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Localized description of superconductivity. II. Strong-coupling formulation

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A localized description of superconductivity in narrow-band metals, proposed by Appel and Kohn, is extended to the strong-coupling case. Equations similar, but not identical, to the Eliashberg equations are obtained. These equations are solved numerically and the results are represented by a semiphenomenological formula for T_c. A microscopic calculation of the electron-phonon coupling constant in the localized representation, based on measured phonon frequency-distribution curves and augmented-plane-wave band calculations, is described. Results for V, Nb, and Ta yield values of λ within a factor of 2 from the expected ones, without any adjustable parameter.

I. INTRODUCTION

Appel and Kohn have suggested in a recent paper[1] (hereafter referred to as AK) that the natural way to describe the Cooper pairing mechanism in transition metals with narrow *d* bands is by employing the Wannier or atomic-site representation rather than the Bloch representation. The former emphasizes the atomic nature of the tightly bound *d* electrons which are generally believed to be responsible for superconductivity in the transition metals.

The AK formulation begins with the homogeneous integral equation for the vertex part of a Cooper pair transformed to the site representation. In the case of a nondegenerate band this equation reads

$$\Gamma(\vec{n}, \omega) = -\frac{1}{\beta} \sum_{\vec{n}', \omega'} \Gamma(\vec{n}', \omega') \sum_{\vec{m}, \vec{m}'} G(\vec{m} + \vec{m}', \omega) \times G(\vec{m}', -\omega)\, I(\vec{n}' - \vec{m}, \vec{n}; \omega - \omega') , \quad (1.1)$$

where $\beta = 1/k_B T$, the frequency sum runs over the values $\omega' = (i\pi/\beta)(2n+1)$, and the Green's function is

$$G(\vec{m}, \omega) = \frac{1}{N} \sum_{\vec{p}} \frac{e^{i \vec{p} \cdot \vec{m}}}{\omega - \epsilon(\vec{p})}, \quad (1.2)$$

where $\epsilon(\vec{p})$ is the single-particle energy. Finally, the factor I in Eq. (1.1) is the contracted irreducible vertex defined by

$$I(\vec{n}', \vec{n}; \omega) = \frac{1}{N} \sum_{\vec{n}_1, \vec{n}_2} I(\vec{n}_2 + \vec{n}', \vec{n}_2; \vec{n}_1 + \vec{n}, \vec{n}_1; \omega) . \quad (1.3)$$

Each term on the right-hand side is the irreducible vertex, describing the transition of two electrons initially at sites $\vec{n}_2$, $\vec{n}_2 + \vec{n}'$, to sites $\vec{n}_1$, $\vec{n}_1 + \vec{n}$. The irreducible vertex, which is the main ingredient in the whole theory, consists of the phonon-exchange vertex and the Coulomb-interaction vertex. The basic approximation of AK is that of the "contact model," which neglects all terms with $\vec{n}, \vec{n}' \neq 0$ in Eq. (1.3). This means that the dominant contribution to the interaction vertex comes from processes in which the two electrons are initially at the same site and are scattered together to another site. In the contact model the set of equations in (1.1) reduces to a single equation, from which one can derive a BCS-like formula for the transition temperature.

In a previous paper[2] (hereafter referred to as I) we described a microscopic calculation along the lines proposed by AK for V, Nb, and Ta. Our main conclusions were that (a) the contact model is a satisfactory first approximation and (b) the Bloch formulation of the electron-phonon interaction vertex adopted in AK has to be modified in a way to allow the *d* functions to follow the ionic motions without appreciable deformation. Such a formulation of the phonon-electron interaction was developed by Mitra[3] and Barisic.[4] In the contact model the phonon-exchange vertex factorizes into a part which depends only on the phonon spectrum and one which is determined by the electron properties. The first part can be calculated from experimental phonon-frequency-distribution curves. The second part involves derivatives of matrix elements of the potentials between localized wave functions. These matrix elements were calculated in I, using the atomic wave functions and potentials given by the Herman-Skillman tables.[5] The atomic potentials were modified by a Thomas-Fermi screening factor to account for the screening by the free *s* electrons in the metal.

The formulation developed by AK does not take into account self-consistently the electron self-energy and is therefore a weak-coupling theory, while narrow-band superconductors are as a rule strong-coupling superconductors. In the present paper the ideas of the localized description proposed by AK are extended to the strong-coupling theory of superconductivity. We start from the self-energy equations and transform the Coulomb and phonon-exchange interactions, which appear in these equations to the atomic-site representation. We then adopt the contact approximation. Following the standard procedure one can subsequently derive equations which are similar, but not identical, to the Eliashberg equations. This is described in Sec. II. In Sec. III we show that T_c derived from these equations may be represented by a McMillan[6]-type formula, or even better by an expression proposed by Leavens.[7] The electron-phonon coupling constant, which appears in these expressions, is calculated in Sec. IV for V, Nb, and Ta. The difference between this calculation and the one described in I is that now the matrix elements in the phonon-exchange vertex are derived from the band structure obtained by an augmented-plane-wave (APW) calculation. The present calculation has no adjustable parameters.

