Phonons and superconducting p-state pairing in Pd

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We present an analytical calculation of the electron-phonon parameters for s- and p-state pairing in Pd, λ_0^{ph} and λ_1^{ph}. The calculation is based on Doniach's six half-sphere Fermi-surface model for the heavy d electrons, a Debye and an Einstein model for intra- and intersphere phonon-scattering processes, respectively, and the LCMTO (linear combination of muffin-tin orbitals) representation to obtain the electron-phonon matrix elements. The group-theoretical method of Allen is employed in solving the anisotropic gap equation at the multiply sheeted Fermi surface for s- and p-state pairing interactions. The phonon-mediated interaction, $I^{ph}(\vec{k},\vec{k}')$, is attractive for all momentum transfers, $\vec{k}-\vec{k}'$, and yields the BCS parameter, $\lambda_0^{ph}=0.153$, in agreement with Papaconstantopoulos *et al.* Our results for p-state pairing is $\lambda_1^{ph}=0$, when Einstein phonon model is used for both intra- and intersheet scattering processes and $\lambda_1^{ph}=0.089\lambda_0^{ph}$ when the Debye model is applied to the small-momentum intrasheet transitions of the Cooper pairs. The weakness of the p-state interaction is due to the cancellation between the contributions from intrasheet scattering and from large-momentum intersheet scattering processes. A detailed discussion of the results is presented in terms of the parameters of our electron-phonon model.

I. INTRODUCTION

Both phonons and spin fluctuations can contribute to the p-state pairing interaction in narrow-band transition metals with strong exchange interactions. For palladium, the spin fluctuations alone lead to a small attractive p-state interaction, $\lambda_1^{SF}\sim 0.08$, yielding a transition temperature $T_{c1}\sim 10^{-5}$–10^{-6} K.[1] This small value indicates that the occurrence of an observable transition hinges on a significant attractive electron-phonon interaction.

For the spin-fluctuation pairing, the physical origin is readily understood in terms of an attractive exchange interaction between two electrons with parallel spins. In the paramagnon model,[2] the attraction given by λ_1^{SF} is a result of the irreducible electron-electron interaction given by the particle-hole ladder diagrams (cf., Fig. 1 of Ref. 2). This electron-electron interaction due to spin fluctuations has a strong lobe in the forward direction, which, as we will discuss shortly, is necessary for a significant p-state component.

The phonon-mediated interaction for p-state pairing in Pd is studied in three recent papers.[3–5] Appel and Fay[3] calculate this interaction using the atomic-site representation for the heavy d electrons and an Einstein model for the phonons; the result is a very small repulsive interaction, $|\lambda_1^{ph}| << \lambda_0^{ph}$. Pinski, Allen, and Butler[4] present a rigorous calculation of the phonon pairing using electron-phonon parameters calculated with the Korringa-Kohn-Rostoker (KKR) method, employing a Born–von Kármán force-constant model fitted to experimental neutron data, and taking the Fermi-surface sheets of both d and s electrons into account, they get $\lambda_0^{ph}=0.44$ and $\lambda_1^{ph}=-0.02$. Finally, Foulkes, and Gyorffy[5] estimate λ_1^{ph} from the high-temperature resistivity of Pd. Their result $\lambda_1^{ph}=0.192$ is too high, one reason being that the effect of small-angle scattering on the electron-electron interaction is overestimated by this procedure. All three of these studies, however, do not readily provide physical insight into the problem, namely, why is the p-state phonon interaction so small compared with the ordinary BCS interaction and what are the pertinent properties of electrons, phonons, and the electron-phonon interaction which are necessary for a significant attractive p-state interaction that would result in a superconducting transition at observable temperatures.

For simple metals, such as the alkalis, the question raised above can be answered as follows. For a spherical Fermi surface, we can write $I^{ph}(\vec{k},\vec{k}')=I^{ph}(|\vec{k}|,|\vec{k}'|,\hat{k}\cdot\hat{k}')$, where $|\vec{k}|=|\vec{k}'|=k_F$. The angular-momentum decomposition of I^{ph} yields the p-state ($l=1$) pairing coefficient $I_1^{ph}=\int \hat{k}\cdot\hat{k}' I^{ph}(\hat{k}\cdot\hat{k}')\,d(\hat{k}\cdot\hat{k}')$. In simple metals, e.g., I_1^{ph} is comparable with I_0^{ph} because the phonon mediated interaction has a strong lobe in the forward direction, $\hat{k}\cdot\hat{k}'\sim 1$, and is small for large angle scattering, $\hat{k}\cdot\hat{k}'\sim 0$. Taking, in addition, into account that for the relative orbital motion in a p-state the Coulomb repulsion between two electrons almost vanishes, we get the p-state transition temperature for Na and K as $T_{c1}\gtrsim 10^{-3}$ and 10^{-4} K, respectively, and furthermore, we have $T_{c1}>>T_{c0}$.[6]

Returning now to the transition metal Pd, we ad-

dress ourselves to the problem of the p-state phonon interaction in the following manner. We assume the *anisotropic* multiply sheeted Fermi-surface model of Doniach[7] for the d electrons. The anisotropic-energy-gap function is expanded in terms of Allen's Fermi-surface harmonics[8,9] and the gap equation is solved for the T_c eigenvalues that correspond to s- and p-state pairing (Sec. II). In Sec. III, we calculate analytically the form of the phonon interaction parameters, assuming spherical Fermi-surface (FS) sheets. The electron-phonon matrix elements entering the interaction parameters are found in Sec. IV by employing the linear combination of muffin-tin orbitals (LCMTO) representation of Andersen.[10,11] The wave functions are written in terms of the structure constants of the Pd lattice and the potential parameters of the canonical d bands. In Sec. V the phonon parameters are evaluated for singlet and for triplet pairing, $\lambda_0^{\rm ph}$ and $\lambda_1^{\rm ph}$, in terms of the p-d and d-f matrix elements of the ion potential gradient. In Sec. VI we discuss the phonon parameters with emphasis on (a) the relative importance of small angle intrasheet and large angle intersheet scattering processes at the FS and (b) the relative contributions of s-p, p-d, and d-f matrix elements of the ion potential gradient to intra- and intersheet scatterings.

II. T_c EQUATION AND ITS EIGENVALUES

In this section we formulate the T_c equation and determine its eigenvalues for s-state and for p-state pairing. The gap equation defining T_c is obtained by the procedure of Butler and Allen.[9] The anisotropic energy gap is written

$$\Delta(\vec{k},\omega)=\sum_L \Delta_L(\omega)F_L(\vec{k}) \ , \tag{2.1}$$

where the basis functions, $F_L(\vec{k})$, with L being the label, are by definition orthonormal on the FS. The properties of the F_L's, the so-called FS harmonics (FSH's), are discussed in Ref. 8. The F_L's are polynomials in the velocity components, $v_{k_x}, v_{k_y}, v_{k_z}$, they have translational symmetry in $\vec{k}$ space, and they transform according to the irreducible representations of the crystal point group.[12]

Using the expansion for $\Delta(\vec{k},\omega)$, Eq. (2.1), and parametrizing the ω dependence in the manner of BCS, the gap equation is given by

$$\rho(\underline{1}+\underline{\Lambda})\cdot\vec{\Delta}=(\underline{\lambda}-\underline{\mu}^*)\cdot\vec{\Delta} \ . \tag{2.2}$$

