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Electron-phonon interaction in cubic systems: Application to niobium*

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To a good approximation the electron-phonon coupling parameter λ, which determines the superconducting transition temperature T_c and the electron-phonon mass enhancement, may be written as the product of two factors: one which depends upon the phonon frequencies, $(M\langle\omega^2\rangle)^{-1}$, and a purely electronic factor η. This latter quantity is determined by the band structure and the electron-phonon matrix elements. In this paper we develop a method of calculating η from first principles making only the rigid muffin-tin approximation to describe the electron-phonon coupling. As an illustration we evaluate η for Nb and discuss the significance of the calculation with regard to the validity of describing the electron-phonon interaction in transition metals by the rigid muffin-tin approximation. We also attempt to isolate those features of the band structure which appear to have the strongest effect on T_c.

I. INTRODUCTION

In a metal, an electron near the Fermi surface can be scattered by the thermal vibrations of the lattice, and it can also emit and absorb virtual phonons. The first of these processes gives rise to electrical resistance and ultrasonic attenuation. The second is responsible for a slowing down of electrons near the Fermi surface, i.e., mass enhancement. It also leads to an effective attractive force between pairs of the electrons via exchange of phonons. This is the pairing force which at sufficiently low temperatures leads to superconductivity.

In order to understand quantitatively these phenomena one needs a proper description of the electron-phonon interaction. Ever since the pioneering work of Bardeen[1] this has been one of the central themes in the theory of metals.[2] For simple metals one can introduce a weak pseudopotential to describe the interaction between the ions and electrons and therefore, this part of the problem can be treated in perturbation theory. Then the only difficult task is to find an adequate way of taking into account the electron-electron interaction, namely, the screening. Thanks to much work in the field this problem appears to be reasonably well understood.[3] On the other hand, for transition metals where the electron-ion interaction potential is in no sense weak, such first-principles theory does not exist. Most work in the past concentrated on the qualitative features of the problem like the temperature dependence of the resistivity, and used the electron-phonon matrix elements as adjustable parameters.[4] Under this circumstance it did not matter much what one took to be the electron-phonon vertex.

Recently it has been suggested[5,6] that in transition metals the electron-phonon interaction may be described by the rigid muffin-tin approximation. That is to say that one may assume that when one atomic nucleus is displaced while the others are held fixed, the total potential change seen by an electron is proportional to the gradient of the muffin-tin potential which appears in the Schrödinger equation of band theory.

This construction simplifies the evaluation of the electron-phonon matrix elements enormously, since it eliminates the necessity for explicit treatment of screening.[7] Therefore, establishing its range of validity, if any, would be a significant step towards understanding the electron-phonon interaction in transition metals. However, even after such drastic simplifications it is still not easy to make sufficiently accurate calculations of physical observables to test the model. Calculation of the electrical resistivity, for example, requires a solution of the Boltzmann equation,[8] and traditional techniques for solving this equation introduce additional uncertainties which make the assessment of the results difficult.

Fortunately, due to recent advances in theory and experiments,[9-11] it now appears to be the case that superconductivity is not only a sensitive probe of the electron-phonon interaction, but the manner of its probing is relatively amenable to theoretical analysis. In particular, the electron mass enhancement parameter λ and its electronic component η are now known for many materials,[11] and these quantities are rapidly becoming accessible to accurate calculations.[12-14] Thus it is now reasonable to hope that such calculations will provide a quantitative testing ground for the rigid muffin-tin approximation.

As was shown by Gaspari and Gyorffy,[6] the evaluation of the electronic factor η is particularly easy. By making use of the rigid muffin-tin approximation they have derived a simple but approximate formula for η in terms of quantities which could be obtained during the course of a fairly standard band-structure calculation. Early approximate evaluations of this theory were encouraging in that they gave a good semiquantitative picture of the trends in the superconducting transition temperature T_c of transition metals, and some of their compounds, without fitting parameters. Subsequently, the formula was evaluated more accurately by Klein and Papanconstantopoulos[12-14] for a variety of systems such as V, Nb, NbC, TaC, PdH, V_3Si, and metallic H. While these calculations demonstrated that the theory gives a useful guide to T_c, among the most interesting superconductors, they brought to light some significant discrepancies between theory and experiment for V, Nb, and Ta. Even though not all of the elements of the puzzle are fully understood at the present, it now seems that a sufficiently accurate evaluation of η will allow a very direct quantitative comparison between the consequences of the rigid muffin-tin approximation and experiments. As we have argued above, such confrontation between theory and experiments would be an important step in establishing an adequate foundation for the theory of electron-phonon interaction in strong-scattering systems.

