# MECHANISMS FOR SUPERCONDUCTIVITY IN THE TRANSITION METALS

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Recent papers[1-5] on superconductivity in the transition metals suggest almost unanimously that it does not arise primarily from the electron-phonon interaction. These papers cite four categories of experimental evidence: (1) the absence or considerable reduction of the isotope effect in the superconducting transition metals,[1] (2) the pressure dependence of the transition temperature $T_c$,[2] (3) observations relating $T_c$ to position in the periodic table and to $N(0)$, the total density of states at the Fermi surface,[3] and (4) impurity effects, especially those due to magnetic impurities.[4] We show here that this experimental evidence is consistent with the BCS[6] theory and supports the idea of phonon-induced superconductivity.

According to the BCS theory, superconductivity arises from an essentially attractive interaction between Landau quasi-particles.[7] This interaction consists only of (1) a part $V_{ph}$ arising from the virtual exchange of phonons, which is attractive for small energy transfers between quasi-particles, and (2) a screened Coulomb interaction.

The Hamiltonian for dynamically screened Coulomb interactions in a periodic structure may be approximated by the following generalization of Englert's[8] result:

$$\mathcal{H}_E = \sum_n \xi_n a_n^\dagger a_n + \Re \sum_{\vec{q}} (2\pi e^2/\Omega q^2)\{\rho_{\vec{q}}\rho_{-\vec{q}c} - N\},$$

where the sum is over all eigenstates $\psi_n$ of the one-electron crystal Hamiltonian $\mathcal{H}_0$; $\xi_n$ is the one-electron normal-state energy; the $a_n^\dagger$ ($a_n$) are creation (destruction) operators for the states $\psi_n$; and $\Omega$ and $N$ are the volume and number of electrons of the system. Finally,

$$\rho_{\vec{q}} = \sum_{n,n'} \langle n | e^{i\vec{q}\cdot\vec{r}} | n' \rangle a_n^\dagger a_{n'}$$

is an electronic density wave, and $\rho_{\vec{q}c}$ is $\rho_{\vec{q}}$ screened and corrected for local field effects:

$$\langle n | \rho_{\vec{q}c} | n' \rangle = \sum_{\vec{G}} \langle n | \rho_{\vec{q}+\vec{G}} | n' \rangle / \epsilon_{\vec{q},\vec{G}}(\omega_{n'n}),$$

where $\vec{G}$ is any reciprocal lattice vector, $\epsilon_{\vec{q},\vec{G}}(\omega)$ is a self-consistent dynamic dielectric function,[9,10] and $\hbar\omega_{n'n} = \xi_{n'} - \xi_n$. We assume a two-band model for the electronic structure of the transition metals: (1) states for nearly-free electrons (here called $s$ electrons) orthogonalized to (2) tightly bound $d$ states of energy $\xi_d(k) = \xi_0 - E_d \cos\frac{1}{2}(\pi k/K)$. Here $k$ is less than $K$, the radius of the first Brillouin zone in the Wigner-Seitz spherical approximation. We associate this simple $d$ band with a subband at the Fermi surface, rather than with the total $d$ band. The model contains only four independent parameters of importance to the theory: $E_d$, the width of the $d$ subband; $n_s$, the number of $s$ electrons per atom; $g_d$, the number of states in the $d$ subband; and $\xi_0$, which determines the relative position of the $d$ subband with respect to the Fermi energy.

The model permits the derivation of a simple, closed expression for the dielectric function and permits numerical calculation of the matrix elements of $\rho_{\vec{q}}$. The computed interband contributions to the dielectric function are negligible except in small regions of the $q$-$\omega$ plane where $\epsilon_{\vec{q},\vec{0}}(\omega)$ is extremely small. We have constructed both a two-gap theory of superconductivity applicable to "clean" transition metals and a single-gap theory applicable to "dirty" transition metals.[11] For a clean transition metal, we approximate the eigenstates $\psi_n$ of $\mathcal{H}_0$ by Bloch states $\varphi_{l,\vec{k},s}$ designated by band index $l$, wave vector $\vec{k}$, and spin direction $s$. Our model implicitly assumes the Fermi surface separable into distinct $s$- and $d$-like regions.[12] There results a set of coupled integral equations similar to those of Suhl, Matthias, and Walker[13] for the gaps on the $s$ and $d$ parts of the Fermi surface:

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

The kernel

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

$$= K_{ph}(l,l';\xi,\xi') + \frac{e^2 k'}{2\pi k \partial\xi'/\partial k'} \sum_{\vec{G}} \int_{|\vec{k}+\vec{G}|-k'|}^{|\vec{k}+\vec{G}|+k'} \frac{dq}{q} \Re\{\langle l,\vec{k},s|\rho_{\vec{q}}|l',\vec{k}',s\rangle\langle l',\vec{k}',s|\rho_{\vec{q}c}|l,\vec{k},s\rangle\} \quad (1)$$

corresponds to the parameter $-N(0)V$ of the BCS theory;

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

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

The Coulomb contribution $K_C(l,l;\xi,\xi')$ 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. This gives rise to a negative dielectric function $\epsilon_{\vec{q},\vec{G}}(\omega)$ for important regions of the $q$-$\omega$ plane and thus, possibly, to an attractive screened Coulomb interaction between $s$ electrons. As both $s$ and $d$ electrons can follow the motion of the $d$ electrons, the Coulomb interaction between $d$ electrons is always repulsive. Detailed numerical calculations bear out these contentions.

Thus, our two-gap theory permits three contributions to the superconductivity of the clean transition metals: (1) the intraband screened Coulomb interaction $V_C(l,l)$, which may be attractive between $s$-band electrons widely separated in energy,[14] (2) the intraband interactions $V_{ph}(l,l)$ arising from the virtual exchange of phonons, and (3) the attractive effective interaction $V(l,l')\Delta_{l'}/\Delta_l$ arising from the small coupling terms between the $s$- and $d$-band gap equations.[13,15]

For dirty transition metals, on the other hand, we must include impurity scattering in the crystal Hamiltonian $\mathcal{H}_0$ before forming pair states. Following Anderson,[11] we choose paired states

$$\psi_{ns} = \sum_{l,\vec{k},s'} b_{l\vec{k}s',ns}\varphi_{l\vec{k}s}$$

and $\psi_{ns}{}^+$ which are linear combinations of all Bloch states within a small energy range. We take coefficients $b_{l\vec{k}s',ns}$ of random phase such that $\sum_{s'}|b_{l\vec{k}s',ns}|^2 = \bar{\delta}(\xi_n - \xi_{l\vec{k}})/N(\xi_n)$, where $\bar{\delta}(\xi_n - \xi_{l\vec{k}})$ is a spread-out delta function of approximate width $2\hbar/\tau$. A single gap $\Delta(\xi)$ results:

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

where

$$K(\xi,\xi') = \sum_l \sum_{l'} [N_l(\xi)/N(\xi)]K(l,l';\xi,\xi'), \quad (2)$$

where $N_l(\xi)$ is an $l$-band density of states, $K(l,l';\xi,\xi')$ was defined in (1), 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. We have 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.

Our numerical calculations of the interactions $V_C(s,s)$ and $V(s,d)$ 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 [$|N_S(0)N_d(0)V^2(s,d)|^{1/2} \lesssim 0.05$]. 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[16] 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 changes 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, even then, the clean state will be experimentally distinguishable from the dirty state by the presence of at least two partially decoupled energy gaps which are, in general, anisotropic. As a result, anomalies in $H_c(T)$ and $C_v(T)$ will appear. If one assumes a large interband interaction $V(s,d)$,[15] contrary to our calculations, one obtains a further anomaly in the $\Delta_l(T)$ and $H_c(T)$ curves, which continue to rise rapidly as $T/T_c$ approaches zero. Thus, we 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,[17] and perhaps molybdenum,[18] have ever been purified sufficiently to approach the clean state.