II. STRONG-COUPLING EQUATIONS

The strong-coupling theory of superconductivity is most conveniently formulated in the Nambu formalism.[8] The starting point is the equation for the self-energy

$$\Sigma(\vec{p}, i\omega_n) = -\frac{1}{\beta}\sum_{\vec{p}',n'} \tau_3\, G(\vec{p}', i\omega_{n'})\, \tau_3 \times\left(\sum_{\lambda} |g_{\vec{p}\vec{p}',\lambda}|^2 D_\lambda(\vec{p}-\vec{p}', i\omega_n - i\omega_{n'}) + V_c(\vec{p}-\vec{p}')\right), \tag{2.1}$$

where τ_3 is the Pauli matrix and the Green's function G and the self-energy Σ are 2×2 matrices. The diagonal elements of these matrices represent the normal Green's function and self-energy, while the off-diagonal terms are the anomalous functions which do not vanish only in the superconducting state. The Green's function G is related to the self-energy through the equation

$$G^{-1}(\vec{p}, i\omega_n) = G_0^{-1}(\vec{p}, i\omega_n) - \Sigma(\vec{p}, i\omega_n)\ , \tag{2.2}$$

where the free-electron Green's function G_0 is

$$G_0(\vec{p}, i\omega_n) = [i\omega_n \underline{1} - \epsilon(\vec{p})\, \tau_3]^{-1}\ . \tag{2.3}$$

The self-energy is conveniently expanded in Pauli matrices

$$\Sigma(\vec{p}, \omega) = [1 - Z(\vec{p}, \omega)]\, \omega \underline{1} + \Phi(\vec{p}, \omega)\, \tau_1 + \chi(\vec{p}, \omega)\, \tau_3\ . \tag{2.4}$$

From the last three equations, one gets

$$G(\vec{p}, \omega) = \frac{\omega Z(\vec{p}, \omega)\, \underline{1} + \bar{\epsilon}(\vec{p}, \omega)\, \tau_3 + \Phi(\vec{p}, \omega)\, \tau_1}{\omega^2 Z^2(\vec{p}, \omega) - \bar{\epsilon}^2(\vec{p}, \omega) - \Phi^2(\vec{p}, \omega)}\ , \tag{2.5}$$

where

$$\bar{\epsilon}(\vec{p}, \omega) = \epsilon(\vec{p}) + \chi(\vec{p}, \omega)\ .$$

The expression in the brackets of Eq. (2.1) represents the interaction, which consists of the phonon part and the Coulomb part. To make contact with previous work on the localized description of superconductivity, we note that this expression may be replaced by the irreducible electron-electron interaction vertex $I(\vec{p}, \vec{p}'; \vec{p}', \vec{p}; i\omega_n - i\omega_{n'})$, as may be seen from Fig. 1. We then transform this interaction vertex from the momentum representation with eigenstates $|\vec{p}\rangle$ to the Wannier (atomic-site) representation with eigenstates $|\vec{n}\rangle$:

$$I(\vec{p}, \vec{p}'; \vec{p}', \vec{p}; \omega) = \frac{1}{N^2} \sum_{\substack{\vec{n}_1', \vec{n}_2' \\ \vec{n}_1, \vec{n}_2}} e^{-i\vec{p}\cdot(\vec{n}_1' - \vec{n}_2)}\, e^{-i\vec{p}'\cdot(\vec{n}_2' - \vec{n}_1)} \times I(\vec{n}_1', \vec{n}_2'; \vec{n}_1, \vec{n}_2; \omega)\ . \tag{2.6}$$

Let us define $\vec{n} = \vec{n}_1 - \vec{n}_2$, $\vec{n}' = \vec{n}_1' - \vec{n}_2'$, and $\vec{m} = \vec{n}_2' - \vec{n}_2$. In terms of the newly defined site indices, one easily gets

$$I(\vec{p}, \vec{p}'; \vec{p}', \vec{p}; \omega) = \frac{1}{N^2} \sum_{\vec{m}, \vec{n}, \vec{n}'} e^{-i\vec{p}\cdot(\vec{m} + \vec{n}')}\, e^{-i\vec{p}'\cdot(\vec{m} - \vec{n})}\, I(\vec{n}', \vec{n}; \omega)\ , \tag{2.7}$$

where the factor I on the right-hand side is now the contracted-interaction vertex, defined in Eq. (1.3). This interaction vertex contains all the processes in which a pair of electrons on two sites separated by the lattice vector $\vec{n}'$ is scattered to two sites separated by the lattice vector $\vec{n}$. At this point we introduce the contact approximation, assuming that the dominant contribution comes from processes for which two electrons on one

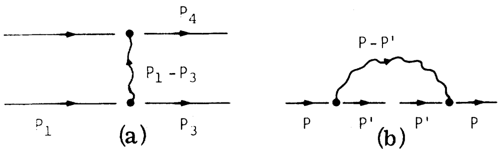

FIG. 1. Connection between the self-energy and the irreducible vertex part: (a) phonon-exchange vertex $I^{\mathrm{ph}}(\vec{p}_1, \vec{p}_2, \vec{p}_3, \vec{p}_4, \omega)$; (b) phonon-exchange self-energy $\Sigma^{\mathrm{ph}}(\vec{p}, \omega)$.

site scatter together to another site:

$$I(\vec{p},\vec{p}\,';\vec{p}\,',\vec{p};\omega)=\frac{1}{N}\sum_{\vec{m}} e^{-i\vec{p}\cdot\vec{m}}\,e^{-i\vec{p}\,'\cdot\vec{m}}\,I(\omega)\ , \tag{2.8}$$

where $I(\omega)\equiv I(0,0;\omega)$.