With the above comments in mind we have generalized the theory of Gaspari and Gyorffy, making the expression for η virtually exact within the rigid muffin-tin approximation. Furthermore, we have developed a rapid and very accurate method for evaluating the new formula using the constant-energy search formulation of the Korringa-Kohn-Rostocker (KKR) band theory due to Faulkner, Davis, and Joy. We illustrate the method by evaluating η for Nb. We then discuss the significance of the new terms in our expression for η, and compare our results with experiments and other calculations. Finally, we make some general remarks concerning the physical significance of the quantities which enter the expression for η, and list some of the conditions necessary to obtain a high value of η.

II. PHONON ENHANCEMENT OF THE ELECTRONIC MASS

As a formal background to our calculation we shall now briefly review the way in which λ arises in the theory of the electron-phonon interaction.[15] Consider an electron with Bloch energy E_k near the Fermi energy E_F. Due to its interaction with the phonons, this electron will acquire a self-energy $\Sigma(k, E)$. Neglecting the imaginary part of this self-energy, the renormalized energy of the electron will be the solution to the equation $E - E_k - \mathrm{Re}\Sigma(k, E) = 0$. It turns out that $\Sigma(k, E)$ does not depend very much on k, and therefore, for $E \sim E_F$, it is customary to replace it with its average value over the Fermi surface $\bar{\Sigma}(E)$. Measuring all energies from E_F, we are interested in $\bar{\Sigma}(E)$ for small E. Thus we write $\mathrm{Re}\bar{\Sigma}(E) = -\lambda E$, where λ is defined by the relation $\lambda = -[d\,\mathrm{Re}\bar{\Sigma}(E)/dE]_{E=E_F}$. Clearly, the renormalized electron energy is $\tilde{E}_k = E_k/(1+\lambda)$. For a free-electron-like band, this means $\tilde{E}_k = h^2k^2/2m^*$, where $m^*/m = 1+\lambda$. Hence the name mass-enhancement parameter.

The interest in λ stems from the fact that it appears directly in a number of expressions for physical observables. For instance, the electronic specific heat is given by $c = \pi^2 k_B T N(E_F)/3(1+\lambda)$, and the superconducting transition temperature T_c is well approximated by[10,16]

$$T_c = \frac{\langle\omega\rangle}{1.2}\exp\left(\frac{-1.04(1+\lambda)}{\lambda - \mu^*(1+.62\lambda)}\right), \tag{2.1}$$

where $\langle\omega\rangle$ is an average phonon frequency defined in Ref. 16, and μ^* is an electron-electron interaction parameter.

Little is known rigorously about μ^* except that it should be small, due to the retarded nature of the electron-phonon interaction,[17] and that it should not vary very much from one metal to another.[11] Tunneling and isotope effect measurements indicate that μ^* is approximately 0.1 to 0.15 for most superconductors.[9,16]

Evaluating $d\,\mathrm{Re}\bar{\Sigma}(E)/dE$ at $E = E_F$ yields the following expression for λ (in atomic units):[3,10]

$$\lambda = \frac{2\Omega^2}{(2\pi)^6 N(E_F)} \int d^3k \int d^3k' \sum_{\nu} |g^{\nu}_{kk'}|^2 \omega^{\nu -1}_{kk'}\, \delta(E_k - E_F) \times \delta(E_{k'} - E_F)\,, \tag{2.2}$$

where Ω is the volume of a Wigner-Seitz cell, $N(E_F)$ is the Fermi energy density of states of one spin, and $g^{\nu}_{kk'}$ is the electron-phonon matrix element for scattering between Bloch states k and k' due to a phonon of mode number ν, frequency $\omega^{\nu}_{k-k'}$, and polarization vector $\vec{\epsilon}^{\,\nu}_{k-k'}$. The electron-phonon matrix element can be written in terms of an operator ∇V, defined so that $\vec{u}\cdot\nabla V$ is the change in crystal potential when an atom experiences a displacement $\vec{u}$:

$$|g^{\nu}_{kk'}|^2 = \left|\int_{\Omega} d^3r\, \psi^*_k(r)\vec{\epsilon}^{\,\nu}_{k-k'}\cdot \nabla V \psi_{k'}(\vec{r})\right|^2 (2M\omega^{\nu}_{k-k})^{-1}\,. \tag{2.3}$$

The wave functions in (2.3) are normalized to unity over the Wigner-Seitz cell Ω.

