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Transition Temperature of Narrow-Band Superconductors

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The equation for the vertex part of a Cooper pair is developed in the Wannier representation to highlight the atomic nature of the electrons responsible for superconductivity in narrow energy bands. For a nondegenerate band and a short-range interaction between two electrons at sites $\vec{n}_1$ and $\vec{n}_2$, the transition temperature T_c is determined by a small set of coupled integral equations in $\vec{n}_1 - \vec{n}_2$ and in the energy variable ω. With contact interaction, $\vec{n}_1 = \vec{n}_2$, only a single equation in ω remains as the defining equation for T_c. The solution has the Bardeen-Cooper-Schrieffer (BCS) form with an attractive interaction depending on a phonon Green's function in site space and with a repulsive interaction determined by the intra-atomic Coulomb integral U. The isotope effect is calculated as a function of U; the result can account for small negative or even positive effects, as observed in transition metals. For a degenerate band, the vertex part depends on the site variables $\vec{n}$ *and* on the orbital indices i, the latter denoting a set of localized orbitals which transform according to a degenerate representation of the crystal group. T_c is calculated in the contact model for a cubic Γ'_{25} band. The result contains the total density of states at the Fermi surface and the intraorbital and interorbital interactions weighted with factors $\frac{1}{3}$ and $\frac{2}{3}$, respectively. The lowering of T_c by long-range Coulomb interactions due to exchange effects is also briefly discussed.

I. INTRODUCTION

Most of the superconducting metals fall into one of two classes: simple metals and transition metals. The conduction electrons of simple metals have a large amplitude between the atoms, and their eigenstates can be found from the orthogonalized-plane-wave (OPW) method or from its pseudopotential formulation. The Fermi surface (FS) in the extended zone scheme is similar to that of free electrons. The phonon spectrum and the electron-phonon interaction can be calculated by using OPW states; the Coulomb interaction between the conduction electrons can be approximately evaluated by using the dielectric screening function of a free-electron gas. The results lead to a reliable estimate of all the parameters which enter into the theory of superconductivity of Bardeen, Cooper, and Schrieffer (BCS).[1] This theory, and its extension to cases of strong electron-phonon interactions,[2] have been remarkably successful in accounting for the superconducting properties of simple or OPW metals.

The BCS mechanism also applies to transition metals, in that Cooper pairing is caused by the virtual exchange of phonons between electrons.[3] However, the evaluation of the pairing parameters in the Bloch representation is so cumbersome that only recently have any attempts been made to do this.[4] The difficulty lies in the presence of unfilled and narrow d bands and the fact that d electrons govern the superconducting properties of most transition metals. The interactions of d electrons with phonons and with one another are conceptually less well understood and mathematically more difficult than those of nearly free electrons. The d-d pairing interaction is usually more important than the s-s or s-d interaction, because of a large d-electron density of states at the Fermi surface. While in the normal state the s electrons carry the electric current, so that the d-electron–phonon interaction is not of much interest here, the Cooper pairs formed from d electrons carry most of the supercurrent below T_c.

The question arises of how suitably to formulate the pairing of tightly bound electrons so that the BCS parameters and especially trends of these parameters with alloying, pressure, etc., can be estimated. It is the purpose of this paper to present such a formulation and to use it, as yet in rather simple model cases, for a discussion of the transition temperature T_c.

To this end, the atomic aspect of itinerant electrons in narrow bands is emphasized. The wave functions of d electrons, in particular, those corresponding to states near the top of a d band, have much larger amplitudes at the atomic sites than between them.[5] The mean time-of-stay for a d electron at a given atom is of the order of $\tau = 1/\Delta E$, where ΔE is an appropriate bandwidth ($\hbar = 1$). For

ΔE values of a few eV, this τ is much larger than the time of revolution $t = 1/E$, where E is the binding energy of a d electron ($\gtrsim 20$ eV). In this situation one can speak of an electron on a particular atom. Note, however, that an electron stays on a site for a time much smaller than the atomic vibration period, except for extremely narrow bands.

In Sec. II we formulate the integral equation for the vertex part of tightly bound electrons, using the Wannier or site representation which emphasizes the atomic character of d electrons. From the vertex equation, the transition temperature can be determined.[6] The crucial ingredient in this equation is the irreducible vertex part. It is derived in Sec. III as a sum of two parts; the first is due to phonon exchange and the second to Coulomb interactions. The irreducible vertex part takes a simple form in the special form of a contact model, which corresponds to a situation where the electron-electron interaction is of short range and the Wannier functions are sufficiently localized. It is noted that our contact interaction due to phonon exchange has some similarity to the pairing interaction used by McMillan[3] and Hopfield[7] in discussing T_c for certain transition metals and alloys. In Sec. IV we discuss the homogeneous integral equation defining T_c and derive an explicit formula in the contact model. In a first step towards the problem of degenerate bands, we formulate in Sec. V the equations for the vertex parts of a threefold-degenerate d band in a cubic crystal.

II. VERTEX EQUATION FOR A COPPER PAIR IN A NONDEGENERATE BAND

Above the superconducting transition temperature T_c, the two-particle Green's function of the electrons can be decomposed into a free and a scattered part, and the vertex Γ, occurring in the scattered part, obeys an inhomogeneous equation of the general form[6]

$$\Gamma = I - \tfrac{1}{2}\Gamma G G I \, . \qquad (2.1)$$

Here the G's are the one-particle Green's functions and I is the irreducible electron-electron interaction vertex.

As the temperature approaches T_c from above, Γ tends to infinity so that at T_c it satisfies the homogeneous equation

$$\Gamma = -\tfrac{1}{2}\Gamma G G I \, . \qquad (2.2)$$

This equation may then be regarded as the defining equation for T_c, which appears in the G's and, though negligibly for our purposes, also in I. Equation (2.2), when written out fully in coordinate space, reads

$$\Gamma(x_1', x_2', x_1, x_2) = -\tfrac{1}{2}\int d^4x_1''' \, d^4x_2''' \, d^4x_1'' \, d^4x_2'' \times \Gamma(x_1', x_2', x_1''', x_2''') G(x_1''', x_1'') \times G(x_2''', x_2'') I(x_1'', x_2'', x_1, x_2) \, . \qquad (2.3)$$

Here x stands for $(\vec{r}, \tau, s)$, where τ is the imaginary time $(0 \le \tau < i/k_B T)$ and s is a spin index; $\int d^4x$ denotes integration over $\vec{r}$ and τ as well as summation over s; the temperature Green's function is defined as usual[8]; and the irreducible interaction I will be discussed in detail below.

We first Fourier transform Eq. (2.3) with respect to the imaginary time variables. The conjugate to τ is

$$\omega_j = i(\pi/\beta)(2j+1) , \quad j = 0 \, , \quad \pm 1 , \; \ldots \, . \qquad (2.4)$$

Using the conventional Fourier transforms of G, I, and Γ,[9] and the notation $z \equiv (\vec{r}, \omega, s)$, we have

$$\Gamma(z_1', z_2', z_1, z_2) = -(1/2\beta) \sum_{\omega_1'', \omega_1''' ; \omega_2'', \omega_2'''} \int d^3r_1''' \, d^3r_2''' \, d^3r_1'' \, d^3r_2'' \times \Gamma(z_1', z_2', z_1''', z_2''') \, G(z_1''', z_1'') \times G(z_2''', z_2'') I(z_1'', z_2'', z_1, z_2) \, , \qquad (2.5)$$

the summations over spins being implied.

Next, we pass from the $\vec{r}$ representation to the Wannier or site representation, characterized by the atomic site vectors $\vec{n}$. The creation operator $\psi^\dagger(\vec{r})$ is expanded as

$$\psi^\dagger(\vec{r}) = \textstyle\sum_{\vec{n}} a^\dagger(\vec{n}) \, w_{\vec{n}}^*(\vec{r}) \, , \qquad (2.6)$$

where the $w_{\vec{n}}(\vec{r})$ are the orthonormal Wannier functions corresponding to sites $\vec{n}$:

$$w_{\vec{n}}(\vec{r}) = w(\vec{r} - \vec{n}) \, . \qquad (2.7)$$

Since we consider here a one-band model, we have omitted summations over band indices. The function $w_{\vec{n}}(\vec{r})$ is related to the normalized Bloch wave $\psi_{\vec{k}}(\vec{r})$ by the equation

$$\psi_{\vec{k}}(\vec{r}) = (1/N^{1/2}) \textstyle\sum_{\vec{n}} w_{\vec{n}}(\vec{r}) \, e^{i\vec{k}\cdot\vec{n}} \, . \qquad (2.8)$$

From Eq. (2.6), the unitary transformation connecting the $\vec{r}$ and $\vec{n}$ representations is

$$\langle \vec{n} \,|\, \vec{r} \rangle = w_{\vec{n}}^*(\vec{r}), \quad \langle \vec{r} \,|\, \vec{n} \rangle = w_{\vec{n}}(\vec{r}) \, . \qquad (2.9)$$

In the site representation, and with the notation $h \equiv (\vec{n}, \omega, s)$, the vertex equation (2.3) has the form

$$\Gamma(h_1', h_2', h_1, h_2) = -(1/2\beta) \sum_{h_1'', h_1''' ; h_2'', h_2'''} \Gamma(h_1', h_2', h_1''', h_2''') \times G(h_1''', h_1'') \, G(h_2''', h_2'') \, I(h_1'', h_2'', h_1, h_2) \, , \qquad (2.10)$$

where, for example,

$$G(h_1''', h_1'')$$

$$= \int \langle h_1''' | z_1''' \rangle G(z_1''', z_1'') \langle z_1'' | h_1'' \rangle d^3r_1''' d^3r_1'''$$

$$= \int w^*_{\vec{n}_1'''}(\vec{r}_1''') G(z_1''', z_1'') w_{\vec{n}_1''}(\vec{r}_1'') d^3r_1''' d^3r_1'' \, . \tag{2.11}$$

A graphical representation of Eq. (2.10) is shown in Fig. 1.

