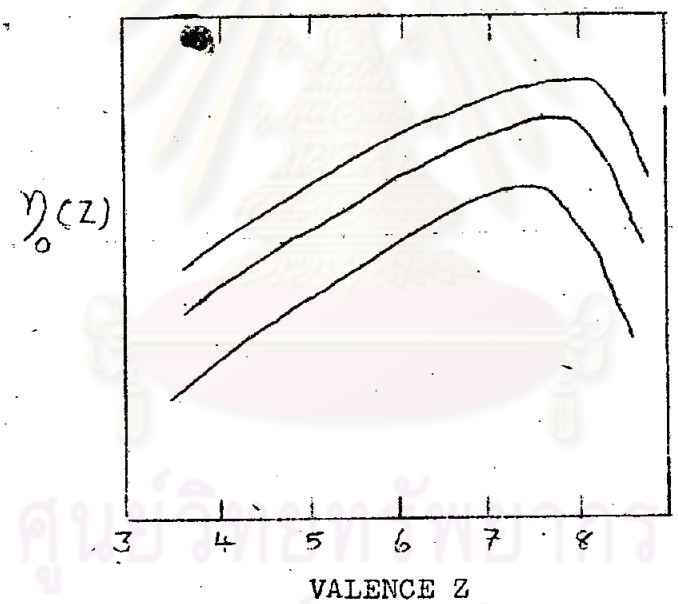


Fig. 3.1. Variation of $\eta_0(Z)$ for the three transition metal series.

Equations(3.7) and (3.8) explain the absence of a consistent correlation between $T_c$ and N(O), $T_c$ depends only weakly on N(O), and it has been shown that this dependence on N(O) is partly cancelled by the dependence of $\mu^*$ on N(O). In general, it has become clear that $T_c$ depends much more strongly on $M\langle\omega^2\rangle$, which

is not primarily determined by N(O), and on $\eta_o$, which is independent of N(O).

Bennemann and Garland have shown that the electron-phonon matrix element between localized d-orbitals leads to an expression for the $T_c$ which allows for the variation in $T_c$ seen in three transition metal series. They have also shown that the McMillan equation, which is based on the virtual exchange of the phonons between the d-electrons, can explain the pressure dependence of the $T_c$ seen in the transition metal superconductors. Appel and Kohn[18](1971) have shown that the vertex function constructed with Wannier function representation of the d-orbital electrons exhibit the singularities which indicate an instability against the formation of Cooper pairs. Appel[19](1976) has given a theoretical discussion of the $T_c$ of superconducting alloys taking into account both the effects of composition and of atomic order. $T_c$ is found from the ensemble-averaged vertex equation for a Cooper pair written in the atomic representation. The application to new experimental data on the effect of long-range order on $T_c$ of $Nb_3Sn$, $V_3Au$, and $V_3Ga$ yields good agreement between theory of d-electron superconductivity and experiment.

III.4 Hamiltonian of the Transition Metal Superconductors

According to sectionIII.3, the mechanism for superconductivity in the transition metals is the electron-phonon interaction between d-electrons. Thus we should add to the Anderson Hamiltonian, Eq.(1.15), the term

$$-\tfrac{1}{2} g \sum_{j,m,\sigma} d^{\dagger}_{j\sigma} d^{\dagger}_{j-\sigma} d_{m-\sigma} d_{m\sigma} , \qquad (3.9)$$

where g is the strength of the electron-phonon interaction between d-orbitals located on the j-th and m-th site and is taken to be the electron-phonon coupling constant in McMillan's work.[16] We have called (3.9) $H_{BCS}$ since it is similar to the term in the BCS theory which leads to the formation of Cooper pairs in simple metal superconductors.

Making use of Hartree-Fock approximation apply to Eq.(3.9), the Hamiltonian of the transition metal superconductors becomes

$$\begin{aligned} H = & \sum_{k,\sigma} \epsilon_k c^{\dagger}_{k\sigma} c_{k\sigma} + \sum_{j,\sigma} (E_j + U\langle n_{\sigma}\rangle) d^{\dagger}_{j\sigma} d_{j\sigma} \\ & + \sum_{j,k,\sigma} (V_{kj} c^{\dagger}_{k\sigma} d_{j\sigma} + V^{*}_{jk} d^{\dagger}_{j\sigma} c_{k\sigma}) \\ & - \tfrac{1}{2} \sum_{j,\sigma} (\Delta^{*}_{g} d_{j-\sigma} d_{j\sigma} + \Delta_g d^{\dagger}_{j\sigma} d^{\dagger}_{j-\sigma}) , \end{aligned} \qquad (3.10)$$

where

$$\Delta_g = g \sum_{j,\sigma} \langle d_{j-\sigma} d_{j\sigma} \rangle + \Delta_d . \qquad (3.11)$$

We shall use the above Hamiltonian to find the Green's function or propagator for the s-electron in the next chapter.