Here

$$\rho^{-1}=\ln(1.13\omega_{\log}/T_c) \ , \tag{2.3}$$

where $\omega_{\log}$ is an average phonon frequency defined elsewhere.[9] The matrices $\underline{\lambda}$, $\underline{\Lambda}$, and $\underline{\mu}^*$ are defined by

$$\lambda_{LL'}=N^{-1}(0)\sum_{\vec{k},\vec{k}'} I^{\rm ph}(\vec{k},\vec{k}')F_L(\vec{k})F_{L'}(\vec{k}')\delta(\epsilon_{\vec{k}})\delta(\epsilon_{\vec{k}'}) \ , \tag{2.4}$$

$$\Lambda_{LL'}=\sum_{L''}\sum_{L'''} C_{LL'L''}\lambda_{L''L'''}\theta_{L'''} \ , \tag{2.5}$$

where

$$C_{LL'L''}=N^{-1}(0)\sum_{\vec{k}} F_L(\vec{k})F_{L'}(\vec{k})F_{L''}(\vec{k})\delta(\epsilon_{\vec{k}}) \ , \tag{2.6}$$

$$\theta_L=N^{-1}(0)\sum_{\vec{k}} F_L(\vec{k})\delta(\epsilon_{\vec{k}}) \ , \tag{2.7}$$

and

$$\mu^*_{LL'}=\mu^*\delta_{L0}\delta_{L'0} \ . \tag{2.8}$$

The column vector $\vec{\Delta}$ has the elements $\Delta_L(\omega=0)$. The FS density of states is given by $N(0)=\sum_{\vec{k}}\delta(\epsilon_{\vec{k}})$. The form of the Coulomb pseudopotential, Eq. (2.8), implies that the Coulomb repulsion is ignored, except for s-state pairing.[13] The gap equation (2.2) has nontrivial solutions, $\vec{\Delta}\neq\vec{0}$, only for discrete eigenvalues ρ

We wish to determine the ρ's which yield the T_c's for s-state and for p-state pairing. To this end we must determine the FSH's for the multiple-sheet FS model shown in Fig. 1. Before this is done let us, for simplicity, discuss the case of a single-sheet FS. In that case, once we have chosen a basis set of F_L's, the matrix $\underline{\lambda}$ becomes block diagonal, each block transforming according to a row of an irreducible representation. Assuming cubic symmetry and restricting ourselves to the two blocks which transform accoring to Γ_1 and the z row of Γ_{15}, the eigenvalues ρ are given by diagonalizing the matrix

$$\begin{pmatrix}[\underline{1}+\underline{\Lambda}(\Gamma_1)]^{-1} & 0\\ 0 & [\underline{1}+\underline{\Lambda}(\Gamma_{15})]^{-1}\end{pmatrix}\begin{pmatrix}\underline{\lambda}(\Gamma_1)-\underline{\mu}^* & 0\\ 0 & \underline{\lambda}(\Gamma_{15}^{(z)})\end{pmatrix} \ , \tag{2.9}$$

where, e.g., $\underline{\lambda}(\Gamma_1)$ is the matrix, Eq. (2.4), in the basis of all FSH's that transform according to Γ_1.

We now turn to the multiply sheeted FS of Fig. 1. There are six half spheres or three full spheres, centered at X, Y, and Z. Hence the number of independent FSH's now increases by a factor of 3. Starting with the disjoint representation of the FSH's,[8]

$$F_L^{(a)}(\vec{k})=\begin{cases}\sqrt{3}F_L(\vec{k}) & \text{for } \vec{k} \text{ on the FS sheet } X,Y,Z\\ & \text{corresponding to } a=1,2,3 \ ;\\ 0 & \text{otherwise} \ ;\end{cases} \tag{2.10}$$

we construct symmetry adapted FSH's by usual projection operator techniques. The three spheres at X,Y,Z transform into one another according to the three-dimensional representation $\Gamma_1\oplus\Gamma_{12}$, the reason

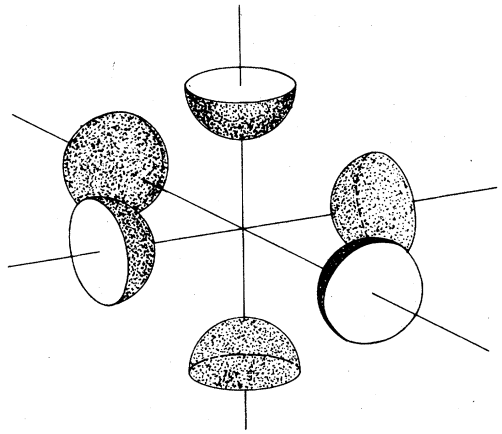

FIG. 1. Six-half-sphere Fermi-surface model for the heavy d electrons of palladium.

being that the spheres at a and $-a$ are equivalent. Taking into account this transformation behavior of the spheres and restricting the set of Γ_1 polynomials on the spheres to the three zeroth-order polynomials, $F_0^{(a)}(\vec{k})=\sqrt{3}$, we get for s-state pairing one symmetrized FSH for Γ_1 and two FSH's for Γ_{12}. These functions are

$$F_0(\Gamma_1;\vec{k})=(F_0^{(1)}+F_0^{(2)}+F_0^{(3)})/\sqrt{3} \ , \tag{2.11}$$

$$F_0(\Gamma_{12}^{(z^2)};\vec{k})=(F_0^{(1)}+F_0^{(2)}-2F_0^{(3)})/\sqrt{6} \ , \tag{2.12}$$

$$F_0(\Gamma_{12}^{(x^2-y^2)};\vec{k})=(F_0^{(1)}-F_0^{(2)})/\sqrt{2} \ , \tag{2.13}$$

where the two Γ_{12} functions transform as $3z^2-r^2$ and x^2-y^2, respectively. Similarly, in determining the FSH's associated with p-state pairing, we restrict the set of Γ_{15} polynomials on the spheres to the three first-order functions $F_1^{(a)}(k)=\sqrt{3}v_{k_z}/|\vec{v}_{\vec{k}}|$ for $a=1,2,3$. The, taking into account that the symmetrized FSH's for p-state pairing transform according to $\Gamma_{15}\otimes(\Gamma_1\oplus\Gamma_{12})=2\Gamma_{15}\oplus\Gamma_{25}$, we get as the z components the following functions:

$$F_1(\Gamma_{15,1}^{(z)};\vec{k})=F_1^{(3)} \ , \tag{2.14}$$

$$F_1(\Gamma_{15,2}^{(z)};\vec{k})=(F_1^{(1)}+F_1^{(2)})/\sqrt{2} \ , \tag{2.15}$$

$$F_1(\Gamma_{25}^{(z)};\vec{k})=(F_1^{(1)}-F_1^{(2)})/\sqrt{2} \ . \tag{2.16}$$

We now use the six functions $F_L(\Gamma;\vec{k})$, Eqs. (2.11)–(2.16), to calculate the eigenvalues ρ of the 6×6 matrix $(\underline{1}+\underline{\Lambda})^{-1}\times(\underline{\lambda}-\underline{\mu}^*)$. The result is

$$\rho(\Gamma_1)=\frac{\lambda_{00}(\Gamma_1)-\mu_{00}^*(\Gamma_1)}{1+\lambda_{00}(\Gamma_1)} \ , \tag{2.17}$$

$$\rho(\Gamma_{12})=\frac{\lambda_{00}(\Gamma_{12})-\mu_{00}^*(\Gamma_{12})}{1+\lambda_{00}(\Gamma_1)} \ , \tag{2.18}$$

$$\rho_\pm(\Gamma_{15})=\frac{\lambda_{11;\pm}(\Gamma_{15})}{1+\lambda_{00}(\Gamma_1)} \ , \tag{2.19}$$

where

$$\lambda_{11;\pm}(\Gamma_{15})=\tfrac{1}{2}[\lambda_{11}(\Gamma_{15},11)+\lambda_{11}(\Gamma_{15},22)] \pm\{\tfrac{1}{4}[\lambda_{11}(\Gamma_{15},11)-\lambda_{11}(\Gamma_{15},22)]^2+\lambda_{11}^2(\Gamma_{15},12)\}^{1/2} \ ,$$

$$\rho(\Gamma_{25})=\frac{\lambda_{11}(\Gamma_{25})}{1+\lambda_{00}(\Gamma_1)} \ . \tag{2.20}$$