This equation can be considerably simplified. Let us begin by eliminating the spin variables. Using the notation $l \equiv (\vec{n}, \omega)$ and writing the spin variables explicitly, we have the antisymmetry property

$$\Gamma_{s_1' s_2' s_1 s_2}(l_1', l_2', l_1, l_2) = -\Gamma_{s_2' s_1' s_1 s_2}(l_2', l_1', l_1, l_2)$$

$$= -\Gamma_{s_1' s_2' s_2 s_1}(l_1', l_2', l_2, l_1) \, , \tag{2.12}$$

which follows from the original definition of Γ. Furthermore, the irreducible interaction I, which has an analogous antisymmetry property, can be separated into a direct part and an exchange part

$$I_{s_1'' s_2'' s_1 s_2}(l_1'', l_2'', l_1, l_2) = I(l_1'', l_2'', l_1, l_2) \delta_{s_1'' s_1} \delta_{s_2'' s_2}$$

$$- I(l_1'', l_2'', l_2, l_1) \delta_{s_2'' s_1} \delta_{s_1'' s_2} \, , \tag{2.13a}$$

where

$$I(l_1'', l_2'', l_1, l_2) = I(l_2'', l_1'', l_2, l_1) \, . \tag{2.13b}$$

Substituting Eqs. (2.12) and (2.12) into Eq. (2.10) gives for the spatial part of the vertex

$$\Gamma(l_1', l_2', l_1, l_2) = -(1/\beta) \sum_{l_1'', l_1''' ; l_2'', l_2'''} \Gamma(l_1', l_2', l_1''', l_2''')$$

$$\times G(l_1''', l_1'') G(l_2''', l_2'') I(l_1'', l_2'', l_1, l_2) \, . \tag{2.14}$$

Next, we note that, in the Bloch representation,

$$G(\vec{k}', \omega'; \vec{k}, \omega) = \delta_{\vec{k}, \vec{k}'} \delta_{\omega, \omega'} [\omega - \epsilon(\vec{k})]^{-1} \, , \tag{2.15}$$

where $\epsilon(\vec{k})$ is the band energy of the electrons with respect to the Fermi energy. (This is the unrenormalized Green's function. Renormalization can be included as discussed in Ref. 2.) The unitary transformation connecting the $\vec{n}$ and $\vec{k}$ representations is [cf. Eqs. (2.6)–(2.9)]

$$\langle \vec{n} | \vec{k} \rangle = (1/N^{1/2}) e^{i\vec{k}\cdot\vec{n}} \, , \quad \langle \vec{k} | \vec{n} \rangle = (1/N^{1/2}) e^{-i\vec{k}\cdot\vec{n}} \, . \tag{2.16}$$

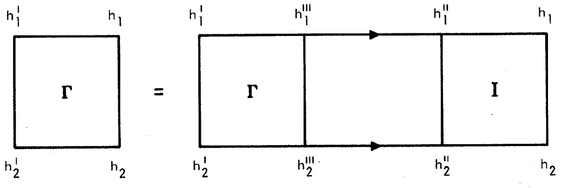

FIG. 1. Graphical representation of the homogeneous vertex equation.

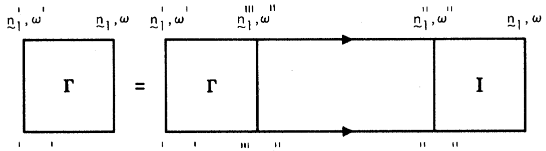

FIG. 2. Graphical representation of the equation for the vertex part of a Cooper pair with zero frequency.

Hence

$$G(\vec{n}', \omega'; \vec{n}, \omega) = \delta_{\omega', \omega} G(\vec{n}' - \vec{n}; \omega) \, , \tag{2.17}$$

where

$$G(\vec{m}, \omega) = (1/N) \sum_{\vec{k}} \{ e^{i\vec{k}\cdot\vec{m}} / [\omega - \epsilon(\vec{k})] \} \, . \tag{2.18}$$

From (2.17) it follows that in Eq. (2.13)

$$\omega_1'' = \omega_1''' \, , \quad \omega_2'' = \omega_2''' \, . \tag{2.19}$$

Further, using conservation of energy (see Fig. 1) and the fact that the superconducting instability occurs first for pairs of zero frequency,[6] we have

$$\omega_1 + \omega_2 = \omega_1'' + \omega_1'' = \omega_1''' + \omega_2''' = \omega_1' + \omega_2' = 0 \, . \tag{2.20}$$

A graphical representation of Eq. (2.14), incorporating the frequency conditions (2.19) and (2.20), is shown in Fig. 2.

Next, we note that the variables l_1', l_2' enter Γ only in the sense of common labels and may therefore be dropped.[10] We write

$$\Gamma(l_1', l_2', l_1, l_2) \rightarrow \Gamma_{l_1', l_2'}(l_1, l_2) \rightarrow \Gamma(l_1, l_2) \rightarrow \Gamma(\vec{n}_1, \vec{n}_2, \omega) \, , \tag{2.21}$$

where

$$\omega = \omega_1 = -\omega_2 \, . \tag{2.22}$$

Equation (2.14) now becomes

$$\Gamma(\vec{n}_1, \vec{n}_2; \omega) = -(1/\beta) \sum_{\omega'''} \sum_{\vec{n}_1'', \vec{n}_1''' ; \vec{n}_2'', \vec{n}_2'''} \Gamma(\vec{n}_1''', \vec{n}_2'', \omega''')$$

$$\times G(\vec{n}_1''' - \vec{n}_1'', \omega''') \, G(\vec{n}_2''' - \vec{n}_2'', -\omega''')$$

$$\times I(\vec{n}_1'', \vec{n}_2'', \omega''' ; \vec{n}_1, \vec{n}_2, \omega). \tag{2.23}$$

In view of the symmetry property (2.13b) of the irreducible interaction I, this equation has solutions symmetric in $\vec{n}_1$ and $\vec{n}_2$ (singlet) or antisymmetric in $\vec{n}_1$ and $\vec{n}_2$ (triplet). In this paper we shall only be concerned with the singlet solutions.

Finally, because of the translational invariance of the system, Γ must have the form

$$\Gamma(\vec{n}_1, \vec{n}_2, \omega) = \Gamma(\vec{n}_1 - \vec{n}_2, \omega) \, e^{i\vec{q}\cdot(\vec{n}_1 + \vec{n}_2)/2} \, . \tag{2.24}$$

Such a solution corresponds to the common pairing momentum $\vec{q}$. The most favorable value of $\vec{q}$, giving rise to the highest value of T_c, is $\vec{q} = 0$.[1] Hence we write

$$\Gamma(\vec{n}_1, \vec{n}_2, \omega) = \Gamma(\vec{n}, \omega), \tag{2.25}$$

where

$$\vec{n} = \vec{n}_1 - \vec{n}_2 . \tag{2.26}$$

Now, the equation for $\Gamma(\vec{n}, \omega)$ [cf. Eq. (2.23)] can be written as

$$\Gamma(\vec{n}, \omega) = (1/\beta) \sum_{\omega'} \sum_{\vec{n}'} \Gamma(\vec{n}', \omega')\, K(\vec{n}', \omega'; \vec{n}, \omega), \tag{2.27}$$

where

$$K(\vec{n}', \omega'; \vec{n}, \omega) = -\sum_{\vec{\mu}} \left(\sum_{\vec{m}_2} G(\vec{m}_2 + \vec{\mu}, \omega')\, G(\vec{m}_2, -\omega') \right) \times \sum_{\vec{n}_2''} I(\vec{n}' + \vec{n}_2'' - \vec{\mu}, \vec{n}_2'', \omega'; \vec{n}, \vec{0}, \omega). \tag{2.28}$$

Or, defining the function

$$F(\vec{\mu}, \omega) \equiv \textstyle\sum_{\vec{m}_2} G(\vec{m}_2 + \vec{\mu}, \omega)\, G(\vec{m}_2, -\omega), \tag{2.29}$$

which describes the propagation of an electron pair, and the contracted interaction vertex

$$I(\vec{n}', \omega'; \vec{n}, \omega) = \textstyle\sum_{\vec{n}_2''} I(\vec{n}' + \vec{n}_2'', \vec{n}_2'', \omega'; \vec{n}, \vec{0}, \omega), \tag{2.30}$$

we may write

$$K(\vec{n}', \omega'; \vec{n}, \omega) = -\textstyle\sum_{\vec{\mu}} F(\vec{\mu}, \omega')\, I(\vec{n}' - \vec{\mu}, \omega'; \vec{n}, \omega). \tag{2.31}$$

Equation (2.27), with K defined in (2.29)–(2.31), represents our final form of the equation which determines the transition temperature T_c.

We shall see in Sec. III that, for the most important interactions, the kernel $I(\vec{n}_1', \vec{n}_2', \vec{n}_1, \vec{n}_2)$ is of short range in the sense that it tends to zero, unless all arguments are near each other, within about a lattice spacing. Consequently, in view of Eq. (2.28), $K(\vec{n}'\vec{n})$ is of short range in $\vec{n}$, and hence, by Eq. (2.27), $\Gamma(\vec{n})$ is substantial only for small values in $\vec{n}$. Therefore, the summation over $\vec{n}'$ in Eq. (2.27) may be truncated after inclusion of only a small number of $\vec{n}'$ vectors. This is important for practical uses of the site point of view which is being developed in this paper.