The function $I(\omega)$ was discussed extensively in AK and I. It is given by

$$I(\omega)=U+J^2\sum_{\vec{m}}\sum_{\alpha,\beta}L_{\alpha\beta}(\vec{m},\omega)\ , \tag{2.9}$$

where U is the Coulomb interaction, $L_{\alpha\beta}$ is essentially the phonon Green's function in the lattice-site representation, and J^2 is a combination of certain matrix elements. Let us now define these factors in greater detail. The Coulomb interaction in the localized representation is

$$U=\sum_{\vec{n}}\int\phi^*(\vec{r}-\vec{n})\,\phi^*(\vec{r}\,'-\vec{n})\,V(|\vec{r}-\vec{r}\,'|)\times\phi(\vec{r})\,\phi(\vec{r}\,')\,d^3r\,d^3r'\ , \tag{2.10}$$

where $\phi(\vec{r}-\vec{n})$ is the Wannier function localized at site $\vec{n}$. In practice $\phi(\vec{r}-\vec{n})$ will be an atomic wave function. The phonon Green's function is

$$L_{\alpha\beta}(\vec{m},\omega)=\frac{1}{N}\sum_{\vec{q},\lambda}\frac{\hbar e_{\lambda\alpha}(\vec{q})\,e_{\lambda\beta}(\vec{q})}{2M\omega_\lambda(\vec{q})}\,D_\lambda(\vec{q},\omega)\,e^{-i\vec{q}\cdot\vec{m}}\ , \tag{2.11}$$

where $e_{\lambda\alpha}(\vec{q})$ is the α Cartesian component of the unit polarization vector describing the phonon $|\vec{q},\lambda\rangle$. For a weak q dependence of ω the $\vec{m}=0$ term makes the largest contribution [for an Einstein phonon $L(\vec{m},\omega)\propto\delta_{\vec{m},0}$] and we shall keep only this term. In a cubic crystal $L_{\alpha\beta}$ is diagonal in α and β and independent of α; so

$$I(\omega)=U+J^2L(\omega)\ , \tag{2.12}$$

with

$$L(\omega)=\frac{1}{M}\int\frac{F(\nu)\,d\nu}{\omega^2-\nu^2}\ , \tag{2.13}$$

where $F(\nu)$ is the normalized phonon-frequency distribution and M is the ionic mass. Finally, it is shown in AK that for a nondegenerate band, neglecting three-center integrals,

$$J^2=\sum_{\vec{n},\alpha}\left(|\langle\vec{n}|\nabla_\alpha V_0|\vec{n}\rangle|^2+2|\langle\vec{n}|\nabla_\alpha V_0|\vec{0}\rangle|^2\right)\ , \tag{2.14}$$

where V_0 is the potential around the atom at the origin. This expression was derived in the usual tight-binding formulation of the electron-phonon coupling, in which the Bloch functions are linear combinations of atomic orbitals around the fixed lattice points. It is shown in I that, starting from atomic orbitals centered around the moving ions, one gets

$$J^2=\sum_{\vec{n},\alpha}\left(|\langle\vec{n}|\nabla_\alpha V_0|\vec{n}\rangle|^2+2|\nabla_{\vec{n},\alpha}\langle\vec{0}|V_0|\vec{n}\rangle|^2\right)\ . \tag{2.15}$$

Let us now replace the expression in the brackets in Eq. (2.1) by $I(\vec{p},\vec{p}\,';\vec{p}\,',\vec{p};i\omega_n-i\omega_{n'})$ given by Eqs. (2.8) and (2.12) and perform in a standard way the frequency sum over n'. We obtain

$$\Sigma(\vec{p},i\omega_n)=-\frac{1}{\pi N}\sum_{\vec{m}}e^{-i\vec{p}\cdot\vec{m}}\sum_{\vec{p}\,'}e^{-i\vec{p}\,'\cdot\vec{m}}\left\{\int_{-\infty}^{\infty}d\omega'\,\mathrm{Im}[\tau_3G(\vec{p}\,',\omega')\tau_3]\left[\frac{J^2}{M}\int\frac{d\nu\,F(\nu)}{2\nu}\left(\frac{f(-\omega')}{i\omega_n-\omega'-\nu}+\frac{f(\omega')}{i\omega_n-\omega'+\nu}\right)+\tfrac{1}{2}U\tanh\frac{\beta\omega'}{2}\right]+\frac{J^2}{M}\int\frac{d\nu\,F(\nu)\,N(\nu)}{2\nu}\,\tau_3[G(\vec{p}\,',i\omega_n+\nu)+G(\vec{p}\,',i\omega_n-\nu)]\,\tau_3\right\}\ , \tag{2.16}$$

where $f(\omega')$ and $N(\nu)$ are the Fermi-Dirac and Bose-Einstein distribution functions. It is easy to proceed from here and obtain a one-dimensional integral equation in the usual way. To do this we neglect the last term with the Bose factor, as is usually done when no soft phonons are involved. (This is done in order to avoid clumsiness and is by no means inevitable.) We consider first the self-energy due to phonon exchange only,

$$\Sigma^{\text{ph}}(\vec{p},\omega)=-\frac{1}{\pi N}\sum_{\vec{m}}e^{-i\vec{p}\cdot\vec{m}}\sum_{\vec{p}\,'}e^{-i\vec{p}\,'\cdot\vec{m}}\times\int_{-\infty}^{\infty}d\omega'\,\mathrm{Im}[\tau_3\,G(\vec{p}\,',\omega')\,\tau_3]\times\frac{J^2}{M}\int_0^{\omega_0}\frac{d\nu\,F(\nu)}{2\nu}\left(\frac{f(-\omega')}{\omega-\omega'-\nu+i\delta}+\frac{f(\omega')}{\omega-\omega'+\nu+i\delta}\right)\ , \tag{2.17}$$