Here, it is taken into account that $\Lambda_{LL'}(\Gamma)=\lambda_{00}(\Gamma_1)\delta_{LL'}$ and, e.g., $\lambda_{11}(\Gamma_{15},12)\equiv\lambda_{11}(\Gamma_{15,1};\Gamma_{15,2})$. The matrix element λ can be decomposed into an intrasheet contribution λ^{ra} $(i=i')$ and an intersheet contribution λ^{er} $(i\neq i')$; hence

$$\lambda_{00}(\Gamma_1)=\tfrac{1}{3}(\lambda_{00}^{ra}+2\lambda_{00}^{er}) \ , \tag{2.21}$$

$$\lambda_{00}(\Gamma_{12})=\tfrac{1}{3}(\lambda_{00}^{ra}-\lambda_{00}^{er}) \ , \tag{2.22}$$

$$\lambda_{11}(\Gamma_{15},11)=\tfrac{1}{3}\lambda_{11}^{ra} \ ,$$

$$\lambda_{11}(\Gamma_{15},12)=\tfrac{1}{3}\sqrt{2}\lambda_{11}^{er} \ , \tag{2.23}$$

$$\lambda_{11}(\Gamma_{15},22)=\tfrac{1}{3}(\lambda_{11}^{ra}+\lambda_{11}^{er}) \ ,$$

$$\lambda_{11,+}(\Gamma_{15})=\tfrac{1}{3}(\lambda_{11}^{ra}+2\lambda_{11}^{er}) \ , \tag{2.24}$$

$$\lambda_{11,-}(\Gamma_{15})=\tfrac{1}{3}(\lambda_{11}^{ra}-\lambda_{11}^{er}) \ , \tag{2.25}$$

$$\lambda_{11}(\Gamma_{25})=\tfrac{1}{3}(\lambda_{11}^{ra}-\lambda_{11}^{er}) \ . \tag{2.26}$$

Similarly, we can decompose the Coulomb pseudopotentials $\mu_{00}^*(\Gamma_1)$ and $\mu_{00}^*(\Gamma_{12})$.

Thus the evaluation of the eigenvalues ρ for s-state and for p-state pairing is reduced to that of a few parameters, λ^{ra} and λ^{er}. We proceed to calculate these parameters for the FS model, Fig. 1.

III. SPHERICAL FERMI-SURFACE SHEET

The matrix elements $\lambda_{LL'}$, Eq. (2.4), depend on the phonon interaction,

$$I^{ph}(\vec{k},\vec{k}')=\sum_i (MN)^{-1}\omega_i^{-2}(\vec{k},\vec{k}')|g_i(\vec{k},\vec{k}')|^2 \ , \tag{3.1}$$

where the electron-phonon matrix element g_i is given by Eq. (4.7), ω_i is the phonon frequency of polarization i, and M is the atomic mass. Note that our g_i does not contain the displacement factor $1/(2MN\omega_i)^{1/2}$. We insert Eq. (3.1) into Eq. (2.4) for $\lambda_{LL'}$ and assume a spherical FS. Then, the density of states is

$$\sum_{\vec{k}}\delta(\epsilon_{\vec{k}})=\frac{m^*Vk_F}{(2\pi)^3}\int_{\text{sphere }(S)} d\hat{k}_F \ , \tag{3.2}$$

(m^* is the d-electron mass, k_F is the Fermi momentum) and we can replace the $F_L(\Gamma,\vec{k})$ by the real

spherical harmonics, $Z_L(\hat{k}_F)$, where $L=(l,m)$ and $\hat{k}_F$ is a unit vector on the FS. The resulting expression for λ is

$$\lambda_{LL'}=\frac{m^*k_FV}{(2\pi)^3}\int_S\int_{S'}d\hat{k}_F\,d\hat{k}_F'I^{\rm ph}(\vec{k}_F,\vec{k}_F')Z_L(\hat{k}_F)Z_{L'}(\hat{k}_F')\,. \tag{3.3}$$

From here we can proceed with the analytic evaluation of the λ's provided we can factorize $I^{\rm ph}$ with respect to $\vec{k}$ and $\vec{k}'$ in such a manner that the integrations over $\vec{k}$ and $\vec{k}'$ become independent of one another.

The matrix element g can be factorized as we shall see below (Sec. IV).

In $I^{\rm ph}$ also occurs the factor $\omega_i^{-2}(\vec{k}-\vec{k}')$. We assume the Einstein model, $\omega_i(\vec{q})=\omega_E$, for intersheet scattering processes, where

$$q=|\vec{k}_F-\vec{k}_F'|\geq(2\pi/a)(\sqrt{2}-ak_F/\pi)\;;$$

here a is the lattice constant and $k_F=2.44a^{-1}$. For intrasheet scattering processes, i.e., $\vec{k}$ and $\vec{k}'$ are on the same sphere, we achieve the factorization by using the Debye model. Here $\omega_i(\vec{q})=u_iq$, where u_i is the phonon phase velocity. We write

$$\begin{aligned}\omega_i^{-2}(\vec{k}_F-\vec{k}_F')&=[2\omega_i(k_F)]^{-2}\sum_{\nu=0}^{\infty}(\hat{k}_F\cdot\hat{k}_F')^\nu\\&=[2\omega_i(k_F)]^{-2}\sum_{\nu=0}^{\infty}(\tfrac{4}{3}\pi)^\nu Z_{\nu0}^\nu(\hat{k}_F)Z_{\nu0}^\nu(\hat{k}_F')\,,\end{aligned} \tag{3.4}$$

where without loss of generality $\hat{k}_F$ is oriented in z direction. Substituting Eq. (3.4) into Eq. (3.1) we get for the Debye (D) model

$$\lambda_{LL'}^D=\omega_E^2[2\omega^2(k_F)]^{-1}\sum_\nu\lambda_{LL'}^{(\nu)}\,, \tag{3.5}$$

where

$$\begin{aligned}\lambda_{LL'}^{(\nu)}=&\frac{3m^*k_FV}{(2\pi)^3M\omega_E^2N}(\tfrac{4}{3}\pi)^\nu\\&\times\int_S\int_{S'}d\hat{k}_F\,d\hat{k}_F'|g(\vec{k}_F,\vec{k}_F')|^2Z_L(\hat{k}_F)Z_{L'}(\hat{k}_F')\\&\times Z_{\nu0}^\nu(\hat{k}_F)Z_{\nu0}^\nu(\hat{k}_F')\end{aligned} \tag{3.6}$$

and

$$\omega^{-2}(k_F)=\tfrac{1}{3}\sum\omega_i^{-2}(k_F)\;.$$

For the Einstein (E) model, we have

$$\lambda_{LL'}^E=\lambda_{LL'}^{(0)}\,. \tag{3.7}$$

Hence, Eq. (3.5) can be written

$$\lambda_{LL'}^D=\omega_E^2[2\omega^2(k_F)]^{-1}\left(\lambda_{LL'}^E+\sum_{\nu=1}^{\infty}\lambda_{LL'}^{(\nu)}\right)\,. \tag{3.8}$$

Returning to the matrix elements $\lambda(\Gamma)$ given by Eqs. (2.21)–(2.26), we now see that the parameters $\lambda^{\rm ra}$ and $\lambda^{\rm er}$ for intrasheet and intersheet scattering can be replaced by λ^D and λ^E, respectively.