λ may also be written in terms of the phonon density of states $F(\omega)$ as

$$\lambda = 2\int \omega^{-1}\alpha^2(\omega)F(\omega)\,d\omega\,, \qquad (2.4)$$

where $\alpha^2(\omega)$ is a measure of the coupling of phonons of frequency ω to the electrons. The function $\alpha^2F(\omega)$ can be obtained from an analysis of tunneling data for many superconductors.

Evidently, λ depends upon the lattice dynamics and upon the electronic band structure. Clearly it would simplify the analysis if we had to deal with only one aspect of the problem at a time. Therefore we follow McMillan[10] and Hopfield[11] and write

$$\lambda = \eta/M\langle\omega^2\rangle\,, \qquad (2.5)$$

where $\langle\omega^2\rangle$ is defined by

$$\langle\omega^2\rangle = \int \omega\alpha^2F\,d\omega \Big/ \int \omega^{-1}\alpha^2F\,d\omega\,, \qquad (2.6)$$

and η is defined by

$$\eta = 2M\int \omega\alpha^2F\,d\omega\,. \qquad (2.7)$$

These somewhat artificial definitions turn out to be useful because it is found experimentally that $\langle\omega^2\rangle$ depends only weakly upon α^2, and thus is primarily determined by the phonon density of states. On the other hand, η is rigorously independent of the phonons, and depends only upon the Fermi-energy electronic structure.

The electronic factor η is given by[10]

$$\eta = \frac{\Omega^2}{(2\pi)^6N(E_F)}\int d^3k\int d^3k'\int d^3r\int d^3r'\,\nabla V(r)\cdot\nabla' V(r')\psi_k^*(r)\psi_{k'}(r)\psi_{k'}^*(r')\psi_k(r')\delta(E_k-E_F)\delta(E_{k'}-E_F)\,. \qquad (2.8)$$

Gaspari and Gyorffy[6] obtained a very simple expression for η,

$$\eta = \frac{2}{N(E_F)}\sum_l (l+1)(V'_{l,l+1})^2T_{ll}T_{l+1,l+1}\,, \qquad (2.9)$$

where

$$V'_{l,l+1} = \int r^2\,dr\,R_l(r)\frac{\partial V}{\partial r}R_{l+1}(r)\,, \qquad (2.10)$$

and

$$T_{ll} = n_l^B \Big/ \int r^2R_l^2(r)\,dr = (\sqrt{E_F}/\pi)n_l^B/n_l^{(1)}\,. \qquad (2.11)$$

n_l^B in (2.11) is the lth-partial-wave contribution to the band-theory density of states at the Fermi energy, $n_l^{(1)}$ is the density of states at the Fermi energy of a single muffin-tin potential in a zero-potential background, and R_l is the regular solution to the radial Schrödinger equation. n_l^B and $n_l^{(1)}$ may be evaluated either within a muffin tin or within a Wigner-Seitz sphere.

Equation (2.9) follows from the assumption that the wave functions $\psi_k(r)$ which enter (2.8) have an angular variation in k space appropriate to spherical bands. We shall derive below an expression for η which avoids this approximation. Gaspari and Gyorffy also showed that if one assumes that V is given by the rigid muffin-tin approximation, then (2.10) may be evaluated exactly in terms of the phase shifts.

$$V'_{l,l+1} = \sin(\delta_l - \delta_{l+1})\,. \qquad (2.12)$$

Equation (2.12) assumes that the radial wave functions are normalized so that for r greater than the muffin-tin radius, $R_l(r) = j_l\cos\delta_l - n_l\sin\delta_l$, where j_l and n_l are the spherical Bessel and Neuman functions, and δ_l is the phase shift for scattering with angular momentum l from the muffin-tin potential V which was used to determine R_l. Note that Eq. (2.12) differs by a sign from the original expression of Gaspari and Gyorffy. This sign error in the original expression does not affect η since the matrix elements always enter bilinearly. In the following we shall retain the rigid muffin-tin approximation for $V'_{l,l+1}$.

Although Gaspari and Gyorffy assumed spherical energy bands in deriving (2.9), it was observed by John[18] that (2.9) is an exact evaluation of (2.8) for cubic systems with one atom per unit cell if there are no contributions for which $l+1$ in Eq. (2.9) exceeds 2. Recently, Boyer *et al.*[19] have used the Gaspari-Gyorffy formula to estimate λ for V, Nb, and Ta. The most surprising result of their calculation was that they found the $l+1=3$ (d-to-f scattering) term in (2.9) to be dominant, so that in fact, the correction terms due to nonspherical bands must be considered.