where we have replaced $i\omega_n$ by $\omega + i\delta$. The main contribution to the integral comes from momenta $\vec{p}'$ such that $|\epsilon_{p'}| \sim \omega_D$; so we may replace $|\vec{p}'|$ by p_F. For an isotropic superconductor we then obtain

$$\frac{1}{N}\sum_{\vec{p}'} e^{-i\vec{p}'\cdot\vec{m}}\,\mathrm{Im}[\tau_3\, G(\vec{p}', \omega')\,\tau_3]$$

$$= \frac{\sin p_F m}{p_F m}\, N(0)\,\pi \int d\epsilon\, \mathrm{Im}[\tau_3\, G(\epsilon, \omega')\,\tau_3] \;, \qquad (2.18)$$

where we used the relations $m\, d\epsilon(p') = p'\, dp'$ and $N(0) = m p_F/2\pi^2$. Extending the integration over ϵ from $-\infty$ to $+\infty$ and using the result

$$\int_{-\infty}^{\infty} d\epsilon(p')\,\tau_3\, G(p', \omega')\,\tau_3$$

$$= -i\pi\, \frac{\omega' Z(\omega')\underline{1} - \Phi(\omega')\,\tau_1}{[\omega'^2 Z^2(\omega') - \Phi^2(\omega')]^{1/2}} \;, \qquad (2.19)$$

and the symmetry properties of the functions Φ and Z, we find for the spherically averaged self-energy

$$\Sigma^{\mathrm{ph}}(\omega) = \frac{1}{4\pi} \int d\Omega_p\, \Sigma^{\mathrm{ph}}(\vec{p}, \omega) \;,$$

at $|\vec{p}| = p_F$,

$$\Sigma^{\mathrm{ph}}(\omega) = \int_0^{\infty} d\omega'\, \mathrm{Re}\left(\frac{\omega' Z(\omega')\underline{1} + \Phi(\omega')\,\tau_1}{[\omega'^2 Z^2(\omega') - \Phi^2(\omega')]^{1/2}}\right)$$
$$\times [K_{\pm}^{\mathrm{ph}}(\omega, \omega') f(-\omega') \mp K_{\pm}^{\mathrm{ph}}(\omega, -\omega') f(\omega')] \;, \qquad (2.20)$$

where

$$K_{\pm}(\omega, \omega') = N(0) \sum_m \left(\frac{\sin p_F m}{p_F m}\right)^2 \frac{J^2}{M} \int \frac{d\nu\, F(\nu)}{2\nu}$$
$$\times \left(\frac{1}{\omega' + \omega + \nu + i\delta} \pm \frac{1}{\omega' - \omega + \nu - i\delta}\right) . \qquad (2.21)$$

In the last two equations the upper sign is used with τ_1 and the lower with the unit matrix.

Finally, let us include the Coulomb part of the interaction. The integration over ω' may be cut off at ω_0 provided that U is replaced by the pseudo-interaction[8]

$$\tilde{U} = \frac{U}{1 + N(0)\, U \ln(\epsilon_F/\omega_0)} \;. \qquad (2.22)$$

Going through the same procedure as before one finds that the Coulomb contribution to the spherically averaged anomalous self-energy is

$$\Phi_c(\omega) = -N(0) \sum_m \left(\frac{\sin p_F m}{p_F m}\right)^2 \tilde{U}$$
$$\times \int_0^{\omega_0} \mathrm{Re}\left(\frac{\Phi(\omega')}{[Z^2(\omega')\,\omega'^2 - \Phi^2(\omega')]^{1/2}}\right)$$
$$\times \tanh\left(\frac{\beta\omega'}{2}\right) \;, \qquad (2.23)$$

and that there is no similar contribution to the normalization function Z. The factor $\sum_m [\sin p_F m / p_F m]^2$ is of order unity, since the dominant term is that with $m = 0$. In what follows we shall omit this factor, approximating it by 1.

We next define the gap function $\Delta(\omega) = \Phi(\omega)/Z(\omega)$ and obtain from Eqs. (2.4), (2.5), (2.20), and (2.23) the two coupled equations for Δ and Z:

$$\Delta(\omega) = \frac{N(0)\, J^2/M}{Z(\omega)} \int_0^{\infty} d\omega'\, \mathrm{Re}\, \frac{\Delta'}{(\omega'^2 - \Delta'^2)^{1/2}} \int_0^{\omega_0} \frac{d\nu\, F(\nu)}{2\nu} \{f(-\omega')[(\omega' + \omega + \nu)^{-1} + (\omega' - \omega + \nu)^{-1}]$$
$$- f(\omega')[(-\omega' + \omega + \nu)^{-1} + (-\omega' - \omega + \nu)^{-1}]\} - \frac{N(0)\,\tilde{U}}{Z(\omega)} \int_0^{\omega_0} \mathrm{Re}\, \frac{\Delta'}{(\omega'^2 - \Delta'^2)^{1/2}} [1 - 2f(\omega')] \;, \qquad (2.24)$$

$$\xi(\omega) = [1 - Z(\omega)]\,\omega = N(0)\, \frac{J^2}{M} \int_0^{\infty} d\omega'\, \mathrm{Re}\, \frac{\omega'}{(\omega'^2 - \Delta'^2)^{1/2}} \int_0^{\omega_0} \frac{d\nu\, F(\nu)}{2\nu}$$
$$\times \{f(-\omega')[(\omega' + \omega + \nu)^{-1} - (\omega' - \omega + \nu)^{-1}] + f(\omega')[(-\omega' + \omega + \nu)^{-1} - (-\omega' - \omega + \nu)^{-1}]\} \;. \qquad (2.25)$$

These equations are very similar to those solved by McMillan.[6] They are further discussed in Sec. III.