IV. ELECTRON-PHONON MATRIX ELEMENT

In Andersen's theory of the electron band structure,[10,11] a Bloch function $\psi_{n\vec{k}}(\vec{r})$ (n is the band index) can be represented by a linear combination of muffin-tin orbitals $\chi_L(\vec{r})$,

$$\begin{aligned}\psi_{n\vec{k}}(\vec{r})&=N^{-1/2}\sum_L B_{Ln}(\vec{k})\left[\chi_L(\vec{r})+\sum_{\vec{R}\neq0}e^{i\vec{k}\cdot\vec{R}}\chi_L(\vec{r}-\vec{R})\right]\\&=N^{-1/2}\sum_L B_{Ln}(\vec{k})\left[\chi_L(\vec{r})-\sum_{L'}\left(\frac{r}{s}\right)^{l'}\frac{i^{l'}Z_{L'}(\hat{r})}{2(2l'+1)}S_{LL'}(\vec{k})\chi_L(s)\right]\,.\end{aligned} \tag{4.1}$$

We employ Andersen's notation, that is, s is the atomic sphere or Wigner-Seitz radius and the $S_{LL'}(\vec{k})$ are the canonical structure constants. By using the LCMTO secular equation,[11] we can write the Bloch function for a canonical d band ($l=2$) with subband index α as

$$\psi_{2\alpha,\vec{k}}(\vec{r})=[N_{2\alpha}(\vec{k})N]^{-1/2}\left[\sum_{m=-2}^{2}B_{2m,2\alpha}(\vec{k})\phi_{2m}(\vec{r})-\sum_{L'}{}'\frac{1}{2l'+1}\left(\frac{\tau_{l'}}{2\mu_2(2l'+3)}\right)^{1/2}\sum_{m=-2}^{2}S_{L',2m}(\vec{k})B_{2m,2\alpha}(\vec{k})\phi_{L'}(\vec{r})\right]\,, \tag{4.2}$$

where the normalization constant $N_{2\alpha}(\vec{k})$ is given by

$$N_{2\alpha}(\vec{k})=1+\frac{1}{2\mu_2}\sum_{L'}{}'\frac{\tau_{l'}}{(2l'+1)^2(2l'+3)}\left|\sum_{m'=-2}^{2}S_{L',2m}(\vec{k})B_{2m,2\alpha}(\vec{k})\right|^2\,. \tag{4.3}$$

Here μ_2 is the mass at the center of gravity of the d band and τ_l is the mass at the bottom of the l band. The radial part of the function $\phi_L(\vec{r})=\phi_l(r)Z_L(\hat{r})$ is the solution of the Schrödinger equation for a single muffin-tin well. In Eq. (4.2), the prime on $\sum_{L'}$ implies that the $L'=2$ term must be omitted.

Now, taking $N_{2\alpha}=1$ because of the large value of μ_2 ($=6.79$ for Pd) and neglecting the weak s-d hybridization at the FS of Pd, we have

$$B_{2m,2\alpha}(\vec{k})=\delta_{m\alpha} \ . \tag{4.4}$$

Hence, the Bloch function is

$$\psi_{2\alpha,\vec{k}}(\vec{r})=N^{-1/2}\sum_L \tilde{S}_{L,2\alpha}(\vec{k})\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}}\Theta(\vec{r}-\vec{R})\phi_L(\vec{r}-\vec{R}) \ , \tag{4.5}$$

where

$$\tilde{S}_{L,2\alpha}(\vec{k})=\begin{cases} -\dfrac{1}{2l+1}\left(\dfrac{\tau_l}{2\mu_2(2l+3)}\right)^{1/2} S_{L,2\alpha}(\vec{k}) & \text{for } l\neq 2 \\ \delta_{m\alpha} \text{ for } l=2 \ . \end{cases} \tag{4.6}$$

The function $\Theta(\vec{r}-\vec{R})$ is unity inside the atomic sphere centered at $\vec{R}$ and zero outside.

In terms of the Bloch functions ψ, Eq. (4.5), the electron-phonon matrix element g for the emission of a phonon with wave vector $\vec{q}=\vec{k}-\vec{k}'$ is given by

$$g_i(\vec{k}\alpha,\vec{k}'\alpha')=\sum_{\vec{R}}\vec{e}_i(\vec{q})e^{i\vec{q}\cdot\vec{R}}\int_V \psi^*_{2\alpha,\vec{k}}(\vec{r})\vec{\nabla}V(\vec{r}-\vec{R})\psi_{2\alpha',\vec{k}'}(\vec{r})\,d^3r \ . \tag{4.7}$$

Assuming that the three phonon branches do not interact (i.e., the dynamical matrix is diagonal for all $\vec{q}$) we get on the basis of the rigid-muffin-tin approximation for $\vec{\nabla}V(\vec{r})$

$$g(\vec{k}\alpha,\vec{k}'\alpha')=\sum_{LL'}\tilde{S}^*_{L,2\alpha}(\vec{k})\tilde{S}_{L',2\alpha'}(\vec{k}')\int_{\text{WS sphere}}\phi_l(r)Z_L(\hat{r})\vec{\nabla}V(\vec{r})\phi_{l'}(r)Z_{L'}(\hat{r})\,d^3r \ , \tag{4.8}$$

independent of i. We now choose the z axis parallel to $\vec{\nabla}V$ and get

$$\begin{aligned} g(\vec{k}\alpha,\vec{k}'\alpha') &= \sum_{LL'}\tilde{S}^*_{L,2\alpha}(\vec{k})\tilde{S}_{L',2\alpha'}(\vec{k}')M_{ll'}\int Z_l(\hat{r})\cos\theta\, Z_{L'}(\hat{r})\,d\hat{r} \\ &= \sum_L[\tilde{S}^*_{L,2\alpha}(\vec{k})\tilde{S}_{L+1,2\alpha'}(\vec{k}')+\tilde{S}_{L+1,2\alpha}(\vec{k})\tilde{S}_{L,2\alpha'}(\vec{k}')]\,M_{l,l+1}(\tfrac{4}{3}\pi)^{1/2}G_{10}(L,L+1) \ , \end{aligned} \tag{4.9}$$

where $L=(l,m)$, $L+1=(l+1,m)$, and

$$M_{l,l+1}=\int_0^s \phi_l(r)\frac{dV}{dr}\phi_{l+1}(r)r^2\,dr \ , \tag{4.10}$$

$$G_L(L',L'')=\int Z_L(\hat{r})Z_{L'}(\hat{r})Z_{L''}(\hat{r})\,d\hat{r} \ . \tag{4.11}$$

We now assume that the symmetry of the Bloch functions is $\alpha=xy$, yz, and zx, according to whether the wave vector $\vec{k}$ is near X, Y, or Z in the fcc Brillouin zone. Summing up to $l=2$ in Eq. (4.9), the final result for g can be written

$$g(\vec{k},xz;\vec{k}',xz)=\sum_{i=1}^{3}T_{i-1,i}M_{i-1,i} \ , \tag{4.12}$$

where

$$T_{01}=[\tilde{S}^*_{00,21}(\vec{k})\tilde{S}_{10,21}(\vec{k}')+\tilde{S}^*_{10,21}(\vec{k})\tilde{S}_{00,21}(\vec{k}')]/\sqrt{3} \ , \tag{4.13}$$

$$T_{12}=[\tilde{S}^*_{11,21}(\vec{k})+\tilde{S}_{11,21}(\vec{k}')]/\sqrt{5} \ , \tag{4.14}$$

$$T_{23}=[\tilde{S}^*_{31,21}(\vec{k})+\tilde{S}_{31,21}(\vec{k}')]/\sqrt{8/35} \ . \tag{4.15}$$

Here we can restrict ourselves to the electron-phonon matrix element g for $\alpha=\alpha'=zx(=1)$ since the expression for λ, Eq. (3.6), is factorized below into an integral over $\vec{k}$ and an integral over $\vec{k}'$.

Furthermore, taking into account that the $\vec{k}$ and $\vec{k}'$ integrations are carried out over a spherical FS sheet, it is convenient to represent the structure constants $\tilde{S}_{LL'}(\vec{k})$ by an expansion in terms of spherical harmonics. The structure constants are evaluated in Appendix A.

Having obtained g, we can now proceed to calculate the interaction parameters λ, Eq. (3.6), relevant for s-state and for p-state pairing.