In view of the fact that their results for η seem to disagree with experiments, we thought it desirable to develop an alternative method for evaluating η. Apart from checking whether their surprisingly large $n_3^B/n_3^{(1)}$ is indeed correct, we also sought to investigate all possible corrections to Eq. (2.9) within the rigid muffin-tin approximation. As is clear from Eq. (2.10), one should not expect to find significant contributions from going to l's higher than 3 in Eq. (2.9), since the phase shifts are known to be small for $l > 2$. Therefore, we attempted to remove the assumption of spherical bands. In fact, we have obtained a generalization of Eq. (2.9) which is exact for systems in which all atoms sit at sites having cubic symmetry. Like Eq. (2.9), the new expression contains the matrix elements (2.10) which in the rigid muffin-tin approximation are expressible in terms of phase shifts. However, the coefficients analogous to (2.11) no longer have the simple interpretation in terms of partial densities of states. Nevertheless, there are only a few of these which are important, and we tabulate them for angular momentum values as high as $l=3$.

To evaluate η we first express (2.8) in terms of the density matrix $\rho(\vec{r},\vec{r}\,',E_F)$. In the following we shall omit vector notation except where necessary to avoid ambiguity. Thus we write

$$\eta = N(E_F)^{-1}\int d^3r\int d^3r'\,\rho(r,r';E_F)\times\nabla V(r)\cdot\nabla' V(r')\rho(r',r;E_F)\,, \tag{2.13}$$

where

$$\rho(r,r';E_F)=\frac{\Omega}{(2\pi)^3}\int d^3k\,\psi_k^*(r)\,\psi_k(r')\delta(E_k-E_F)\,. \tag{2.14}$$

We find it convenient to expand the wave functions and density matrix in terms of Kubic harmonics.[20]

$$\psi_k(\vec{r})=\sum_{l\mu t} i^l R_l(r)C^t_{l\mu}(k)K^t_{l\mu}(\hat{r})\,, \tag{2.15}$$

$$\rho(\vec{r},\vec{r}\,';E_F)=\sum_{l\mu t}\sum_{l'\mu't'} i^{l-l'}R_l(r)R_{l'}(r')\times K^t_{l\mu}(\hat{r})K^{t'}_{l'\mu'}(\hat{r}')T^{tt'}_{l\mu,l'\mu'}\,, \tag{2.16}$$

where R_l is the regular solution to the radial Schrödinger equation, and $K^t_{l\mu}$ is a cubic harmonic of orbital quantum number l and row μ of irreducible representation t. $C^t_{l\mu}$ and $T^{tt'}_{l\mu,l'\mu'}$ are real coefficients. The wave-function coefficients $C^t_{l\mu}$ are determined from the symmetrized KKR equations,

$$\sum_{l'\mu'}\Lambda^t_{l\mu l'\mu'}(E,k)C^t_{l'\mu'}(E,k)=0\,, \tag{2.17}$$

and from the requirement that the wave functions be normalized to unity over the Wigner-Seitz cell. $T^{tt'}_{l\mu,l'\mu'}$ is a Brillouin-zone average of products of C's:

$$T^{tt'}_{l\mu,l'\mu'}=(2\pi)^{-3}\sum_n\int_{\text{FS}} k_n^2\,d\hat{k}\,\frac{C^t_{l\mu}(k)C^{t'}_{l'\mu'}(k)}{\hat{k}\cdot\nabla_k E_{k_n}}\,. \tag{2.18}$$

$\vec{k}_n$ is a solution to (2.17) for $E=E_F$. If the Fermi surface has more than one sheet, the integral is carried out over each and then the summation indicated in (2.18) is performed.

Clearly the diagonal part of the density matrix $\rho(r,r;E_F)$ is just the density of states per unit volume at point r, and must therefore have cubic symmetry. Imposition of cubic symmetry on the products of Kubic harmonics in (2.16) leads to the requirement that