III. TRANSITION TEMPERATURE

Following McMillan, one can solve Eqs. (2.24) and (2.25) by starting from the trial function

$$\Delta(\omega) = \begin{cases} \Delta_0, & 0 < \omega < \omega_0 \\ 0, & \omega_0 < \omega \end{cases}$$

and get

$$T_c = \langle \omega \rangle \exp\left(\frac{1 + \lambda}{\lambda - \mu^* + \lambda\mu^*(\langle \omega \rangle/\omega_0)}\right), \qquad (3.1)$$

where

$$\lambda = \frac{N(0)J^2}{M}\int \frac{F(\nu)\,d\nu}{\nu^2}\;, \tag{3.2}$$

$$\mu^* = N(0)\,\tilde{U}\,, \tag{3.3}$$

$$\langle\,\omega\,\rangle = \int \frac{F(\nu)\,d\nu}{\nu} \bigg/ \int \frac{F(\nu)\,d\nu}{\nu^2}\;. \tag{3.4}$$

McMillan obtains a similar expression for T_c, however, with a somewhat different expression of the constants λ and $\langle\,\omega\,\rangle$:

$$\lambda = 2\int \frac{\alpha^2(\nu)\,F(\nu)\,d\nu}{\nu}\;, \tag{3.5}$$

$$\langle\,\omega\,\rangle = \int \alpha^2(\nu)\,F(\nu)\,d\nu \bigg/ \int \frac{\alpha^2(\nu)\,F(\nu)\,d\nu}{\nu}\;. \tag{3.6}$$

The function $\alpha^2(\nu)\,F(\nu)$ is usually derived from tunneling experiments.[9] A microscopic calculation of this quantity would involve a complicated Fermi-surface averaging of matrix elements of the crystal potential gradient between electron Bloch functions. From this point of view the expression in Eq. (3.2) looks very appealing. The calculation of J^2 involves matrix elements between atomic orbitals and avoids the Fermi-surface averaging. The frequency integrals in Eqs. (3.2) and (3.4) contain the phonon-distribution function, which is more elementary than the quantity $\alpha^2(\nu)\,F(\nu)$.

TABLE I. Values of the coupling constant λ for the Nb phonon spectrum for various values of the Coulomb term μ^* and transition temperature T_c (in °K), appearing in McMillan's table.

$T_c \diagdown \mu^*$	0	0.088	0.149	0.157	0.245
20	1.34	1.79	2.15		
15	1.05	1.41	1.69		2.19
10	0.78	1.08	1.29		1.67
5	0.54	0.76		0.94	

We have solved Eqs. (2.24) and (2.25) numerically using the experimentally measured phonon-frequency distribution curves for V,[10] Nb,[11] and Ta.[12] Unlike McMillan, we have not eliminated the phonons below 100 °K, because in our equations we have the factor $F(\nu)/2\nu$ instead of $F(\nu)$ in McMillan equations, which weighs more strongly the low-frequency region of the phonon spectrum. The values of λ as a function of T_c and μ^* for the Nb phonon spectrum are listed in Table I. Compared with the corresponding values of λ given by McMillan for given T_c and μ^*, our value of λ is always larger than that of McMillan. Similar results were obtained for Ta (which has a similar phonon spectrum), while somewhat smaller numbers results from the phonon spectrum of V. These results may be parametrized by an expression of the form

$$T_c = a\langle\,\omega\,\rangle\exp\left(\frac{-b(1+\lambda)}{\lambda - \mu^*(1+c\lambda)}\right)\;. \tag{3.7}$$

However, we find that different values of the parameters a, b, c are required to fit the numerical results for Nb, V, and Ta. For comparison we give here the resulting formula for Nb, which is the analog of McMillan's formula:

$$T_c = 1.35\langle\,\omega\,\rangle\exp\left(\frac{-1.31(1+\lambda)}{\lambda - \mu^*(1+0.56\lambda)}\right).$$

A more uniform fit is obtained with an expression of the form suggested by Leavens,[7]

$$T_c = a\omega_0\exp\left(\frac{-b\,[1+\lambda+\bar{\lambda}(T_c)]}{\lambda - c\mu^*}\right)\;, \tag{3.8}$$

where, in our case,

$$\bar{\lambda}(T_c) = N(0)\,\frac{J^2}{M}\int\frac{d\nu\,F(\nu)}{\nu^2}\ln\frac{\omega_0+\nu}{T_c/1.134+\nu}\;. \tag{3.9}$$

The ratio $\bar{\lambda}(T_c)/\lambda$ may be computed directly for a given phonon spectrum. In Fig. 2, $\ln(\omega_0/T_c)$ is plotted for $\mu^*=0$ as a function of $[1+\lambda+\bar{\lambda}(T_c)]/\lambda$, with λ and $\bar{\lambda}(T_c)/\lambda$ computed for V (circles), Nb (dots), and Ta (triangles). All the points fall approximately on a straight line from which we find $a = 1.78$, $b = 1.13$. To get the value of c we plot the right-hand side of the equation,

$$c\mu^* = \lambda - \frac{b[1+\lambda+\bar{\lambda}(T_c)]}{\ln(a\omega_0/T_c)} \tag{3.10}$$

as a function of μ^*. The 42 points we used for the three elements under consideration fall quite nicely on a straight line through the origin with a slope $c = 1.30$. Hence, we find that the transition temperature determined by Eqs. (2.24) and (2.25) is fairly accurately described by the formula

$$T_c = 1.78\,\omega_0\exp\left(\frac{-1.13\,[1+\lambda+\bar{\lambda}(T_c)]}{\lambda - 1.30\mu^*}\right)\;. \tag{3.11}$$