The function $F(\vec{\mu}, \omega)$, defined by Eq. (2.29), may be written, by virtue of Eq. (2.18), as

$$\begin{aligned} F(\vec{\mu}, \omega) &= \frac{1}{N^2} \sum_{\vec{m}_2} \sum_{\vec{k}, \vec{k}'} \frac{e^{i\vec{k}\cdot(\vec{m}_2 + \vec{\mu})}\, e^{i\vec{k}'\cdot\vec{m}_2}}{[\omega - \epsilon(\vec{k})][-\omega - \epsilon(\vec{k}')]} \\ &= \frac{1}{N} \sum_{\vec{k}} \frac{e^{i\vec{k}\cdot\vec{\mu}}}{|\omega|^2 + \epsilon^2(\vec{k})} . \end{aligned} \tag{2.32}$$

Since the factor $[|\omega|^2 + \epsilon^2(\vec{k})]^{-1}$ in Eq. (2.32) is positive definite, F (regarded as a function of $\vec{\mu}$) attains its maximum for $\vec{\mu} = \vec{0}$; dimensional considerations show that it becomes negligible as soon as $|\vec{\mu}|$ is much larger than a lattice parameter. An alternative form for $F(\vec{\mu}, \omega)$ is obtained by first summing over energy shells:

$$F(\vec{\mu}, \omega) = \int_{\epsilon_{\min}}^{\epsilon_{\max}} \frac{d\epsilon}{\epsilon^2 + |\omega|^2}\, N_{\vec{\mu}}(\epsilon), \tag{2.33}$$

where

$$N_{\vec{\mu}}(\epsilon) = \frac{1}{8\pi^3} \int_{\substack{\text{surface}\\ \epsilon=\text{const}}} \frac{\cos(\vec{k}\cdot\vec{\mu})}{|\vec{\nabla}_{\vec{k}}\epsilon|}\, dS . \tag{2.34}$$

$N_{\vec{0}}(\epsilon)$, the largest of the $N_{\vec{\mu}}(\epsilon)$, is just equal to the electronic density of states $N(\epsilon)$.

III. ELECTRON-ELECTRON INTERACTION

A. Phonon Exchange

In this section we shall discuss the phonon contribution to the irreducible interaction vertex $I(\vec{n}_1', \vec{n}_2', \omega'; \vec{n}_1, \vec{n}_2, \omega)$. This vertex is well known in the Bloch representation. We shall simply have to transform it into the site representation, interpret it, and finally form the contracted kernel $I(\vec{n}', \omega'; \vec{n}, \omega)$, Eq. (2.30), required for the solution of Eq. (2.27).

The phonon vertex consists of only one diagram since vertex corrections may be ignored.[11] According to Fig. 3, and using the notation $p \equiv (\vec{k}, \omega)$,

$$I_{\text{ph}}(p_1', p_2', p_1, p_2) = \textstyle\sum_\lambda g_\lambda(\vec{k}_1', \vec{k}_1)\, g_\lambda(\vec{k}_2', \vec{k}_2)\, D_\lambda(p_1' - p_1)\, \delta_{p_1' - p_1, p_2 - p_2'} . \tag{3.1}$$

Here λ is the polarization index and

$$D_\lambda(\vec{q}) = 2\omega_\lambda(\vec{q})/[\omega^2 - \omega_\lambda^2(\vec{q})] \tag{3.2}$$

is the phonon Green's function, given in terms of the vibration frequency $\omega_\lambda(\vec{q})$. The matrix element for the emission of a phonon with momentum $\vec{q} = \vec{k}_1' - \vec{k}_1$ is given by

$$\begin{aligned} g_\lambda(\vec{k}_1', \vec{k}_1) &= -\left(\frac{1}{2MN\omega_\lambda(\vec{q})}\right)^{1/2} \sum_{\vec{m}} \vec{e}_\lambda(\vec{q})\, e^{i\vec{q}\cdot\vec{m}} \times \int_{\mathcal{V}} \psi_{\vec{k}_1'}^*(\vec{r})\, \vec{\nabla} V(\vec{r} - \vec{m})\, \psi_{\vec{k}_1}(\vec{r})\, d^3r \\ &= -\left(\frac{1}{2MN\omega_\lambda(\vec{q})}\right)^{1/2} \sum_{\vec{m};\vec{n}_1,\vec{n}_1'} e_\lambda(\vec{q})\, e^{i\vec{q}\cdot\vec{m}}\, e^{i(-\vec{k}_1'\cdot\vec{n}_1' + \vec{k}_1\cdot\vec{n}_1)} \\ &\quad \times \frac{1}{N} \int_{\mathcal{V}} w^*(\vec{r} - \vec{n}_1')\, \vec{\nabla} V(\vec{r} - \vec{m})\, w(\vec{r} - \vec{n}_1)\, d^3r. \end{aligned} \tag{3.3}$$

Here M is the atomic mass and $\vec{e}_\lambda(\vec{q})$ is the polarization vector; $V(\vec{r} - \vec{m})$ is the effective ionic potential at site $\vec{m}$; and $\mathcal{V}$ is the crystal volume. The matrix element for an absorption process has the same form, except that $\vec{q}$ is replaced by $-\vec{q}$. Mo-

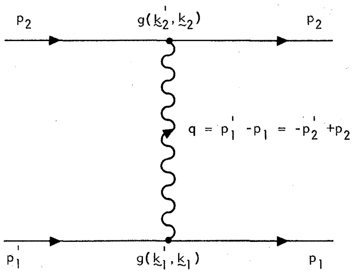

FIG. 3. Diagram for the phonon exchange between two electrons; $g(\vec{k}_1', \vec{k}_1)$ and $g(\vec{k}_2', \vec{k}_2)$ are the matrix elements for an emission and an absorption process.

mentum conservation follows from the translational invariance of the last integral against equal displacements of all three sites.

We now substitute Eqs. (3.2) and (3.3) in (3.1) and transform to the site representation. This gives

$$I_{\text{ph}}(\vec{n}_1', \vec{n}_2', \vec{n}_1, \vec{n}_2, \omega)$$

$$= \sum_{\vec{k}_1, \vec{k}_1'; \vec{k}_2, \vec{k}_2'} e^{i(\vec{k}_1' \cdot \vec{n}_1' + \vec{k}_2' \cdot \vec{n}_2' - \vec{k}_1 \cdot \vec{n}_1 - \vec{k}_2 \cdot \vec{n}_2)} \times I_{\text{ph}}(\vec{k}_1', \vec{k}_2', \vec{k}_1, \vec{k}_2; \omega)$$

$$= \sum_{\vec{l}, \vec{m}} \sum_{\alpha, \beta} L_{\alpha\beta}(\vec{m}; \omega) (\vec{n}_1' | \nabla_\alpha V_{\vec{l}} | \vec{n}_1) (\vec{n}_2' | \nabla_\beta V_{\vec{l} - \vec{m}} | \vec{n}_2). \tag{3.4}$$

Here $\omega = \omega_1 - \omega_1' = \omega_2 - \omega_2'$; $L_{\alpha\beta}(\vec{m}; \omega)$ is a lattice Green's function in site space,

$$L_{\alpha\beta}(\vec{m}; \omega) \equiv \frac{1}{N} \sum_{\lambda} \sum_{\vec{q}} \frac{e_{\lambda\alpha}(\vec{q})\, e_{\lambda\beta}(\vec{q})}{2M\omega_\lambda(\vec{q})} D_\lambda(\vec{q}, \omega)\, e^{-i\vec{q} \cdot \vec{m}}; \tag{3.5}$$

and

$$(\vec{n}' | \nabla_\alpha V_{\vec{l}} | \vec{n}) = \int_{\upsilon} w^*(\vec{r} - \vec{n}')\, \nabla_\alpha V(\vec{r} - \vec{l})\, w(\vec{r} - \vec{n})\, d^3 r, \tag{3.6}$$

where $\nabla_\alpha \equiv \nabla_{r_\alpha}$. A graphical representation of the phonon vertex in the site representation, Eq. (3.4), is shown in Fig. 4. Two electrons initially at sites $\vec{n}_1'$ and $\vec{n}_2'$ are scattered to $\vec{n}_1$ and $\vec{n}_2$ by an atomic displacement which propagates between $\vec{l} - \vec{m}$ and $\vec{l}$. The summation is over the sites $\vec{l}$ and $\vec{m}$.

According to Eq. (2.30), the required vertex $I_{\text{ph}}(\vec{n}', \omega'; \vec{n}, \omega)$ is obtained from $I_{\text{ph}}(\vec{n}_1', \vec{n}_2', \vec{n}_1, \vec{n}_2; \omega)$ by partial summation. Since the latter is invariant under simultaneous translation of $\vec{n}_1'$, $\vec{n}_2'$, $\vec{n}_1$, and $\vec{n}_2$, it can be written as

$$I_{\text{ph}}(\vec{n}', \vec{n}; \omega) = \sum_{\vec{m}} \sum_{\alpha, \beta} L_{\alpha\beta}(\vec{m}; \omega) \times \sum_{\vec{n}_2, \vec{n}_2'} (\vec{n}_2' + \vec{n}' | \nabla_\alpha V_{\vec{0}} | \vec{n}_2 + \vec{n}) (\vec{n}_2' | \nabla_\beta V_{-\vec{m}} | \vec{n}_2). \tag{3.7}$$

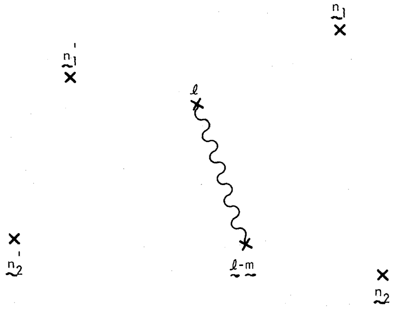

FIG. 4. Phonon vertex; electron 1 transfers from $\vec{n}_1'$ to $\vec{n}_1$, electron 2 from $\vec{n}_2'$ to $\vec{n}_2$. A lattice distortion propagates between $\vec{l}$ and $\vec{l} - \vec{m}$.