$$T^{tt'}_{l\mu,l'\mu'}=T^t_{ll'}\delta_{\mu\mu'}\delta_{tt'}\,. \tag{2.19}$$

In fact, (2.16) may be written through terms with $l=3$ as

$$\begin{aligned}\rho(\vec{r},\vec{r}\,';E_F)={}&T^{(1)}_{00}F^{(1)}_{00}(\hat{r},\hat{r}')R_0(r)R_0(r')+T^{(15)}_{11}F^{(15)}_{11}(\hat{r},\hat{r}')R_1(r)R_1(r')+[T^{(25')}_{22}F^{(25')}_{22}(\hat{r},\hat{r}')+T^{(12)}_{22}F^{(12)}_{22}(\hat{r},\hat{r}')]R_2(r)R_2(r')\\&+[T^{(25)}_{33}F^{(25)}_{33}(\hat{r},\hat{r}')+T^{(15)}_{33}F^{(15)}_{33}(\hat{r},\hat{r}')+T^{(2')}_{33}F^{(2')}_{33}(\hat{r},\hat{r}')]R_3(r)R_3(r')\\&-T^{(15)}_{13}F^{(15)}_{13}(\hat{r},\hat{r}')R_1(r)R_3(r')-T^{(15)}_{31}F^{(15)}_{31}(\hat{r},\hat{r}')R_3(r)R_1(r')\,.\end{aligned} \tag{2.20}$$

The angular terms $F^t_{ll'}(\hat{r},\hat{r}')$ are defined by

$$F^t_{ll'}(\hat{r},\hat{r}')=\sum_\mu K^t_{l\mu}(\hat{r})K^t_{l'\mu}(\hat{r}')\,. \tag{2.21}$$

Explicit forms are listed in Table I.

Substituting (2.20) into (2.13), and writing the gradients as

$$\nabla V(r)\cdot\nabla' V(r')=\frac{\partial V(r)}{\partial r}\,\frac{\partial V(r')}{\partial r'}\,\frac{xx'+yy'+zz'}{rr'}\,, \tag{2.22}$$

we have

$$\eta=N(E_F)^{-1}\sum_{l_1l_2l_3l_4}\sum_{t_1t_2}T^{t_1}_{l_1l_2}T^{t_2}_{l_3l_4}V'_{l_1l_4}V'_{l_2l_3}i^{l_1-l_2}i^{l_3-l_4}\mathfrak{F}^{t_1t_2}(l_1l_2;l_3l_4)\,, \tag{2.23}$$

where

TABLE I. Angular functions appearing in the expansion of the density matrix for cubic systems $F^{t}_{ll'}(\hat{r},\hat{r}')$.

l	l'	t	$F^{t}_{ll'}(\hat{r},\hat{r}')*4\pi$
0	0	Γ_1	1
1	1	Γ_{15}	$3(xx'+yy'+zz')/rr'$
2	2	$\Gamma_{25'}$	$15(yzy'z'+xzx'z'+xyx'y')/r^2r'^2$
2	2	Γ_{12}	$\frac{15}{2}(x^2x'^2+y^2y'^2+z^2z'^2)/r^2r'^2-\frac{5}{2}$
3	3	Γ_{25}	$\frac{105}{4}[xx'(z^2-y^2)(z'^2-y'^2)+yy'(x^2-z^2)(x'^2-z'^2)+zz'(x^2-y^2)(x'^2-y'^2)]/r^3r'^3$
3	3	Γ_{15}	$\frac{175}{4}[x(x^2-\frac{3}{5}r^2)x'(x'^2-\frac{3}{5}r'^2)+y(y^2-\frac{3}{5}r^2)y'(y'^2-\frac{3}{5}r'^2)+z(z^2-\frac{3}{5}r^2)z'(z'^2-\frac{3}{5}r'^2)]/r^3r'^3$
3	3	$\Gamma_{2'}$	$105(xyzx'y'z')/r^3r'^3$
1	3	Γ_{15}	$-\frac{5}{2}\sqrt{21}[xx'(x'^2-\frac{3}{5}r'^2)+yy'(y'^2-\frac{3}{5}r'^2)+zz'(z'^2-\frac{3}{5}r'^2)]/rr'^3$
3	1	Γ_{15}	$-\frac{5}{2}\sqrt{21}[x(x^2-\frac{3}{5}r^2)x'+y(y^2-\frac{3}{5}r^2)y'+z(z^2-\frac{3}{5}r^2)z']/r^3r'$

$$\mathfrak{F}^{t_1t_2}(l_1l_2;l_3l_4)=\int d\Omega\int d\Omega' F^{t_1}_{l_1l_2}(\hat{r},\hat{r}')F^{t_2}_{l_3l_4}(\hat{r}',\hat{r})\frac{xx'+yy'+zz'}{rr'}\,. \tag{2.24}$$

These integrals have been evaluated and are listed in Table II.