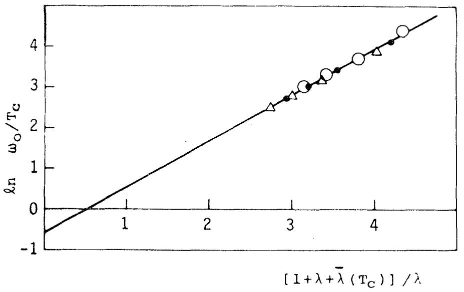

FIG. 2. Plot of $\ln(\omega_0/T_c)$ vs $[1+\lambda+\bar{\lambda}(T_c)]/\lambda$ which yields the values $a = 1.78$, $b = 1.13$ appearing in Eq. (3.11).

This expression fits the results for such different phonon spectra as of Ta (two narrow peaks and $\omega_0 = 245\,^\circ\mathrm{K}$) and V (a broad maximum and $\omega_0 = 410\,^\circ\mathrm{K}$).

IV. CALCULATION OF COUPLING CONSTANT

In the present section we describe a microscopic calculation of the constant λ [Eq. (3.2)] for V, Nb, and Ta. The inverse second moment of $F(\nu)$ may be obtained from measured phonon-frequency-distribution curves, as was done in our previous paper (I). The main problem lies in computing the factor J^2. We assume again (as was done in I) that the d electrons occupy the threefold-degenerate Γ'_{25} band in a cubic crystal. It was shown in I that in this case

$$J^2 = \tfrac{1}{3}(J_{11}^2 + 2J_{12}^2) , \qquad (4.1)$$

where

$$J_{1i}^2 = \sum_{\vec{n},\alpha} \left[2\,|\nabla_{\vec{n},\alpha} J_{\vec{n}}(1,i)|^2 + |\nabla_{\vec{n},\alpha} K_{\vec{n}}(1,i)|^2 \right] \qquad (i = 1, 2) , \quad (4.2)$$

where

$$\begin{aligned} J_{\vec{n}}(1,i) &= \int \phi_1^*(\vec{r})\, V(\vec{r})\, \phi_i(\vec{r}-\vec{n})\, d\vec{r} , \\ K_{\vec{n}}(1,i) &= \int \phi_1^*(\vec{r}-\vec{n})\, V(\vec{r})\, \phi_i(\vec{r}-\vec{n})\, d\vec{r} . \end{aligned} \qquad (4.3)$$

The function $\phi_i(\vec{r}-\vec{n})$ is the atomic orbital centered at the lattice point $\vec{n}$, and the indices 1, 2 refer to the d subbands,

$$\phi_\delta(\vec{r}) \propto xyf(r), \quad \phi_\pi(\vec{r}) \propto xzf(r) ,$$

respectively. The indices of the gradient symbol are the differentiation variable ($\vec{n}$) and the Cartesian component of the gradient vector (α). The derivation of Eq. (4.2) rests on the assumption that the d electrons follow adiabatically the motion of the ions. It was argued extensively by Barisic[4] and in I that this is the appropriate formulation of the electron-phonon interaction in narrow-band metals.

The crystal structure under consideration is bcc; so the nearest neighbors are not located along the crystal symmetry axes. It is therefore convenient to use the Koster-Slater[13] method and express the integrals in Eqs. (4.3) in terms of similar integrals in which the two lattice points involved are on the z axis. The J (and K) integrals in Eq. (4.3) may be expressed as linear combinations of the three integrals $\bar{J}_\rho(\sigma,\sigma)$, $\bar{J}_\rho(\delta,\delta)$, and $\bar{J}_\rho(\pi,\pi)$ [or $\bar{K}_\rho(\sigma,\sigma)$, $\bar{K}_\rho(\delta,\delta)$, and $\bar{K}_\rho(\pi,\pi)$] in the rotated coordinate system, which otherwise have the same form as in Eq. (4.3). The index ρ now represents the distance between the two lattice points, and σ denotes the atomic orbital

$$\phi_\sigma \propto (3z^2 - r^2) f(r) .$$

The $\bar{J}_\rho$ and $\bar{K}_\rho$ integrals and their derivatives were computed numerically in I with the radial wave functions taken from the Herman-Skillman tables.[5] The potentials were the Herman-Skillman potentials multiplied by the Thomas-Fermi screening factor $e^{-\kappa r}$ to account for the screening of the atomic potentials by the s electrons in the crystal. The screening length κ^{-1} was treated as an adjustable parameter. In the present paper we describe a different procedure. The essence of the present approach is a derivation of the $\bar{J}_\rho$ (and possibly $\bar{K}_\rho$) integrals from some given band structure. We shall demonstrate how this is done for the two-center integrals $\bar{J}_\rho$ using the results of APW band calculations. The procedure is quite straightforward. One constructs the tight-binding Hamiltonian matrix for a general crystal momentum $\vec{k}$. This is a 6×6 matrix in view of the five d functions and one s function. Diagonalizing this matrix one obtains the energy levels as a linear combination of the transfer integrals $\bar{J}_\rho$ and the crystal-field integrals (or degenerate three-center integrals) $\bar{K}_\rho$. The calculation is simple at certain symmetry points in the Brillouin zone when the Hamiltonian matrix is reducible. We shall now skip the details of constructing and diagonalizing this matrix and simply write down the energy levels at the symmetry points Γ (0, 0, 0), H (0, 0, π), and N (0, $\frac{1}{2}\pi$, $\frac{1}{2}\pi$). These points were chosen because the corresponding energy levels contain combinations of the three integrals $\bar{J}_\rho(\delta,\delta)$, $\bar{J}_\rho(\pi,\pi)$, and $\bar{J}_\rho(\sigma,\sigma)$. Keeping terms up to second nearest neighbors, we find