It describes an atomic displacement of frequency ω propagating between, say, site 0 and all possible sites $-\vec{m}$, while two electrons, initially separated by the lattice vector $\vec{n}'$, scatter into new positions, where they are separated by the lattice vector $\vec{n}$.

The interaction I_{ph} is significant only when all four site variables are near each other. This may be seen as follows. Clearly the matrix element (3.6) is small unless all three sites are near each other. Furthermore, the function $L_{\alpha\beta}(\vec{m}, \omega)$ is, Eq. (3.5), the Fourier transform of a function of $\vec{q}$ with a characteristic scale of a^{-1}, where a is the lattice constant. Therefore $L_{\alpha\beta}(\vec{m}, \omega)$ is negligible for $|\vec{m}| \gg a$. With these facts, inspection of Eq. (3.4) now yields immediately the asserted short range of $I_{\text{ph}}(\vec{n}_1', \vec{n}_2', \vec{n}_1, \vec{n}_2; \omega)$. The contracted vertex $I_{\text{ph}}(\vec{n}', \vec{n}; \omega)$, defined by Eq. (2.30), is then also evidently of short range in both site variables.

B. Short-Range Coulomb Interaction

We now seek the Coulomb contribution to the irreducible vertex part. As is well known, in simple metals the effective Coulomb interaction is given by the bare interaction screened by a dielectric func-

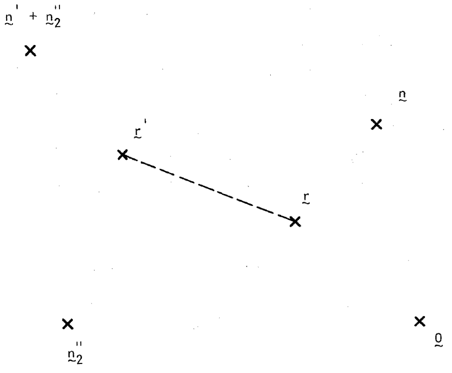

FIG. 5. Short-range Coulomb vertex.

tion.[12] This interaction is of short range and may be assumed to be frequency independent.

In the present case the interaction has the form

$$I_c(\vec{n}_1', \vec{n}_2', \vec{n}_1, \vec{n}_2) = \int d^3r\, d^3r'\, w^*(\vec{r} - \vec{n}_1')\, w^*(\vec{r}\,' - \vec{n}_2') \times V_c(|\vec{r}\,' - \vec{r}|)\, w(\vec{r} - \vec{n}_1)\, w(\vec{r}\,' - \vec{n}_2), \tag{3.8}$$

where $V_c(\vec{r})$ is the effective interaction between d electrons. The contracted Coulomb vertex, Eq. (2.29), is given by (see Fig. 5)

$$I_c(\vec{n}\,', \vec{n}) = \sum_{n_2''} \int d^3r\, d^3r'\, w^*(\vec{r} - \vec{n}\,' - \vec{n}_2'')\, w^*(\vec{r}\,' - \vec{n}_2'') \times V_c(|\vec{r}\,' - \vec{r}|)\, w(\vec{r} - \vec{n})\, w(\vec{r} - \vec{0}). \tag{3.9}$$

It is evident that $I_c(\vec{n}_1', \vec{n}_2', \vec{n}_1, \vec{n}_2)$ is negligible unless all site variables are near each other, and that $I_c(\vec{n}, \vec{n}\,')$ is negligible unless $\vec{n}$ and $\vec{n}\,'$ are small.

We mention that in some narrow-band superconductors, the Coulomb interaction has, in addition, a long-range part due to exchange effects (see Appendix B).

C. Contact Model

Equation (2.27), in general, represents a set of coupled integral equations for the quantities $\Gamma(n; \omega)$. We believe that these may in the future be useful for quantitative calculations of the transition temperature of d- and f-band superconductors. However, for qualitative insight, we now adopt the so-called contact model characterized by the assumption

$$I(0, 0; \omega) \gg I(\vec{n}\,', \vec{n}; \omega) \quad \text{for } \vec{n} \text{ or } \vec{n}\,' \neq 0. \tag{3.10}$$

Thus we set

$$I(\vec{n}\,', \vec{n}; \omega) = \delta_{\vec{n},0}\, \delta_{\vec{n}\,',0}\, I(\omega). \tag{3.11}$$

With this assumption and the notation $\Gamma(0; \omega) \equiv \Gamma(\omega)$, Eq. (2.27) reduces to a single integral equation, which will be discussed in detail in Sec. IV.

The assumption (3.11) means physically that we consider only scattering processes in which the two electrons are initially both on one site, say, $\vec{n}_1' = \vec{n}_2'$, and finally again both on one site, $\vec{n}_1 = \vec{n}_2$.

This is certainly a reasonable assumption for the Coulomb vertex, Eqs. (3.8) and (3.9), for which, when $\vec{n} = \vec{n}\,' = 0$,

$$I_c(\omega) = \textstyle\sum_{\vec{s}} \int d^3r\, d^3r'\, w^*(\vec{r} - \vec{s})\, w^*(\vec{r}\,' - \vec{s}) \times V_c(|\vec{r}\,' - \vec{r}|)\, w(\vec{r})\, w(\vec{r}\,'). \tag{3.12}$$

In fact, here the leading term corresponds to $\vec{s} = 0$,

$$I_c(w) \approx U \equiv \int d^3r\, d^3r'\, |w(\vec{r}\,')|^2\, V_c(|\vec{r}\,' - \vec{r}|)\, |w(\vec{r})|^2, \tag{3.13}$$

the screened interaction between the charges of the two electrons on the same atom.

For the phonon vertex we have in the contact model

$$I_{\text{ph}}(\omega) = \sum_{\vec{m}} \sum_{\alpha,\beta} L_{\alpha\beta}(\vec{m}; \omega) \times \sum_{\vec{s},\vec{s}\,'} (\vec{s}\,' | \nabla_\alpha V(\vec{0}) | \vec{s})\, (\vec{s}\,' | \nabla_\alpha V(-\vec{m}) | \vec{s}). \tag{3.14}$$

Here the contributions from $\vec{s} - \vec{s}\,' = 0$ vanish because of the parity selection rule. The phonon Green's function $L_{\alpha\beta}(\vec{m}; \omega)$, defined in Eqs. (3.5) and (3.2), is of short range in $\vec{m}$; in fact, for an Einstein model, it vanishes unless $\vec{m} = 0$. It is reasonable therefore to assume that the dominant contribution to (3.14) will come from $\vec{m} = 0$. For a cubic lattice,

$$L_{\alpha\beta}(0; \omega) = \delta_{\alpha\beta}\, L(\omega), \tag{3.15}$$

where

$$L(\omega) \equiv (1/M) \int_0^{\omega_0} [g(z)\, dz / (\omega^2 - z^2)], \tag{3.16}$$

ω_0 is the maximum phonon frequency, and $g(z)$ is the normalized density of frequencies,

$$\int_0^{\omega_0} g(z)\, dz = 1. \tag{3.17}$$

Keeping only the $\vec{m} = 0$ term then gives

$$I_{\text{ph}}(\omega) \approx L(\omega) \sum_{\vec{s},\vec{s}\,'} \sum_{\alpha} |(\vec{s} | \nabla_\alpha V(\vec{r}) | \vec{s}\,')|^2. \tag{3.18}$$

We now offer some additional remarks on the contact model. The term $I_{\text{ph}}(0, 0; \omega)$ $[= I_{\text{ph}}(\vec{n}\,' = 0, \vec{n} = 0; \omega)]$ is related to the interaction in momentum space as follows:

$$I_{\text{ph}}(0, 0; \omega) = (1/N^2) \sum_{\vec{k},\vec{k}\,'} I_{\text{ph}}(\vec{k}\,', \vec{k}; \omega), \tag{3.19}$$

where the sum goes over the Brillouin zone. The contact approximation (3.11) is equivalent to the approximation

$$I_{\text{ph}}(\vec{k}\,', \vec{k}; \omega) = I_{\text{ph}}(0, 0; \omega), \tag{3.20}$$

independent of $\vec{k}$ and $\vec{k}\,'$. As we have seen, this is a good approximation for a very short-range interaction and for sufficiently localized Wannier functions. In a more typical situation, $I_{\text{ph}}(\vec{k}\,', \vec{k}; \omega)$ varies somewhat as a function of the momentum variables on a scale of the order of a reciprocal-lattice vector. To allow for this variation in site space would require including interaction matrix elements $I_{\text{ph}}(\vec{n}\,', \vec{n}; \omega)$, where $|\vec{n}\,'|$ and $|\vec{n}|$ are of the order of a lattice parameter, in addition to the term with $\vec{n}\,' = \vec{n} = 0$.

Our contact approximation has some similarity to approximations used by other authors, especially McMillan[3] and Hopfield,[7] in which also a single effective interaction is used. However, Hopfield, after writing the phonon interaction in an angular momentum representation, makes the approximation Eq. (21) in order to derive his main conclusion, Eq. (26). In our development the only approximation is the truncation of the coupled system of equations.