We conclude that the experimentally observed superconducting properties of the transition metals must be explained by the single-gap theory appropriate to dirty materials. Moreover, the assumption of Cooper pairing in any single-gap theory implies (in the absence of magnetic impurities) that superconductivity must arise primarily from the exchange of virtual phonons.

We have found our single-gap theory to yield isotope-effect coefficients in agreement with experiment (a consequence of the narrowness of the $d$ band) and have shown the near-zero isotope effect of ruthenium to provide the basis for a theoretical argument against the existence of any strong contribution to superconductivity other than the virtual exchange of phonons.[19] Although we have been unable to perform a good, quantitative calculation of the pressure dependence of the transition temperature, we have shown the observed pressure effects in both the transition metals and the nontransition metals to be consistent with our simple models for phonon-induced superconductivity.[19]

From the experimental ratio $T_c/\theta_D$ and the theoretical $K_C$, we have computed the effective phonon contribution[20] $\langle K_{ph}\rangle$ to the kernel by means of the formula $\langle K_{ph}\rangle = K_{eff} - K_C^*$, where $K_{eff} = 1/[2\ln(T_c/1.14\,\theta_D)]$ and[20] $K_C^*$ is a function of $K_C$ determined by an approximate solution of Eq. (2). From this we estimate the average unscreened phonon interaction $\langle V_{ph}'\rangle = \langle V_{ph}\rangle/S_{ph}$ arising from the virtual exchange of phonons, where $\langle V_{ph}\rangle = \langle K_{ph}\rangle/N(0)$ is the corresponding screened interaction, and where we expect the screening factor $S_{ph}$ to have the approximate form $S_{ph} \approx [1 + \alpha N(0)]^{-2}$.[21] We should expect $\langle V_{ph}'\rangle$, not $\langle V_{ph}\rangle$ or $\langle K_{ph}\rangle$, to be independent of $N(0)$ and to vary only slightly as a function of position in the periodic table. We have calculated the fluctuations in $\langle V_{ph}'\rangle$ as a function of position in the periodic table for all transition elements and alloy systems for which $N(0)$ and $K_{eff}$ are known experimentally with $3\times10^{23}\,\alpha$ equal to 0.9, 1.0, and 1.1 eV-cm$^3$. We find the fluctuations to be less than 20% of the average $\langle V_{ph}'\rangle$. The fluctuations appear to be regular but bear no relationship to the Matthias rules.[22] This approximate constancy of the empirical $\langle V_{ph}'\rangle$ deduced from $T_c$ suggests that there are no large, unknown additional contributions to the superconductivity of the transition metals. We believe even the small fluctuations observed in $\langle V_{ph}'\rangle$ to arise primarily from rapid changes in band structure near the Fermi surface which render inaccurate both the equation $\langle V_{ph}\rangle = \langle K_{ph}\rangle/N(0)$ and the assumed form of the screening factor $S_{ph}$.

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$$\alpha \sim \frac{4\pi e^2}{Q^2}\sum_{n'}\sum_{\vec{G}}|\langle n|\rho_{\vec{Q}+\vec{G}}|n'\rangle|^2 < \frac{4\pi e^2}{Q^2},$$

where $Q$ is a typical phonon wave number, and the state $n$ is on the Fermi surface.

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## ISOTOPE EFFECT IN SUPERCONDUCTIVITY

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The transition temperature $T_c$ of a superconductor depends upon the average atomic mass $M$ of its constituents:

$$T_c \propto M^{-z} = M^{-0.5(1-\zeta)}. \qquad (1)$$

Although the existence of this isotope effect has played an important role in the development of the theory of superconductivity, the experimentally observed values of $\zeta$ have never been properly explained. Here we present calculated values of $\zeta$ in agreement with experiment and show the observed qualitative difference between the reduced isotope effect ($\zeta \geq 0.3$) of the transition metals and the nearly complete isotope effect ($\zeta \sim 0.1$) of the simple[1] metals to follow from elementary ideas of band structure.

We have assumed an isotropic free-electron model for the simple metals and a two-band model consisting of nearly free electronic states or-