$$\begin{aligned} \Gamma'_{25} &= d_0 + a + 4\bar{J}_{\rho_2}(\pi,\pi) + 2\bar{J}_{\rho_2}(\delta,\delta) , \\ \Gamma_{12} &= d_0 + c + 3\bar{J}_{\rho_2}(\sigma,\sigma) + 3\bar{J}_{\rho_2}(\delta,\delta) , \\ H'_{25} &= d_0 - a + 4\bar{J}_{\rho_2}(\pi,\pi) + 2\bar{J}_{\rho_2}(\delta,\delta) , \\ H_{12} &= d_0 - c + 3\bar{J}_{\rho_2}(\sigma,\sigma) + 3\bar{J}_{\rho_2}(\delta,\delta) , \\ N_3 &= d_0 + b - 2\bar{J}_{\rho_2}(\delta,\delta) , \\ N_2 &= d_0 - b - 2\bar{J}_{\rho_2}(\delta,\delta) , \end{aligned} \qquad (4.4)$$

where

$$\begin{aligned} a &= \tfrac{8}{3}\bar{J}_{\rho_1}(\sigma,\sigma) + \tfrac{16}{9}\bar{J}_{\rho_1}(\pi,\pi) + \tfrac{32}{9}\bar{J}_{\rho_1}(\delta,\delta) , \\ b &= -\tfrac{8}{3}\bar{J}_{\rho_1}(\sigma,\sigma) + \tfrac{8}{9}\bar{J}_{\rho_1}(\pi,\pi) + \tfrac{16}{9}\bar{J}_{\rho_1}(\delta,\delta) , \\ c &= \tfrac{16}{3}\bar{J}_{\rho_1}(\pi,\pi) + \tfrac{8}{3}\bar{J}_{\rho_1}(\delta,\delta) . \end{aligned} \qquad (4.5)$$

The index ρ_1 (ρ_2) denotes the distance to the first (second) nearest neighbor. We have neglected the possible small difference between the crystal-field integrals in the π and σ states as is also done by Koster-Slater.[13] These integrals appear only in the diagonal and are absorbed in the constant d_0, and their values cannot be obtained in this way. The identification of the computed energy levels at the various symmetry points is not difficult but should, nevertheless, be done with care. Once this is done one can calculate from Eqs. (4.4) and (4.5) the $\bar{J}$ integrals for the first and second nearest neighbors.

The next step is to evaluate the derivatives of these integrals. This may be done analytically using the expressions for the tight-binding transfer integrals proposed by Ashkenazi and Weger.[14] Expanding the asymptotic form of the atomic orbitals,

$$\phi_i(\vec{r}-\vec{n}) \propto A e^{-Q|\vec{r}-\vec{n}|}/|\vec{r}-\vec{n}| ,$$

these authors get

$$\begin{aligned} \bar{J}_\rho(\sigma,\sigma) &= (B/\rho^3)\, e^{-Q\rho}[2+Q\rho+\tfrac{1}{3}(Q\rho)^2] , \\ \bar{J}_\rho(\delta,\delta) &= (B/\rho^3)\, e^{-Q\rho}, \\ \bar{J}_\rho(\pi,\pi) &= -(B/\rho^3)\, e^{-Q\rho}(2+Q\rho) , \end{aligned} \tag{4.6}$$

where B is a certain integral over the radial wave functions and serves here, together with Q, as an adjustable parameter. Using the relation between the J and $\bar{J}$ integrals[13] for the nearest neighbor $\vec{\rho}=\frac{1}{2}(a,a,a)$ and Eqs. (4.6) to obtain the relevant derivatives, one finds

$$\begin{aligned} \frac{\partial}{\partial\rho_y} J(\delta,\pi) = \frac{\partial}{\partial\rho_z} J(\delta,\delta) &= \frac{\partial}{\partial\rho_z} J(\delta,\pi) \\ &= A[14+8(Q\rho)+2(Q\rho)^2+\tfrac{1}{3}(Q\rho)^3] , \\ \frac{\partial}{\partial\rho_x} J(\delta,\delta) = \frac{\partial}{\partial\rho_y} J(\delta,\delta) &= A[2+\tfrac{1}{3}(Q\rho)^3] , \\ \frac{\partial}{\partial\rho_x} J(\delta,\pi) &= A[-10-2(Q\rho)+(Q\rho)^2+\tfrac{1}{3}(Q\rho)^3] , \end{aligned} \tag{4.7}$$

where $A=-(\sqrt{3}\,B/9\rho^4)\,e^{-Q\rho}$. The parameters B, Q may be obtained, using Eqs. (4.6), with the integrals $\bar{J}_\rho$ derived from the APW band structure using Eqs. (4.4) and (4.5). The derivatives in Eq. (4.7) are then computed and substituted into Eq. (4.2) to obtain J^2. In order to check this procedure we calculated J^2 first directly by differentiating the $\bar{J}$'s defined in Eq. (4.3) with the wave functions and potential of Herman and Skillman,[5] and compared the results to those obtained by solving Eq. (4.6) with the same values of $\bar{J}$ and substituting into Eq. (4.7). The agreement was excellent for V and Ta, while for Nb we got a deviation of 20% in J^2. Thus we conclude that having the transfer integrals from any reliable source we may get J^2 within an accuracy of about 20%.