IV. TRANSITION TEMPERATURE

At this point we turn back to Eqs. (2.27)–(2.31), defining the transition temperature T_c. We make the contact approximation for the Coulomb repulsion

$$I_c(\vec{n}', \vec{n}; \omega) = \delta_{\vec{n},0}\delta_{\vec{n}',0}U , \tag{4.1}$$

where U is given by Eq. (2.13) and is independent of ω. As we have remarked, this is certainly a reasonable approximation for the short-range Coulomb interaction (we do not make the contact approximation for I_{ph}). Inspection of Eqs. (2.27)–(2.31) shows that since I does not have a frequency cutoff, $\Gamma(\vec{n}, \omega)$ tends to a finite limit when $\omega \to \infty$. With Eq. (4.1), we may write

$$\Gamma(\vec{n}, \omega) = \Gamma_1(\vec{n}, \omega) + \Gamma_2(0)\delta_{\vec{n},0} , \tag{4.2}$$

where

$$\lim \Gamma_1(\vec{n}, \omega) = 0 \quad \text{as } |\omega| \to \infty . \tag{4.3}$$

The quantity $\Gamma_2(0)$ can be eliminated from Eq. (2.27). We take the limit $\omega \to \infty$, which gives

$$\Gamma_2(0) = -(1/\beta) \sum_{\omega'} \sum_{\vec{n}'} [\Gamma_1(\vec{n}', \omega') + \Gamma_2(0)\, \delta_{\vec{n}',0}] F(\vec{n}', \omega')\, U . \tag{4.4}$$

Hence

$$\Gamma_2(0) = -\frac{U}{\beta} \sum_{\omega'} \sum_{\vec{n}'} \Gamma_1(\vec{n}', \omega') F(\vec{n}', \omega') \Big/ \left(1 + \frac{U}{\beta} \sum_{\omega'} F(0, \omega')\right) . \tag{4.5}$$

Now going back to Eq. (2.27) for arbitrary ω, we find the following equation for $\Gamma_1(\vec{n}, \omega)$:

$$\Gamma_1(\vec{n}, \omega) = -\frac{1}{\beta} \sum_{\omega'} \sum_{\vec{n}', \vec{\mu}} F(\vec{\mu}, \omega')\, I_{ph}(\vec{n}' - \vec{\mu}, \vec{n};\ \omega' - \omega) \times \left[\Gamma_1(\vec{n}', \omega') - \delta_{\vec{n}',0} \frac{U}{\beta} \sum_{\omega''} \sum_{\vec{n}''} \Gamma_1(\vec{n}'', \omega'') \times F(\vec{n}'', \omega'') \Big/ \left(1 + \frac{U}{\beta} \sum_{\omega''} F(0, \omega'')\right)\right] . \tag{4.6}$$

The denominator in this equation can be evaluated (see Appendix A):

$$1 + (U/\beta)\textstyle\sum_{\omega''} F(0, \omega'') = 1 + U\, N(0) \ln(\alpha\beta\epsilon_b) , \tag{4.7}$$

where α is a positive dimensionless constant, of order unity [see Eq. (A16)], and ϵ_b is an effective half-width of the energy band [see Eq. (A11)].

To continue further, we now make the contact approximation, Eq. (3.11), also for I_{ph}. Then (4.6) reduces to the following equation for $\Gamma_1(\omega)$ [$= \Gamma_1(0, \omega)$]:

$$\Gamma_1(\omega) = -\frac{1}{\beta} \sum_{\omega'} F(0, \omega')\, I_{ph}(\omega - \omega') \times \left(\Gamma_1(\omega') - \frac{U}{\beta} \sum_{\omega''} \Gamma_1(\omega'')\, F(0, \omega'') \Big/ [1 + U(0) \ln(\alpha\beta\epsilon_b)]\right) . \tag{4.8}$$

This is still an integral equation which, through I_{ph}, involves the details of the phonon spectrum and requires numerical solution for each case.

We may, however, roughly parametrize I_{ph} by writing, in the manner of BCS,

$$I_{ph}(\omega - \omega') = \begin{cases} -I_{ph}, & |\omega| \text{ and } |\omega'| \le \omega_0 \\ 0, & \text{otherwise.} \end{cases} \tag{4.9}$$

This gives

$$\Gamma_1(\omega) = \begin{cases} \Gamma_1, & |\omega| \le \omega_0 \\ 0, & |\omega| > \omega_0 \end{cases} \tag{4.10}$$

where Γ_1 satisfies the equation

$$\Gamma_1 = \frac{I_{ph}}{\beta} \sum_{|\omega'| \le \omega_0} F(0, \omega')\, \Gamma_1 \times \left(1 - \frac{U}{\beta} \sum_{|\omega'| \le \omega_0} F(0, \omega') \Big/ [1 + U N(0) \ln(\alpha\beta\epsilon_b)]\right). \tag{4.11}$$

Now the sum over ω' is easily evaluated [$N(\epsilon)$ may be replaced by $N(0)$] and gives

$$(1/\beta) \sum_{|\omega'| \le \omega_0} F(0, \omega') = N(0) \ln(\alpha'\beta\omega_0) , \tag{4.12}$$

where

$$\alpha' = 2e^{\gamma}/\pi = 1.13 \tag{4.13}$$

(γ = Euler's constant). Substituting this expression into (4.10) and dividing by Γ_1 gives

$$1 = N(0)\, I_{ph} \ln(\alpha'\beta\omega_0) \left(1 - \frac{N(0)\, U \ln(\alpha'\beta\omega_0)}{1 + N(0)\, U \ln(\alpha\beta\epsilon_b)}\right) \tag{4.14}$$

or

$$1 = N(0) \ln(\alpha'\beta\omega_0)\, (I_{ph} - \tilde{U}) , \tag{4.15}$$

where

$$\tilde{U} = \frac{U}{1 + N(0)\, U \ln[(\alpha/\alpha')(\epsilon_b/\omega_0)]} . \tag{4.16}$$

From (4.15) and (4.16) we see that the frequency-independent repulsion U is equivalent to a much weaker effective repulsion $\tilde{U}$ limited to the frequency range $|\omega|$, $|\omega'| \le \omega_0$.[13]

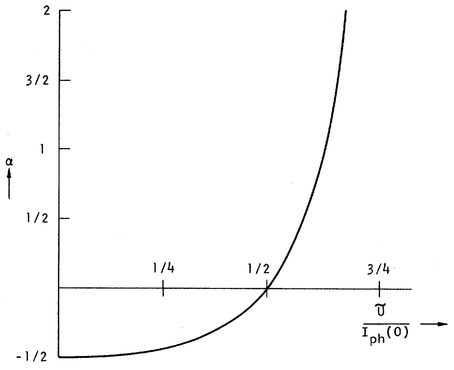

FIG. 6. Isotope effect for the contact model.

Solving (4.15) for T_c gives

$$k_B T_c = 1.13\,\omega_0 \exp\left(-\frac{1}{N(\sigma)\,(I_{ph}-\tilde{U})}\right) . \tag{4.17}$$

The isotope effect arises from the dependence of ω_0 and $\tilde{U}$ on M, in Eq. (4.17). Using Eq. (4.16) one finds

$$a \equiv \frac{d \ln T_c}{dM} = -\frac{1}{2}\left(1 - \frac{\tilde{U}^2}{(I_{ph}-\tilde{U})^2}\right) . \tag{4.18}$$

This expression is of the form discussed in Ref. 14. It is clear that, in a narrow-band superconductor, a small negative or even positive isotope effect may well occur. For in these materials the Coulomb repulsion U is primarily an intra-atomic effect, and may be expected to be considerably larger than the screened Coulomb interaction between the conduction electrons of simple metals. Figure 6 shows a as a function of $\tilde{U}/I_{ph}$. α is positive provided that

$$\frac{\tilde{U}}{I_{ph}} \geq \frac{1}{2} . \tag{4.19}$$

For $\tilde{U}/I_{ph} = 0.69$ we see from Fig. 6 that $\alpha = 2$. Such a large positive value of α will be accompanied by a small value of T_c.

For some metals, at the ends of the transition periods (Pd, Pt), the Coulomb interaction is not adequately described by I_c. Exchange interactions can lead to a long-range Coulomb interaction I_{spin}. Their effect on T_c is calculated in Appendix B, based on a model interaction for I_{spin} which takes into account its long-range and low-frequency behavior.

V. DEGENERATE BAND

A. Vertex Equation for a Copper Pair

In the preceding part of this paper, a theory of the transition temperature was developed for the case of a nondegenerate s band. For such a band the central equations (2.27)–(2.31) for the vertex part of a Cooper pair are mathematically relatively simple. However, as mentioned in the Introduction, of real interest are the superconductors with d and f bands, that is, the transition, rare-earth, and actinide metals and their alloys and compounds. Therefore, we would like to extend the previous discussion to the case of degenerate band structures. As a first step in this direction we consider in some detail a threefold-degenerate d band in a cubic crystal. Possible hybridization with an overlapping s-p band is not taken into account.