V. PHONON INTERACTION λ FOR s- AND p-STATE PAIRING

In order to get the s-state and p-state parameters $\lambda(\Gamma)$, Eqs. (2.21)–(2.26), we need the following ma-

trix elements, Eq. (3.6) ($\hat{Z}_L = [4\pi/(2l+1)]^{1/2} Z_L$):

$$\lambda_{00}^{(0)} = \lambda_{00}^{E} = \left(\frac{A}{4\pi}\right) \int_S \int_{S'} d\hat{k}_F \, d\hat{k}_F' \, |g(\vec{k}_F, \vec{k}_F')|^2 \ , \quad (5.1)$$

$$\lambda_{11}^{(0)} = \lambda_{11}^{E} = \frac{3A}{4\pi} \int_S \int_{S'} d\hat{k}_F \, d\hat{k}_F' \, |g(\vec{k}_F, \vec{k}_F')|^2 \times \hat{Z}_{10}(\hat{k}_F) \hat{Z}_{10}(\hat{k}_F') \ , \quad (5.2)$$

$$\lambda_{00}^{(\nu)} = \left(\frac{A}{4\pi}\right) \int_S \int_{S'} d\hat{k}_F \, d\hat{k}_F' \, |g(\vec{k}_F, \vec{k}_F')|^2 \times \hat{Z}_{10}^{\nu}(\hat{k}_F) \hat{Z}_{10}^{\nu}(\hat{k}_F') \ . \quad (5.3)$$

Here is $A = 3m^* k_F V / M\omega_E^2 (2\pi)^3 N$. The matrix elements for the Debye model, Eq. (3.8), are then given by

$$\lambda_{00}^{D} = C\left(\lambda_{00}^{E} + \tfrac{1}{3}\lambda_{11}^{E} + \sum_{\nu=2}^{\infty} \lambda_{00}^{(\nu)}\right) \ , \quad (5.4)$$

$$\lambda_{11}^{D} = C\left(\lambda_{11}^{E} + 3 \sum_{\nu=2}^{\infty} \lambda_{00}^{(\nu)}\right) \ , \quad (5.5)$$

where $C = \omega_E^2 / 2\omega^2(k_F)$ and where it is taken into account that $\lambda_{11}^{(\nu)} = 3\lambda_{00}^{(\nu+1)}$.

When now the electron-phonon matrix element g, Eq. (4.12), is substituted into the equations above, the following integral must be dealt with:

$$K_{ij}^{(\nu)} = \int_S \int_{S'} d\hat{k}_F \, d\hat{k}_F' \, \hat{Z}_{10}^{\nu}(\hat{k}_F) \hat{Z}_{10}^{\nu}(\hat{k}_F') \, T_{i-1,i}^{*} T_{j-1,j} \ . \quad (5.6)$$

These integrals are calculated in Appendix B. There it is seen that only the $K_{ij}^{(\nu)}$ for $ij = 22, 23, 33$ contribute significantly to the λ's so that we may restrict ourselves to p-d and d-f transitions in the electron-phonon interaction. These $K_{ij}^{(\nu)}$ can be written

$$K_{ij}^{(\nu)} = \begin{cases} -\dfrac{3}{(\nu+2)^2} K_{ij}^{(0)} \ , & \nu \text{ odd} \\ \dfrac{3}{(\nu+1)(\nu+3)} K_{ij}^{(0)} \ , & \nu \text{ even} \ . \end{cases} \quad (5.7)$$

In terms of $K_{ij}^{(\nu)}$ the parameter $\lambda_{00}^{(\nu)}$ is given by

$$\lambda_{00}^{(\nu)} = \left(\frac{A}{4\pi}\right) \sum_{i=2}^{3} \sum_{j=2}^{3} K_{ij}^{(\nu)} M_{i-1,i} \, M_{j-1,j} \quad (5.8)$$

and, hence the ν summation in Eq. (5.4) yields

$$\sum_{\nu=2}^{\infty} \lambda_{00}^{(\nu)} = \left(\frac{A}{4\pi}\right) \sum_{ij} M_{i-1,i} M_{j-1,i} K_{ij}^{(0)} \sum_{\nu=1}^{\infty} \frac{6}{(2\nu+1)(2\nu+3)^2} = 0.135 \lambda_{00}^{E} \ . \quad (5.9)$$

As the result of Eq. (5.9) we can now express all of the matrix elements, Eqs. (5.2)–(5.5), in terms of λ_{00}^{E}, i.e., we have

$$\lambda_{11}^{E} = -\lambda_{00}^{E} \ , \quad (5.10)$$

$$\lambda_{00}^{D} = 0.802 C \lambda_{00}^{E} \ , \quad (5.11)$$

$$\lambda_{11}^{D} = -0.595 C \lambda_{00}^{E} = -0.742 \lambda_{00}^{D} \ . \quad (5.12)$$

Substituting the intra- and intersheet interactions, $\lambda_{LL'}^{ra}$ and $\lambda_{LL'}^{er}$ by $\lambda_{LL'}^{D}$ and $\lambda_{LL'}^{E}$, respectively, we finally get the explicit form of the $\lambda(\Gamma)$, Eqs. (2.21)–(2.26). Then we can determine from Eqs. (2.17) and (2.19) the ratio between the eigenvalues ρ for s-state and for p-state pairing; we have

$$\frac{\rho_-(\Gamma_{15})}{\rho(\Gamma_1)} = \frac{(1 - 0.595C)\lambda_{00}^{E}}{(2 + 0.802C)\lambda_{00}^{E} - \mu^*} \ , \quad (5.13)$$

where $\mu^* \equiv \mu_{00}(\Gamma_1)$ and

$$\lambda_{00}^{E} = \frac{3m^* k_F V}{(2\pi)^3 M \omega_E^2 N} \frac{1}{4\pi} \times (K_{22}^{(0)} M_{pd}^2 + 2K_{23}^{(0)} M_{pd} M_{df} + K_{33}^{(0)} M_{df}^2) \ . \quad (5.14)$$

VI. RESULTS AND DISCUSSION

Let us recall that Doniach's FS model is a basic assumption employed in setting up the gap equation and in determining its electron-phonon kernel. This model, shown in Fig. 1, is a simplification of the actual d-electron FS found by Andersen[14] and Mueller *et al.*[15(a)] from energy-band calculations. Recently, the d-electron FS has been experimentally confirmed with high precision measurements of de Haas–van Alphen orbits.[15(b)] Despite the complexity of the actual FS geometry, the simple FS model of Fig. 1 allows for what is perhaps the most pertinent physical aspect here for s-state vs p-state pairing, namely, a reasonable separation of the pairing interaction, $I^{ph}(\vec{k}, \vec{k}')$, into two types: (a) intrasheet scattering, where the Cooper pair stays on one and the same sphere (or on one set of conjugated half spheres) and (b) intersheet scattering, where a pair is scattered between two different spheres. For the first type, the scattering angle between $\vec{k}$ and $\vec{k}'$ is small, $\leq 45.7°$; for the second type, the angle is large, $> 44.3°$ ($\vec{k}, \vec{k}'$ are referred to the center of the Brillouin zone). Furthermore, this simple multiply-sheeted FS model allows for a straightforward application of the group-theoretical method of Butler and Allen[9] in solving the *anisotropic* gap equation. We expand $\Delta(\vec{k}, \omega)$ in terms of our symmetry-adapted FS harmonics, which in our case are linear combinations of spherical harmonics, and get as eigenvalues of the gap matrix equation the results, Eqs. (2.17)–(2.20). It follows

from the eigenvalues, $\rho(\Gamma_1)$ and $\rho(\Gamma_{15})$, that the electron-phonon coupling parameters for s-state and for p-state pairing are respectively given by

$$\lambda_0^{\rm ph} \equiv \lambda_{00}(\Gamma_1) = \tfrac{1}{3}(\lambda_{00}^{\rm ra} + 2\lambda_{00}^{\rm er}) \ , \tag{6.1}$$

$$\lambda_1^{\rm ph} \equiv \lambda_{11;-}(\Gamma_{15}) = \tfrac{1}{3}(\lambda_{11}^{\rm ra} - \lambda_{11}^{\rm er}) \ , \tag{6.2}$$

where $\lambda_{00}^{\rm ra}$ and $\lambda_{00}^{\rm er}$ are the ordinary BCS parameters for intra- and intersheet scattering and where $\lambda_{11}^{\rm ra}$ and $\lambda_{11}^{\rm er}$ are obtained from the $\lambda_{LL'}$, Eq. (2.4), when the Γ_{15} functions, Eqs. (2.14) and (2.15), are substituted for the FS harmonics F_L and $F_{L'}$. What bedevils the p-state pairing interaction in Pd is the fact that for the *intra*sheet (i.e., small momentum) scattering of the d electrons the dominant d-f contribution to the squared electron-phonon matrix element, $|g(\vec{k},\vec{k}')|^2$, is proportional to $|\vec{k}-\vec{k}'|^2$. This dependence is responsible for $\lambda_{11}^{\rm ra} \approx -\lambda_{00}^{\rm ra}$, Eq. (5.12). On the other hand, for simple metals with a single spherical FS the dominant s-p contribution to $|g|^2$ results in a strong forward lobe of $I^{\rm ph}(\vec{k},\vec{k}')$ yielding $\lambda_1^{\rm ph} \approx \frac{1}{2}\lambda_0^{\rm ph}$.[6] As for the *inter*sheet (i.e., large angle) scattering, we get $\lambda_{11}^{\rm er} = -\lambda_{00}^{\rm er}$, Eq. (5.10), and therefore the p-state eigenvalue $\lambda_1^{\rm ph}$, Eq. (6.2), almost vanishes.