To complete the calculation of λ, we still need the density of states at the Fermi energy, $N(0)$. The later may be obtained from the measured heat-capacity constant γ, which is proportional to the "band-structure" density of states which appears in Eq. (3.2) times the electron-phonon enhancement factor[6] $(1+\lambda)$:

$$N(0) = 3\gamma/2\pi^2 k_B^2(1+\lambda) . \tag{4.8}$$

Together with the equation for

$$\lambda = [N(0)J^2/M]\,\langle 1/\nu^2\rangle , \tag{4.9}$$

this yields two coupled equations for $N(0)$ and λ.

The whole procedure described above was performed for Nb, V, and Ta. The APW band-structure calculations are described in Refs. 15 (for V) and 16 (for Nb and Ta). The measured phonon-distribution curves are given in Refs. 10 (for V), 11 (for Nb), and 12 (for Ta), and the heat-capacity constant γ is given in Ref. 17. The results are listed in Table II. The values of λ obtained by this procedure should be compared with the values of λ_c which yield the experimental values of T_c in Eqs. (2.24), (2.25), or in the semiphenomenological formula (3.11) with $\mu^*=0.15$. These values of λ_c are as a rule larger than those obtained by McMillan (the later are listed for comparison) because of the inclusion of phonons up to 100 °K and the fact that the replacement of $F(\nu)$ by $F(\nu)/2\nu$ attributes more weight to the lower modes.

One should keep in mind that we have not included in our calculations the degenerate three-center integrals K. Although these integrals are neglected in the treatment of Barisic[4] and Mitra,[3] we have argued previously that they are of the same order of magnitude as the two-center transfer integrals. Taking into account these integrals would increase J^2 additively; however, their effect on λ would be smaller because they would further reduce $N(0)$ through the renormalization in Eq. (4.8). It is interesting to note that such a simple (in principle) procedure without a single adjustable parameter yields values of λ which differ from the expected ones (λ_c) by less than a factor of 2.

TABLE II. Experimental data and coupling constant λ obtained in Sec. IV, compared with λ_c, the expected value from the solution described in Sec. III.

	V	Nb	Ta
T_c	5.30	9.22	4.48
$\gamma\left(\frac{mJ}{\text{mole °K}}\right)$	9.04	7.66	5.84
J^2 (10^{-2}a.u.)	0.59	2.14	2.96
$\langle\nu^{-2}\rangle$ (10^{-5} °K^{-2})	2.22	3.79	4.85
$N(0)$ (eV atom)$^{-1}$	0.99	0.57	0.50
λ (present calc)	0.94	1.83	1.47
λ_c	0.79	1.29	0.92
λ (McMillan)	0.60	0.82	0.65

V. SUMMARY

In the first part of this paper we have modified the strong-coupling equations of superconductivity in a way which emphasizes the atomic nature of the d electrons in a narrow-band metal. The starting point is the ordinary self-energy equation in which the electron-electron interaction vertex is expressed in the atomic-site representation and then simplified greatly by the use of the "contact model." This approximation was discussed and justified in our previous paper (I).

In the localized description there is a decoupling of the phonon-interaction vertex into a part which depends only on the phonon spectrum and one which involves electron matrix elements. As a result of this, the phonon spectrum $F(\nu)$ appears in our final equations in comparison with the function $\alpha^2(\nu)F(\nu)$ in the ordinary strong-coupling equations. Although it is easy to obtain this function from tunneling experiments, its theoretical derivation requires complicated averages over the Fermi surface, which is avoided in the present formulation. Actually, the kernel in our equations contains $F(\nu)/2\nu$, which attributes more weight to the low-frequency phonons in accordance with what one generally finds[18] on comparing $\alpha^2(\nu)F(\nu)$ with $F(\nu)$.

We have solved the gap equations numerically for various values of μ^* and T_c and obtained the corresponding values of the coupling constant λ. The attempt to represent all the results for the three transition elements considered led us to a formula proposed by Leavens, rather than the McMillan formula. The former takes into account the finer details of the phonon spectrum and can therefore describe T_c in materials with phonon spectra as different as in Ta and V.

In the second part of this paper we describe a microscopic calculation of λ. The calculation of the phonon part from experimental data is straightforward. To get the electronic part, we used a procedure of extracting the matrix elements in J^2 from band-structure calculations. In the form presented here this procedure, as well as the expression for J^2, is suitable only for the Γ'_{25} band. This may be a reasonable approximation as long as the number of d electrons is small, but it will have to be abandoned for metals with more d electrons, when all five d functions have to be taken into account. This is not a serious problem and may be solved quite easily.[19,20] Another limitation of the present calculation is the neglect of the contribution of the crystal-field integrals to λ. In principle these may also be derived from the band structure, but we have not been able to do so in our case. We have argued that because of the renormalization in Eqs. (4.8) and (4.9) the effect of these integrals on increasing λ will be much smaller than their additive contribution to J^2.

In conclusion we have derived an expression of the coupling constant λ in the localized representation, obtained the theoretical values of λ which give the observed values of T_c in the modified Eliashberg equations, and, finally, presented a microscopic calculation of this λ. This calculation is based on the experimental phonon spectrum, the measured heat capacity constant, and given energy bands, without any adjustable parameter. The agreement is reasonably good. The simplicity of this procedure gives hope that it will be possible to correlate systematically the various factors which affect T_c as one goes from one transition element to another, as soon as more experimental phonon distribution curves and reliable band-structure calculations are available.

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