We write the Bloch waves for our degenerate bands as

$$\psi_{\nu,\vec{k}}(\vec{r}) = (1/N^{1/2}) \sum_{\vec{n}} \sum_{i} a_i(\nu,\vec{k})\, e^{i\vec{k}\cdot\vec{n}}\, w_i(\vec{r}-\vec{n}) . \tag{5.1}$$

Here ν is the band index. The (real) Wannier functions $w_i(\vec{r})$ are characterized by an orbital index i and transform according to a degenerate representation of the crystal point group. We choose band indices ν and wave-function phases in such a way that

$$\begin{aligned} \epsilon(\nu,-\vec{k}) &= \epsilon(\nu,\vec{k}) , \\ \psi_{\nu,-\vec{k}}(\vec{r}) &= \Psi^{*}_{\nu,\vec{k}}(\vec{r}) , \\ a_i(\nu,-\vec{k}) &= a_i^{*}(\nu,\vec{k}) . \end{aligned} \tag{5.2}$$

Since the Bloch waves and the Wannier functions form orthonormal sets, the coefficients $a_i(\nu,\vec{k})$ satisfy the condition

$$\textstyle\sum_i a_i^{*}(\nu,\vec{k})\, a_i(\nu',\vec{k}) = \delta_{\nu\nu'} . \tag{5.3}$$

The generalization of Eqs. (2.27)–(2.31) to the case of a degenerate band is straightforward. The result is

$$\Gamma_{ij}(\vec{n},\omega) = (1/\beta) \sum_{\omega'} \sum_{n'} \sum_{i',j'} \Gamma_{i'j'}(\vec{n}',\omega') \times K_{i'j';ij}(\vec{n}',\omega';\vec{n},\omega) . \tag{5.4}$$

Here

$$K_{i'j';ij}(\vec{n}'\omega';\vec{n},\omega) = -\sum_{\vec{\mu}} \sum_{i'',j''} F_{i'j';i''j''}(\vec{\mu},\omega')\, I_{i''j'';ij} \times (\vec{n}'-\vec{\mu},\omega';\vec{n},\omega) , \tag{5.5}$$

where

$$F_{i'j';i''j''}(\vec{\mu},\omega) = \sum_{\vec{m}_2} G_{i'i''}(\vec{m}_2+\vec{\mu},\omega)\, G_{j'j''}(\vec{m}_2,-\omega) \tag{5.6}$$

and

$$I_{i''j'';ij}(\vec{n}'-\vec{\mu},\omega';\vec{n},\omega)$$

$$=\sum_{\vec{n}_2''} I_{i''j'';ij}(\vec{n}'+\vec{n}_2'',\vec{n}_2',\omega';\vec{n},0,\omega). \tag{5.7}$$

Matrices in $(\vec{n}, i)$ space can be related to the Bloch or $(\nu, \vec{k})$ space by the unitary transformation

$$(i,\vec{n}\,|\,\nu,\vec{k}) = N^{-1/2}\, a_i(\nu,\vec{k})\, e^{i\vec{k}\cdot\vec{n}}. \tag{5.8}$$

For example, the Green's function $G_{i'i}(\vec{n}'-\vec{n},\omega)$ describing propagation from $\vec{n}', i'$ to $\vec{n}, i$ is given by

$$G_{i'i}(\vec{n}'-\vec{n},\omega) = \frac{1}{N}\sum_{\nu,\vec{k}} \frac{e^{i\vec{k}\cdot(\vec{n}'-\vec{n})}}{\omega-\epsilon(\nu,\vec{k})}\, a_{i'}(\nu,\vec{k})\, a_i^*(\nu,\vec{k}), \tag{5.9}$$

where $\epsilon(\nu,\vec{k})$ is the energy associated with $\psi_{\nu,\vec{k}}(\vec{r})$.

B. Transition Temperature for a Γ_{25}' Band

As an example of the use of Eq. (5.4), we shall now calculate, in the contact approximation, the transition temperature of a threefold-degenerate *d* band in a cubic crystal. The corresponding Wannier functions, centered at the origin, are

$$w_1(\vec{r}) = xy\, f(\vec{r}),\quad \omega_2(\vec{r}) = yz\, f(\vec{r}),\quad \omega_3(\vec{r}) = zx\, f(\vec{r}), \tag{5.10}$$

where $f(\vec{r})$ has cubic symmetry.[15]

The phonon vertex is, in the approximation corresponding to Eq. (3.18),

$$I^{\mathrm{ph}}_{i'j';ij}(\omega) = F(\omega)\sum_{\vec{s},\vec{s}'}\sum_{\alpha}(i',\vec{s}'\,|\,\nabla_\alpha V(\vec{r})\,|\,i,\vec{s})$$

$$\times(j',\vec{s}'\,|\,\nabla_\alpha V(\vec{r})\,|\,j,\vec{s}), \tag{5.11}$$

where the phonon function $F(\omega)$ is given by Eq. (3.6) and the matrix elements are defined in analogy with Eq. (3.6). The Coulomb vertex is

$$I^{c}_{i'j';ij} = \int d^3r\, d^3r'\, w_{i'}^*(\vec{r})\, w_{j'}^*(\vec{r}')$$

$$\times V_c(|\vec{r}'-\vec{r}|)\, w_i(\vec{r})\, w_j(\vec{r}'). \tag{5.12}$$

Equation (5.4) now becomes

$$\Gamma_{ij}(\omega) = (1/\beta)\sum_{\omega'}\sum_{i',j'}\Gamma_{i'j'}(\omega')\, K_{i'j';ij}(\omega',\omega), \tag{5.13}$$

where

$$K_{i'j';ij}(\omega',\omega) = -\sum_{i'',j''} F_{i'j';i''j''}(0,\omega')$$

$$\times I_{i''j'';ij}(\omega'-\omega). \tag{5.14}$$

From the cubic symmetry it follows that K has at most four nonvanishing independent components, viz.,

$$K_1 = K_{11;11},\quad K_2 = K_{11;22},\quad K_3 = K_{12;12},\quad K_4 = K_{12;21}. \tag{5.15}$$

Equation (5.13) has solutions corresponding to irreducible representations which are symmetric in i and j (singlet). Denoting the dimensionality of the representations by n, they have the form

$$\Gamma_{11}^{(1)} = \Gamma_{22}^{(1)} = \Gamma_{33}^{(1)} = \Gamma^{(1)},\quad n=1$$

$$\Gamma_{11}^{(2)} = -\Gamma_{22}^{(2)} = \Gamma^{(2)},\quad n=2 \tag{5.16}$$

$$\Gamma_{12}^{(3)} = \Gamma_{21}^{(3)} = \Gamma^{(3)},\quad n=3.$$

All components of Γ_{ij} not explicitly shown vanish. The equations satisfied by $\Gamma^{(1)}$, $\Gamma^{(2)}$, and $\Gamma^{(3)}$ are obtained by substitution of (5.16) in (5.13):

$$\Gamma^{(1)}(\omega) = (1/\beta)\textstyle\sum_{\omega'}\Gamma^{(1)}(\omega')\,[K_1(\omega',\omega)+2K_2(\omega',\omega)],$$

$$\Gamma^{(2)}(\omega) = (1/\beta)\textstyle\sum_{\omega'}\Gamma^{(2)}(\omega')\,[K_1(\omega',\omega)-K_2(\omega',\omega)], \tag{5.17}$$

$$\Gamma^{(3)}(\omega) = (1/\beta)\textstyle\sum_{\omega'}\Gamma^{(3)}(\omega')\,[K_3(\omega',\omega)+K_4(\omega',\omega)].$$

The first solution $\Gamma^{(1)}$ has complete cubic symmetry while the others have directional properties. Since no experimental evidence for cubic superconductors of the latter type exists, we shall from here on only consider $\Gamma_{ij}^{(1)}$.

By (5.14), and again using cubic symmetry, we have

$$K_1(\omega',\omega) \equiv K_{11;11}(\omega',\omega)$$

$$= -\textstyle\sum_j F_{11;jj}(0,\omega')\, I_{jj;11}(\omega'-\omega) \tag{5.18}$$

and

$$K_2(\omega',\omega) \equiv K_{11;22}(\omega',\omega)$$

$$= -\textstyle\sum_j F_{11;jj}(0,\omega')\, I_{jj;22}(\omega'-\omega). \tag{5.19}$$

Substitution of (5.18) and (5.19) in (5.17) gives

$$\Gamma^{(1)}(\omega) = -(1/\beta)\textstyle\sum_\omega \Gamma^{(1)}(\omega')\sum_j F_{11;jj}(0,\omega')$$

$$\times[I_{11,11}(\omega'-\omega)+2I_{11;22}(\omega'-\omega)]. \tag{5.20}$$

Now, using cubic symmetry and Eqs. (5.6) and (5.9) we find

$$\sum_j F_{11;jj}(0,\omega')$$

$$=\tfrac{1}{3}\sum_{i,j} F_{ii;jj}(0,\omega')$$

$$=(1/3N)\sum_{\nu,\nu'}\sum_{\vec{k}}\{[\omega'-\epsilon(\nu,\vec{k})][-\omega'-\epsilon(\nu',\vec{k})]\}^{-1}$$

$$\times\sum_i a_i(\nu,\vec{k})\, a_i(\nu',-\vec{k})\sum_j a_j^*(\nu,\vec{k})\, a_j^*(\nu',-\vec{k}). \tag{5.21}$$

With the symmetry relations (5.2) and the orthogonality condition (5.3), the summations over i and j

can be carried out. This leads, in analogy with Eqs. (2.33) and (2.34), to

$$\sum_j F_{11;jj} = \frac{1}{3N}\sum_{\nu}\sum_{\vec{k}} \frac{1}{|\omega'|^2+\epsilon^2(\nu,\vec{k})}$$

$$= \frac{1}{3}\int_{\epsilon_{\min}}^{\epsilon_{\max}} \frac{N(\epsilon)\,d\epsilon}{|\omega'|^2+\epsilon^2}\,, \qquad (5.22)$$

where $N(\epsilon)$ is the total density of states.

Using Eq. (5.22), the integral equation (5.20) has the same structure as in the contact model for a nondegenerate band if we make the identification

$$I(\omega'-\omega) \equiv \tfrac{1}{3}\,(I_{11;11}+2I_{11;22}). \qquad (5.23)$$

Hence the transition temperature in a BCS-like theory is given by

$$k_B T_c = 1.13\,\omega_0 \exp\left(-\frac{1}{N(0)\,(I_{\text{ph}}-\tilde{U})}\right)\,, \qquad (5.24)$$

as in Eq. (4.16). I_{ph} is the average defined by (5.23), and $\tilde{U}$, the effective Coulomb repulsion, is given by

$$\tilde{U} = \frac{U}{1+N(0)\,U\ln[(\alpha/\alpha')(\epsilon_b/\omega_0)]}\,, \qquad (5.25)$$

where U is the average Coulomb matrix element, in the sense of Eq. (5.23), and the other quantities have the same meaning as in Sec. IV.