To actually calculate the $\lambda^{\rm ra}$ and $\lambda^{\rm er}$ from $I^{\rm ph}(\vec{k},\vec{k}')$, Eq. (3.1), we must also simplify the phonon dispersion, $\omega_i(\vec{k}-\vec{k}')$. For the [100] and [110] directions the dispersions are known from neutron scattering data.[16] For $\lambda^{\rm ra}$ we use a Debye model, $\omega_i(\vec{q}) = u_i q$, and estimate u_i as described in the text following Eq. (3.6); we then get $\omega(k_F) = 2.1 \times 10^{13}$ sec^{-1}, where $k_F = 2.44a^{-1}$ is the radius of a sphere. The parameters $\lambda^{\rm er}$ are determined by momentum transfers, $|\vec{k}-\vec{k}'| \geq 1.27(\pi/a)$, and, therefore, we use here the Einstein model, estimating from the experimental data the proper frequency ω_E. If, however, the Einstein model were applied to both intra- and intersheet scattering processes, the result would be

$$\lambda_1^{\rm ph} = 0 \ . \tag{6.3}$$

The phonon interaction, $I^{\rm ph}(\vec{k},\vec{k}')$, also depends on the electron-phonon matrix element $g(\vec{k},\vec{k}')$, Eq. (4.7). This is factorized into $\vec{k}$ and $\vec{k}'$-dependent functions by using the LCMTO representation for the Bloch waves.

Then, the coupling parameters $\lambda^{\rm ra} = \lambda^{\rm Debye}$ and $\lambda^{\rm er} = \lambda^{\rm Einstein}$ can be calculated analytically, since the $\vec{k}$ and $\vec{k}'$ integration on the FS are now independent.

The ratio between the p-state and s-state pairing interactions, $\lambda_1^{\rm ph}/\lambda_0^{\rm ph}$, is given by Eq. (5.13), setting $\mu^* = 0$. The result depends only on the value of $C = \omega_E^2/2\omega^2(k_F)$ and is shown in Fig. 2. From the experimental phonon data, we take $C = 1.235$ yielding a weak attractive p-state interaction.

Finally, the numerical value for the BCS parameter $\lambda_0^{\rm ph}$ depends on two parameters, C and λ_{00}^E, the latter given by Eq. (5.14). With the $K^{(0)}$ values given in

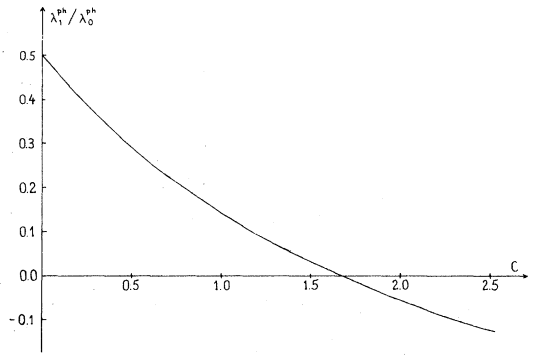

FIG. 2. Ratio between s- and p-state pairing parameters, $\lambda_1^{\rm ph}/\lambda_0^{\rm ph}$, as a function of the phonon parameter, $C = \omega_E^2/2\omega^2(k_F)$, where ω_E is the Einstein frequency for intersheet scattering and $\omega(k_F)$ is the Debye frequency for the momentum k_F corresponding to the radius of a subsphere.

Appendix B, λ_{00}^E can be written

$$\lambda_{00}^E = \frac{N(0)}{M\omega_E^2}\left(\frac{1}{4\pi}\right)^2 (0.0862M_{pd}^2 + 0.2382|M_{pd}M_{df}| + 0.1646M_{df}^2) \ . \tag{6.4}$$

To evaluate λ_{00}^E we need the following parameter values: $N(0)$ (density of states; $3m^*k_F V/2\pi^2 N$) $=14.15$ states/atom Ry; μ_2 (band mass at the center of gravity) $=6.79$ a.u.; ω_E (Einstein frequency for intersheet scattering) $=3.3 \times 10^{13}$ sec^{-1}; k_F (Fermi momentum of a subsheet sphere) $=0.627$ Å^{-1}; M (atomic mass of Pd) $=106.4$ amu; M_{pd}^2 (squared unscreened p-d matrix element) $=27.4$ (ev/Å)^2; M_{df}^2 (squared d-f matrix element, screened by a factor of 2) $=1402.8$ (eV/Å)^2. Here M_{pd} is the unscreened matrix element calculated by Pettifor.[17] M_{df} is Pettifor's value reduced by a factor $\sqrt{2}$, by virtue of screening effects. This reduction is used by Papaconstantopoulos *et al.*[18] in their calculation of T_c for 32 metals. With the above parameter values and the values found for the $K^{(0)}$ integrals in Appendix B, we get λ_{00}^E and $\lambda_0^{\rm ph} = 0.153$,[19] in perfect agreement with the value of 0.148 of Ref. 18.

In summary, based on a simple electron-phonon model, that yields a reliable value for the BCS parameter $\lambda_0^{\rm ph}$, we find the p-state pairing interaction $\lambda_1^{\rm ph}$ to be almost zero ($\lambda_1^{\rm ph} = 0$ for the Einstein model). The reason for the smallness of $\lambda_1^{\rm ph}$ is the cancellation between the contributions from the small-angle intrasheet and the large-momentum intersheet scattering. Both of these contributions, $\lambda_{11}^{\rm ra}$ and $\lambda_{11}^{\rm er}$, are repulsive and it is evident from the eigenvalues for p-state pairing, Eqs. (2.24)–(2.26), that either $\lambda_{11}^{\rm ra}$ must be sufficiently attractive or $\lambda_{11}^{\rm er}$ must be sufficiently repulsive in order to arrive at an attractive p-state interaction due to phonon exchange.

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APPENDIX A: STRUCTURE CONSTANTS

The structure constants $\tilde{S}_{LL'}(\vec{k})$ defined by Eq. (4.6) can be written

$$\tilde{S}_{L,2\alpha}(\vec{k}) = -\frac{1}{2l+1}\left(\frac{\tau_l}{2\mu_2(2l+3)}\right)^{1/2} \times \sum_{\vec{R}\neq\vec{0}} e^{i\vec{k}\cdot\vec{R}} S(L,2\alpha;\vec{R}) \ , \tag{A1}$$

where the $S(L,2\alpha;\vec{R})$ are given by Andersen *et al.*, Table II.[20] Expanding $\tilde{S}$ in terms of spherical harmonics we have

$$\tilde{S}_{L,2\alpha}(\vec{k}) = -\frac{1}{2l+1}\left(\frac{\tau_l}{2\mu_2(2l+3)}\right)^{1/2} \times \sum_{L'} i^{l'} j_{l'}(kR) Z_{L'}(\hat{k}) \times \sum_{\vec{R}\neq\vec{0}} Z_{L'}(\hat{R}) S(L,2\alpha;\vec{R}) \ . \tag{A2}$$

The following structure constants are of interest here:

$$S(s,xz;\vec{R}) = -2(4\pi)^{1/2}\left(\frac{s}{R}\right)^3 Z_{21}(\hat{R}) \ , \tag{A3}$$

$$S(z,xz;\vec{R}) = -12\left(\frac{40\pi}{21}\right)^{1/2}\left(\frac{s}{R}\right)^4 Z_{31}(\hat{R}) \ , \tag{A4}$$

$$S(x,xz;\vec{R}) = -12\left(\frac{40\pi}{21}\right)^{1/2}\left(\frac{s}{R}\right)^4 Z_{31}(\sigma_{\bar{x}z}\hat{R}) \ , \tag{A5}$$

$$S(xz^2,xz;\vec{R}) = -10\left(\frac{280\pi}{11}\right)^{1/2}\left(\frac{s}{R}\right)^6 \times [Z_{50}(\hat{R}) + (\tfrac{21}{20})^{1/2} Z_{52}(\hat{R})] \ . \tag{A6}$$

[$\sigma_{\bar{x}z}$ is a reflection at a plane normal to $(-x,0,z)$.]