VI. SUMMARY

Generally the discussions of the superconducting transition temperature are based on theories formulated in terms of Bloch wave functions. However, there is a great deal of experimental evidence[16] that there is a strong correlation between atomic properties and the superconducting transition temperatures. This is especially true for *d*-band transition metals and alloys.[14] Therefore, in this paper we have developed a theory of the transition temperature in terms of wave functions localized at atomic sites.

The central equations are Eq. (2.27), for the vertex part of a nondegenerate band, and its generalization to a degenerate band, Eq. (5.4). The kernel appearing in (2.27) is of short range provided the electron-electron interaction in coordinate space is appreciable only for small distances and the Wannier functions are sufficiently localized. The short-range *e-e* interaction has two parts, the first of which, caused by the electron-lattice interactions, is attractive, whereas the second, caused by the screened Coulomb interaction, is repulsive. When the kernel is of short range, the vertex equation reduces to a small number of coupled integral equations in site space. In particular, only a single equation remains in the contact model. This model means physically that we consider only scattering processes where the two electrons are initially both at one site, say $\vec{n}_1' = \vec{n}_2'$, and finally again both at one site, $\vec{n}_1 = \vec{n}_2$.

Assuming the contact model, we calculate T_c for a nondegenerate band in the manner of BCS. The result contains the Coulomb pseudointeraction $\tilde{U}$ which is caused by the intra-atomic Coulomb interaction U. Thus, U takes the place of the screened interaction between nearly free electrons in *s-p* metals. When U is large, the isotope effect can have either sign. It is positive if $2\tilde{U}$ is greater than the attractive interaction; in such a case T_c is found to be small. Geballe, Matthias, Hull, and Corenzwit[17] have first observed that in transition metals the isotope effect is not proportional to $M^{-1/2}$, as in simple metals. In Ru there is no observable effect, in Mo the effect is proportional to $M^{-0.33}$, and in uranium it is positive. These variations in the isotope exponents were considered as indications for an attractive mechanism other than phonon exchange. We believe, however, that they may be accounted for by variations in the intra-atomic Coulomb interaction U and, to a smaller extent, in the electronic bandwidth.

The generalized vertex equation (5.4) in the contact approximation is applied to the case of a threefold-degenerate *d* band of cubic symmetry Γ_{25}'. The corresponding localized functions are similar to *xy*, *yz*, and *zx* atomic orbitals. The vertex equation has one solution with full cubic symmetry which is presumably the physically significant one. The associated transition temperature depends on the total density of states of all three bands at the Fermi surface and on a pairing constant which weighs the intraorbital and interorbital interactions with $\frac{1}{3}$ and $\frac{2}{3}$, respectively. This calculation is considered as a first step towards a treatment of real *d*-band materials.

The lowering of T_c due to a long-range Coulomb interaction, which can occur in transition metals with nearly filled *d* bands, is discussed in Appendix B. The interaction, due to exchange effects, is given by an approximation that takes into account its low-frequency and long-range behavior. For weak exchange effects, the T_c formula is of the same form as that given by Berk and Schrieffer.[18]

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APPENDIX A: DENOMINATOR IN EQ. (4.5)

The denominator in Eq. (4.5) can be easily calculated. We write, from (2.33) and (2.34),

$$\frac{1}{\beta}\sum_{\omega}^{+\infty} F(0,\omega)=\frac{1}{\beta}\sum_{\omega}\int_{\epsilon_{\min}}^{\epsilon_{\max}} d\epsilon\,\frac{N(\epsilon)}{\epsilon^2+|\omega|^2}=J_1+J_2\,, \tag{A1}$$

where

$$J_1=\frac{1}{\beta}\sum_{\omega}\int_{\epsilon_{\min}}^{\epsilon_{\max}} d\epsilon\,\frac{N(0)}{\epsilon^2+|\omega|^2}\,, \tag{A2}$$

$$J_2=\frac{1}{\beta}\sum_{\omega}\int_{\epsilon_{\min}}^{\epsilon_{\max}} d\epsilon\,\frac{N(\epsilon)-N(0)}{\epsilon^2+|\omega|^2}\,, \tag{A3}$$

and $\omega_j=i\pi(2j+1)/\beta$.

In J_1, consider first contributions from $\epsilon>0$. These are

$$\begin{aligned}J_1^+&=\frac{N(0)}{\beta}\sum_{j=-\infty}^{\infty}\int_0^{\epsilon_{\max}}\frac{d\epsilon}{\epsilon^2+|\omega_j|^2}\\&=\frac{N(0)}{\beta}\sum_j\frac{1}{|\omega_j|}\tan^{-1}\frac{\epsilon_{\max}}{|\omega_j|}\\&=\frac{N(0)}{\beta}\lim_{J\to\infty}2\left\{\sum_{j=0}^{J}\frac{\pi}{2}\,\frac{1}{|\omega_j|}\right.\\&\qquad\left.+\sum_{j=0}^{J}\frac{1}{|\omega_j|}\left[\left(\tan^{-1}\frac{\epsilon_{\max}}{|\omega_j|}-\frac{\pi}{2}\right)\right]\right\}\\&=\frac{N(0)}{\beta}\lim_{J\to\infty}\left\{\beta\sum_0^J\frac{1}{(2j+1)}+\int_\sigma^J\frac{2\,dx}{(\pi/\beta)(2x+1)}\right.\\&\qquad\left.\times\left(\tan^{-1}\frac{\epsilon_{\max}}{(\pi/\beta)(2x+1)}-\frac{\pi}{2}\right)\right\}.\end{aligned} \tag{A4}$$

Now

$$\sum_0^J\frac{1}{2j+1}\to\tfrac{1}{2}\ln(2J+1)+\tfrac{1}{2}(\gamma+\ln 2), \tag{A5}$$

where $\gamma=0.57721$ is Euler's constant. In the integral in (A4) we introduce the variable $y=(2x+1)\pi/\beta\epsilon_{\max}$. This gives for the integral in question

$$\begin{aligned}Q&\equiv\int_0^J\frac{2\,dx}{(\pi/\beta)(2x+1)}\left(\tan^{-1}\frac{\epsilon_{\max}}{(\pi/\beta)(2x+1)}-\frac{\pi}{2}\right)\\&=\frac{\beta}{\pi}\int_0^{(2J+1)\pi/\beta\epsilon_{\max}}\frac{dy}{y}\left(\tan^{-1}\frac{1}{y}-\frac{\pi}{2}\right)\\&\to\frac{\beta}{\pi}\left\{\int_0^1\frac{dy}{y}\left(\tanh^{-1}\frac{1}{y}-\frac{\pi}{2}\right)\right.\\&\qquad\left.+\int_1^\infty\frac{dy}{y}\tanh^{-1}\frac{1}{y}+\int_1^{(2J+1)\pi/\beta\epsilon_{\max}}\frac{dy}{y}\left(-\frac{\pi}{2}\right)\right\}.\end{aligned} \tag{A6}$$

The first two integrals cancel each other, as may be seen by the substitution $y=1/z$ in the first, so that, as $J\to\infty$,

$$Q\to-(\beta/2)\,[\ln(2J+1)+\ln\pi-\ln\beta\epsilon_{\max}]. \tag{A7}$$

Substituting (A5) and (A7) into (A4) gives

$$J_1^+=[N(0)/2]\;[\ln(\beta\epsilon_{\max})+\eta], \tag{A8}$$

where

$$\eta=\gamma+\ln 2-\ln\pi=0.12563. \tag{A9}$$

Hence,

$$J_1=N(0)\;[\ln(\beta\epsilon_b)+\eta], \tag{A10}$$

where ϵ_b is an effective "half-width" of the band defined by

$$\ln\epsilon_b=\tfrac{1}{2}\,(\ln|\epsilon_{\max}|+\ln|\epsilon_{\min}|). \tag{A11}$$

In J_2, the sum over ω can be replaced by an integral, because of the factor $N(\epsilon)-N(0)$, which vanishes at $\epsilon=0$:

$$\sum_{j=-\infty}^{+\infty}\frac{1}{\epsilon^2+|\omega_j|^2}=\int_{-\infty}^{+\infty}\frac{dx}{\epsilon^2+[(\pi/\beta)(2x+1)]^2}=\frac{\beta}{2|\epsilon|}\,. \tag{A12}$$

Hence,

$$J_2=\int_{\epsilon_{\min}}^{\epsilon_{\max}} d\epsilon\,\frac{N(\epsilon)-N(0)}{2|\epsilon|}=N(0)\kappa, \tag{A13}$$

where κ is a dimensionless constant, depending on the band of interest, given by

$$\kappa=\int_{\epsilon_{\min}}^{\epsilon_{\max}}\left(\frac{N(\epsilon)}{N(0)}-1\right)\frac{1}{2|\epsilon|}\,d\epsilon. \tag{A14}$$

Finally, substituting (A10) and (A13) in (A1),

$$(1/\beta)\textstyle\sum_\omega F(0,\omega)=N(0)\ln(\alpha\beta\epsilon_b), \tag{A15}$$

where $N(0)$ is the density of states at the Fermi surface, α is a dimensionless positive constant of order unity given by

$$\ln\alpha=\eta+\kappa=0.12563+\kappa \tag{A16}$$

[see Eqs. (A9) and (A14)], and ϵ_b is an effective-band half-width [see Eq. (A11)].

APPENDIX B: EFFECT OF LONG-RANGE COULOMB INTERACTION ON T_c

For certain real metals which are narrow-band superconductors (e.g., metals at the end of the transition periods) the Coulomb interaction has a long-range part that reduces T_c. This part is due to strong exchange interactions between electron spins.[18-20] Its quantitative effect on T_c depends rather sensitively on both the electronic band structure and the exchange potential. For a qualitative understanding, from the site point of view, we adopt the following model for the exchange interaction:

$$I_{\text{spin}}(\vec{n}', \omega'; \vec{n}, \omega) = \begin{cases} I_s, & |\omega| \text{ and } |\omega'| \leq \omega_s \\ 0, & \text{otherwise.} \end{cases} \tag{B 1}$$

This approximation, with I_s being a constant and ω_s being a cutoff frequency which is a small fraction of the Fermi energy, is reasonable because of the long-wavelength low-frequency nature of I_{spin}. It means that the interaction is of infinite range, which is strictly true only in the magnetic state, and that it is retarded. In the latter respect it is similar to I_{ph}.

With (B 1), in addition to a short-range interaction, we may write the solution of Eq. (2. 27) as

$$\Gamma(\vec{n}_1, \omega) = \Gamma_I(\vec{n}, \omega) + \Gamma_{II}(\omega) \ , \tag{B 2}$$

where

$$\lim \Gamma_I(\vec{n}, \omega) = 0 \quad \text{as } \vec{n} \to \infty \ . \tag{B 3}$$

The quantity $\Gamma_{II}(\omega)$ can be eliminated from (2. 27). To this end we write $\Gamma_{II}(\omega)$ in the following form, implied by (B 1):

$$\Gamma_{II}(\omega) = \begin{cases} \Gamma_{II} & \text{for } |\omega| \leq \omega_s \\ 0 & \text{for } |\omega| > \omega_s \ , \end{cases} \tag{B 4}$$

and take in (2. 27) the limit $\vec{n} \to \infty$. This gives

$$\Gamma_{II} = -(1/\beta) \sum_{|\omega'| \leq \omega_s} \sum_{\vec{n}'} [\Gamma_I(\vec{n}', \omega') + \Gamma_{II}] \times F(\vec{n}', \omega') I_s \ . \tag{B 5}$$

Hence,

$$\Gamma_{II} = -\frac{I_s}{\beta} \sum_{|\omega| \leq \omega_s} \sum_{\vec{n}} \Gamma_I(\vec{n}, \omega) F(\vec{n}, \omega) \bigg/ \left(1 + \frac{I_s}{\beta} \sum_{|\omega| \leq \omega_s} \sum_{\vec{n}} F(\vec{n}, \omega)\right) \ . \tag{B 6}$$

Now we return to Eq. (2. 27) and substitute in it Eqs. (B 2) and (B 6). The result is

$$\Gamma_I(\vec{n}, \omega) = -\frac{1}{\beta} \sum_{\omega'} \sum_{\vec{n}'} K(\vec{n}', \omega'; \vec{n}, \omega) \times \left[\Gamma_I(\vec{n}', \omega') - H(|\omega'| - \omega_s) \frac{I_s}{\beta} \times \sum_{|\omega''| \leq \omega_s} \sum_{\vec{\mu}} \Gamma_I(\vec{\mu}, \omega'') F(\vec{\mu}, \omega'') \bigg/ \left(1 + \frac{I_s}{\beta} \sum_{|\omega''| \leq \omega_s} \sum_{\vec{\mu}} F(\vec{\mu}, \omega)\right)\right] \ . \tag{B 7}$$

Here

$$H(x) = \begin{cases} 1 & \text{for } x \leq 0 \\ 0 & \text{for } x > 0 \end{cases} \tag{B 8}$$

is the Heaviside unit step function. K in (B 7) contains only the short-range electron-electron interaction.

For simplicity, let us take $K \equiv I_{\text{ph}}$ and ignore the short-range Coulomb repulsion I_c. Furthermore, to determine T_c we introduce the contact model for I_{ph}, Eq. (3. 11). Then $\Gamma_I(0, \omega)$ has the form [cf. (4. 10)]

$$\Gamma_I(\omega) = \begin{cases} \Gamma_I & \text{for } |\omega| \leq \omega_0 \\ 0 & \text{for } |\omega| > \omega_0 \ , \end{cases} \tag{B 9}$$

and, according to (B 7), Γ_I is given by

$$\Gamma_I = \frac{I_{\text{ph}}}{\beta} \sum_{|\omega'| \leq \omega_0} F(0, \omega') \Gamma_I \left[1 - H(|\omega'| - \omega_s) \frac{I_s}{\beta} \times \sum_{|\omega''| \leq \omega_s} F(0, \omega'') \bigg/ \left(1 + \frac{I_s}{\beta} \sum_{|\omega''| \leq \omega_s} \sum_{\vec{\mu}} F(\vec{\mu}, \omega'')\right)\right] \ . \tag{B 10}$$

The denominator in (B 10) contains

$$\frac{1}{\beta} \sum_{|\omega| \leq \omega_s} \sum_{\vec{\mu}} F(\vec{\mu}, \omega) = \frac{1}{\beta} \sum_{|\omega| \leq \omega_s} \sum_{\vec{\mu}} \frac{1}{N} \sum_{\vec{k}} \frac{e^{i\vec{k} \cdot \vec{\mu}}}{|\omega|^2 + \epsilon^2(\vec{k})} = \frac{1}{\beta} \sum_{|\omega| \leq \omega_s} \frac{1}{|\omega|^2 + \epsilon^2(0)} = \frac{1}{\pi\epsilon(0)} \tan^{-1} \frac{\omega_s}{\epsilon(0)} \ . \tag{B 11}$$

Substituting (B 11) and the sum (A 15) in (B 10) and dividing by Γ_1 gives

$$1 = N(0) I_{\text{ph}} \ln(\alpha' \beta \omega_0) [1 - N(0) J_s \ln(\alpha' \beta \omega_s)] \ , \tag{B 12}$$

where

$$J_s = I_s \bigg/ \left(1 + \frac{1}{\pi} \frac{I_s}{\epsilon(0)} \tan^{-1} \frac{\omega_s}{\epsilon(0)}\right) \ , \tag{B 13}$$

and $\alpha' = 1.13$ [cf. (4. 13)]. Equation (B 12) may be rewritten in the form

$$\frac{1}{N(0) I_{\text{ph}}} = \ln \frac{1.13\, \omega_0}{k_B T_c} \times \left[1 - N(0) J_s \left(\ln \frac{\omega_s}{\omega_0} + \ln \frac{1.13\, \omega_0}{k_B T_c}\right)\right] \ . \tag{B 14}$$

This is a quadratic equation with the solution

$$\ln \frac{1.13\, \omega_0}{k_B T_c} = \frac{1}{2N(0) J_s} [1 - (1 - 4 J_s / I_{\text{ph}})^{1/2}] \ . \tag{B15}$$

A solution exists for

$$I_{\text{ph}} > 4 J_s \ . \tag{B 16}$$

For small J_s one gets

$$k_B T_c = 1.13\, \omega_0 \exp\left(-\frac{1}{N(0)(I_{\text{ph}} - J_s)}\right) , \quad \frac{J_s}{I_{\text{ph}}} \ll 1 . \tag{B 17}$$

This result is of the same form as the T_c equation given by Berk and Schrieffer.[18]

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$$G_{s's}(x', x) = -\langle T_\tau(\varphi_{s'}(x')\varphi_s^+(x))\rangle,$$

where T_τ is the Wick ordering operator and

$$\varphi_s^+(x) = e^{(H-\mu N)\tau}\varphi_s(\vec{r})e^{-(H-\mu N)\tau}$$

is the Heisenberg operator for the creation of a particle; H is the Hamiltonian, N is the number operator, and μ denotes the chemical potential. The angular bracket represents a thermal average over a grand canonical ensemble.

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$$G_{s's}(x', x) = \frac{1}{\beta}\sum_{j',=-\infty}^{+\infty} G_{s's}(\vec{r}', \omega_{j'};\ \vec{r}, \omega_j)\, e^{-i(\omega_j\tau - \omega_{j'}\tau')},$$

$$I_{s_1' s_2' s_1 s_2}(x_1', x_2', x_1, x_2) = \frac{1}{\beta^3}\sum_{j_1', j_1, j_2', j_2=-\infty}^{+\infty} I_{s_1' s_2' s_1 s_2}$$
$$\times(\vec{r}_1', \omega_{j_1'}; \vec{r}_2', \omega_{j_2'}; \vec{r}_1, \omega_{j_1}, \vec{r}_2, \omega_{j_2})$$
$$\times\exp[-i(\omega_{j_1}\tau_1 + \omega_{j_2}\tau_2 - \omega_{j_1'}\tau_1' - \omega_{j_2'}\tau_2')].$$

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Surface Density of Normal Metal in the Intermediate State of Superconducting Aluminum[†]

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Surface-impedance measurements have been made at 0.5 MHz on the intermediate state of aluminum and indicate an increased fraction of normal metal near the surface as compared with the bulk. This result confirms Landau's prediction of the surface structure in the intermediate state and suggests a similar interpretation for Pippard's early observation of the surface resistance of tin at 10 GHz. Surface-impedance techniques are thus seen to provide accurate information on domain broadening near the surface, and to corroborate the effective-field reduction there suggested qualitatively by bismuth-probe and magneto-optic methods.

The nonbranching Landau theory of the intermediate state[1] of an infinite parallel-sided slab of a type-I superconductor in a magnetic field H applied normal to the slab surface postulates a structure consisting of alternating laminar layers of normal and superconducting metal parallel to the field direction. The azimuthal orientation of the parallel-layer structure is arbitrary, but can be imagined to be set up, in practice, by a slight tilt of the applied field from the direction normal to the slab. The thicknesses a_N and a_S of the normal and superconducting domains give rise to a total repeat distance a whose scale depends on the surface energy $+\frac{1}{2}\mu_0 H_c^2 \Delta$ between the normal and superconduct-