Substitution into Eq. (A1) gives

$$\tilde{S}_{00,xz}(\vec{k}) = \left(\frac{2(4\pi)^3}{3\mu_2}\right)^{1/2}\left(\frac{s}{R}\right)^3 \sum_L i^l j_l(kR) Z_L(\hat{k}) A_{L,00} \ , \tag{A7}$$

$$\tilde{S}_{z,xz}(\vec{k}) = 4\left(\frac{(4\pi)^3}{21\mu_2}\right)^{1/2}\left(\frac{s}{R}\right)^4 \sum_L i^l j_l(kR) Z_L(\hat{k}) A_{L,10} \ , \tag{A8}$$

$$\tilde{S}_{xz^2,xz}(\vec{k}) = \frac{10}{3}\left(\frac{5(4\pi)^3}{77\mu_2}\right)^{1/2}\left(\frac{s}{R}\right)^6 \times \sum_L i^l j_l(kR) Z_L(\hat{k}) A_{L,31} \ , \tag{A9}$$

where τ_l is set equal to unity[21] and

$$A_{L,00} = \sum_{\vec{R}\neq\vec{0}} Z_L(\hat{R}) Z_{21}(\hat{R}) \ , \tag{A10}$$

$$A_{L,10} = \sum_{\vec{R}\neq\vec{0}} Z_L(\hat{R}) Z_{31}(\hat{R}) \ , \tag{A11}$$

$$A_{L,31} = \sum_{\vec{R}\neq\vec{0}} Z_L(\hat{R}) [Z_{50}(\hat{R}) + (\tfrac{21}{20}) Z_{52}(\hat{R})] \ . \tag{A12}$$

In general, the structure constants $\tilde{S}_{L,xz}(\vec{k})$ can be written

$$\tilde{S}_{L,xz}(\vec{k}) = c_L \sum_{L'} i^{l'} j_{l'}(kR) Z_{L'}(\hat{k}) A_{L'L} \ , \tag{A13}$$

where the coefficients c_L depend on s/R and μ_2 and where the $A_{L'L}$ have nonvanishing values only for certain parameter combinations L,L' (cf. Table I).

APPENDIX B: INTEGRALS $K_{ij}^{(\nu)}$

These integrals which appear in the parameters $\lambda_{00}^{(\nu)}$ are defined by Eq. (5.6). This equation contains the functions $T_{i-1,i}(\vec{k},\vec{k}')$ defined by Eq. (4.12) for the electron-phonon matrix element g.

TABLE I. L,L' combinations for which the reduced structure constants $A_{L'L}$ do not vanish [$L=(l,m), L'=(l',m')$].

l	m	(l',m')						
0	0	(2,1)	(4,1)	(4,3)	(6,1)	(6,3)	(6,5)	···
1	0	(1,1)	(3,1)	(3,3)	(5,1)	(5,3)	(5,5)	···
1	1	(1,0)	(3,0)	(3,2)	(5,0)	(5,2)	(5,4)	···
3	1	(1,0)	(3,0)	(3,2)	(5,0)	(5,2)	(5,4)	···

The $T_{i-1,i}$ given by Eqs. (4.13)–(4.15) depend on the structure constants $\tilde{S}$. When we substitute $\tilde{S}$, Eq. (A13), into Eqs. (4.13)–(4.15) we get T_{01}, T_{12}, and T_{23} and we can proceed to evaluate the integrals $K_{ij}^{(\nu)}$.

The result for $\nu=0$ is given by

$$K_{11}^{(0)} = \tfrac{2}{3} c_{00}^2 c_{10}^2 \sum_{LL'} j_l^2 j_{l'}^2 A_{L,00}^2 A_{L',10}^2 \ , \tag{B1}$$

$$K_{22}^{(0)} = 4\pi \times 2 d_{10}^2 c_{10}^2 \sum_{L} J_l^2 A_{L,11}^2 \ , \tag{B2}$$

$$K_{33}^{(0)} = 4\pi \times 2 d_{31}^2 c_{31}^2 \sum_{L} j_l^2 A_{L,31}^2 \ , \tag{B3}$$

$$K_{23}^{(0)} = 4\pi \times 2 d_{10} d_{31} c_{10} c_{31} \sum_{L} j_l^2 A_{L,11} A_{L,31} \ , \tag{B4}$$

$$K_{12}^{(0)} = K_{13}^{(0)} = 0 \ . \tag{B5}$$

Here

$$j_l = j_l(k_F R) \ , \quad d_{10} = (\tfrac{1}{5})^{1/2} \ , \quad d_{31} = (\tfrac{8}{35})^{1/2} \ ,$$

$$c_{10} = c_{11} = 4 \left(\frac{(4\pi)^3}{21 \mu_2} \right)^{1/2} \left(\frac{s}{R} \right)^4 \ ,$$

$$c_{00} = (\tfrac{7}{8})^{1/2} (R/s) c_{10} \ , \tag{B6}$$

$$c_{31} = (\tfrac{5}{2})(\tfrac{5}{33})^{1/2} (s/R)^2 c_{10} \ , \quad \frac{s}{R} = \frac{1}{2} \left(\frac{3\sqrt{2}}{\pi} \right)^{1/3} \ .$$

First, we show that in Eqs. (B2)–(B4) only the first term of the L summation has to be taken into account. Then, we demonstrate that $K_{11}^{(0)}$ is negligible compared with the other $K_{ij}^{(0)}$, Eqs. (B2)–(B4). Finally, we give a proof for the relation (5.7) for the $K_{ij}^{(\nu)}$.

In evaluating Eqs. (B1)–(B4), we need the following reduced structure constants $A_{LL'}$, Eqs. (A10)–(A12):

$$\left.\begin{matrix} A_{21,00} \\ A_{41,00} \\ A_{43,00} \end{matrix}\right\} = \frac{15\sqrt{3}}{4\pi \times 4\sqrt{2}} \left\{ \begin{matrix} 4(\frac{2}{3})^{1/2} \\ 1 \\ \sqrt{7} \end{matrix} \right. ;$$

$$\left.\begin{matrix} A_{11,10} \\ A_{31,10} \\ A_{33,10} \end{matrix}\right\} = \frac{7}{16 \times 4\pi} \left\{ \begin{matrix} \frac{12}{7}\sqrt{2} \\ 39 \\ 7\sqrt{15} \end{matrix} \right. ; \tag{B7}$$

$$\left.\begin{matrix} A_{10,11} \\ A_{30,11} \\ A_{32,11} \end{matrix}\right\} = \frac{7\sqrt{3}}{4\pi \times 8\sqrt{2}} \left\{ \begin{matrix} 4(\frac{3}{7})^{1/2} \\ -1 \\ 5\sqrt{15} \end{matrix} \right. ;$$

$$\left.\begin{matrix} A_{10,31} \\ A_{30,31} \\ A_{32,31} \end{matrix}\right\} = \frac{17\sqrt{77}}{31 \times 4\pi} \left\{ \begin{matrix} -4(\frac{3}{7})^{1/2} \\ 1 \\ \frac{21}{17}\sqrt{15} \end{matrix} \right. .$$

When only terms with $l \leq 4$ are considered in the expansion of $K_{ij}^{(0)}$ we have

$$K_{22}^{(0)} = 4\pi \tfrac{2}{5} c_{10}^2 [j_1^2 A_{10,11}^2 + j_3^2 (A_{30,11}^2 + A_{32,11}^2)]$$
$$= \frac{3.15}{4\pi} (c_{10} j_1)^2 [1 + 54.8333 (j_3/j_1)^2] \ , \tag{B8}$$

$$K_{33}^{(0)} = 4\pi \tfrac{16}{35} c_{31}^2 [j_1^2 A_{10,31}^2 + j_3^2 (A_{30,31}^2 + A_{32,31}^2)]$$
$$= \frac{3.15}{4\pi} (c_{10} j_1)^2 [1.9106 + 6.6562 (j_3/j_1)^2] \ , \tag{B9}$$

$$K_{23}^{(0)} = 4\pi \frac{8\sqrt{2}}{5\sqrt{7}} c_{10} c_{31} [j_1^2 A_{10,11} A_{10,31} + j_3^2 (A_{30,11} A_{30,31} + A_{32,11} A_{32,31})]$$
$$= -\frac{3.15}{4\pi} (c_{10} j_1)^2 [2.7645 - 36.9481 (j_3/j_1)^2] \ . \tag{B10}$$

Now, using the fact that M_{pd} and M_{df} have opposite sign,[17] we get

$$\sum_{i,j=2,3} K_{ij}^{(0)} M_{l-1,i} M_{j-1,j} = \frac{3.15 (c_{10} j_1 M_{pd})^2}{4\pi} \left\{ 1 + 1.9106 \left(\frac{M_{df}}{M_{pd}} \right)^2 + 2.7645 \left| \frac{M_{df}}{M_{pd}} \right| + 0.5282 \left[1 + 0.1214 \left(\frac{M_{df}}{M_{pd}} \right)^2 - 0.6738 \left| \frac{M_{df}}{M_{pd}} \right| \right] \right\} \ . \tag{B11}$$

Since $(M_{df}/M_{pd})^2 \approx 50$, the term proportional to j_3 contributes only 1% to the curly bracket and is therefore ignored. The general formulas for $K_{ij}^{(0)} (i,j = 2,3)$ are thus given by

$$K_{ij}^{(0)} = 4\pi \times 2 d_{L_i} d_{L_j} c_{L_i} c_{L_j} j_1^2 (k_F R) A_{10,L_i} A_{10,L_j} \ , \tag{B12}$$

where L_i and L_j are (11) and (31), respectively.

Next, we show that $K_{11}^{(0)}$ is negligible. By summing in Eq. (B1) up to $l=4$ we get

$$K_{11}^{(0)} = \tfrac{2}{3} c_{00}^2 c_{10}^2 \{ j_1^2 A_{11,10}^2 [j_2^2 A_{21,00}^2 + j_4^2 (A_{41,00}^2 + A_{43,00}^2)] + j_3^2 (A_{31,00}^2 + A_{33,10}^2 [j_2^2 A_{21,00}^2 + j_4^2 (A_{41,00}^2 + A_{43,00}^2)] \}$$
$$= \frac{3.15}{4\pi} (c_{10} j_1)^2 \tfrac{1}{24} \ . \tag{B13}$$

This value of $K_{11}^{(0)}$ is small compared to the $K_{ij}^{(0)}$ given by Eqs. (B8)–(B10). Furthermore, $M_{sp}^2 \ll M_{df}^2$ and, therefore, we can neglect the s-p contribution to $\lambda_{00}^{(\nu)}$, Eq. (5.8).[18]

Finally, we have to evaluate the $K_{ij}^{(\nu)}$ for $i,j=2,3$ and $\nu>0$. Using the Gaunt numbers,

$$G_1(l,l+1)=(3/4\pi)^{1/2}(l+1)\,[(2l+1)(2l+3)]^{-1/2}\ , \tag{B14}$$

$$G_2(l,l)=(5/4\pi)^{1/2}l(l+1)\,[(2l-1)(2l+3)]^{-1}\ , \tag{B15}$$

$$G_2(l,l+1)=(5/4\pi)^{1/2}3(l+1)(l+2)\,\{2(2l+3)[(2l+1)(2l+5)]^{1/2}\}^{-1}\ , \tag{B16}$$

the following expansion for the powers of $Z_{10}(\hat{k})$ can be verified:

$$\hat{Z}_{10}^{\nu}=\begin{cases}(\nu+1)^{-1}\left[1+\dfrac{5\nu}{\nu+3}\hat{Z}_{20}+\dfrac{9\nu(\nu-2)}{(\nu+3)(\nu+5)}\hat{Z}_{40}+\dfrac{13\nu(\nu-2)(\nu-4)}{(\nu+3)(\nu+5)(\nu+7)}\hat{Z}_{60}+\cdots\right], & \nu \text{ even}\\ (\nu+2)^{-1}\left[3\hat{Z}_{10}+\dfrac{7(\nu-1)}{\nu+4}\hat{Z}_{30}+\dfrac{11(\nu-1)(\nu-3)}{(\nu+4)(\nu+6)}\hat{Z}_{50}+\cdots\right], & \nu \text{ odd}\ .\end{cases} \tag{B17}$$

Here $\hat{Z}_L=[4\pi/(2l+1)]^{1/2}Z_L$. Substituting these expansions in $K_{ij}^{(\nu)}$, Eq. (5.6), and keeping only the terms with $l<3$—which is consistent with Eq. (B12) for $K_{ij}^{(0)}$—one gets three types of integrals. For $\nu=1$, we have

$$K_{ij}^{(1)}=-(4\pi/3)\times 2d_{L_i}d_{L_j}c_{L_i}c_{L_j}j_1^2A_{10,L_i}A_{10,L_j}=-\tfrac{1}{3}K_{ij}^{(0)}\ . \tag{B18}$$

For even ν two types of integrals occur in $K_{ij}^{(\nu)}$

$$\begin{aligned}\int d\hat{k}'\,d\hat{k}\,[\hat{Z}_{20}(\hat{k})+\hat{Z}_{20}(\hat{k}')]\,T_{i-1,i}^{*}T_{j-1,j}\ &=2d_{L_i}d_{L_j}\int d\hat{k}\,\hat{Z}_{20}(\hat{k})\tilde{S}_{L_i}\tilde{S}_{L_j}\int d\hat{k}'\\ &=2\times 4\pi d_{L_i}d_{L_j}c_{L_i}c_{L_j}\sum_{LL'}i^{l-l'}j_lj_{l'}A_{LL_i}A_{L'L_j}G_{20}(LL')\left(\frac{4\pi}{5}\right)^{1/2}\\ &\cong 2\times 4\pi d_{L_i}d_{L_j}c_{L_i}c_{L_j}j_1^2A_{10,L_i}A_{10,L_j}\times\tfrac{2}{5}=\tfrac{2}{5}K_{ij}^{(0)}\ ,\end{aligned} \tag{B19}$$

and

$$\int d\hat{k}\,d\hat{k}'\,\hat{Z}_{20}(\hat{k})\,\hat{Z}_{20}(\hat{k}')\,T_{i-1,i}^{*}T_{j-1,j}=0\ . \tag{B20}$$

Again L_i and L_j can take the values (11) and (31), respectively, and the last equation follows from $A_{20,L_i}=0$ (cf. Table I). Using Eqs. (B18)–(B20), one arrives at Eq. (5.7).

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[13]For p-state pairing, electron 1 has vanishing amplitude at the site of electron 2, and vice versa. Hence, in the atomic-site representation, where the s-state Coulomb interaction is governed by the intra-atomic Coulomb integral, the p-state interaction for a nondegenerate band is determined by the interatomic Coulomb interaction; it is $\frac{1}{3}U$ (interatomic) for Pd.

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