Because of cubic symmetry, the coefficients $T^{t}_{ll'}$ are diagonal in l and l' for l and l' less than 3. For l and l' less than or equal to 3 only one off-diagonal term enters, $T^{(15)}_{13}$. This coefficient determines the amount of electronic density which arises from the product of wave functions having Γ_{15} symmetry for both the $l=1$ and $l=3$ orbital quantum numbers. Note also that l_1 and l_4, and l_2 and l_3 must differ by ±1 if $\mathfrak{F}^{t_1t_2}(l_1l_2;l_3l_4)$ is to be nonzero.

Using the explicit results for the angular integrals listed in Table II, we have

$$\begin{aligned}\eta=2N(E_F)^{-1}\{&T^{(1)}_{00}T^{(15)}_{11}V'^2_{01}+T^{(15)}_{11}[\tfrac{6}{5}T^{(25')}_{22}+\tfrac{4}{5}T^{(12)}_{22}]V'^2_{12}+\tfrac{1}{35}[30T^{(25')}_{22}T^{(25)}_{33}+18T^{(25')}_{22}T^{(15)}_{33}+15T^{(25')}_{22}T^{(2')}_{33}+15T^{(12)}_{22}T^{(25)}_{33}\\&+27T^{(12)}_{22}T^{(15)}_{33}]V'^2_{23}\\&+\tfrac{12}{5}\sqrt{\tfrac{3}{7}}[T^{(15)}_{13}T^{(25')}_{22}-T^{(15)}_{13}T^{(12)}_{22}]V'_{12}V'_{23}\}\,.\end{aligned} \tag{2.25}$$

Equation (2.25) can be written so as to show explicitly the corrections introduced by the assumption of cubic rather than spherical symmetry.

$$\begin{aligned}\eta=2N(E_F)^{-1}\Big(&\sum_{l=0,1,2}(l+1)V'^2_{l,l+1}\overline{T}_{ll}\overline{T}_{l+1,l+1}+\tfrac{3}{35}V'^2_{23}[T^{(25')}_{22}-T^{(12)}_{22}][T^{(25)}_{33}-3T^{(15)}_{33}+2T^{(2')}_{33}]\\&+\tfrac{12}{5}\sqrt{\tfrac{3}{7}}\,V'_{12}V'_{32}[T^{(25')}_{22}-T^{(12)}_{22}]T^{(15)}_{13}\Big)\,,\end{aligned} \tag{2.26}$$

TABLE II. Angular integrals appearing in the expansion of η for cubic systems, $\mathfrak{F}^{t_1t_2}(l_1l_2;l_3l_4)$.

		l_3l_4	11	22	22	33	33	33	13	31
l_1	l_2	t_1 \ t_2	Γ_{15}	$\Gamma_{25'}$	Γ_{12}	Γ_{25}	Γ_{15}	$\Gamma_{2'}$	Γ_{15}	Γ_{15}
0	0	Γ_1	1	0	0	0	0	0	0	0
1	1	Γ_{15}		$\frac{6}{5}$	$\frac{4}{5}$	0	0	0	0	0
2	2	$\Gamma_{25'}$			0	$\frac{30}{35}$	$\frac{18}{35}$	$\frac{15}{35}$	$\frac{6}{5}\sqrt{3/7}$	$\frac{6}{5}\sqrt{3/7}$
2	2	Γ_{12}				$\frac{15}{35}$	$\frac{27}{35}$	0	$-\frac{6}{5}\sqrt{3/7}$	$-\frac{6}{5}\sqrt{3/7}$

where

$$\begin{aligned}\overline{T}_{00}&=T_{00}^{(1)}\,,\\ \overline{T}_{11}&=T_{11}^{(15)}\,,\\ \overline{T}_{22}&=\tfrac{1}{5}(3T_{22}^{(25')}+2T_{22}^{(12)})\,,\\ \overline{T}_{33}&=\tfrac{1}{7}(3T_{33}^{(25)}+3T_{33}^{(15)}+T_{33}^{(2')})\,.\end{aligned}\tag{2.27}$$

The first term in (2.26) is equivalent to (2.9). The two correction terms involve *d*-to-*f* scattering and *p*-to-*d*-to-*f* scattering. These nonspherical terms can in principle be quite large, especially since the $l=2$ term tends to be the dominant one. For example, if the density of *d* states at the Fermi energy were pure Γ_{12} and the *f* states were pure $\Gamma_{2'}$, the nonspherical correction would be -100% of the *d*-to-*f* spherical contribution. We will show, however, that for Nb the two correction terms are small and of opposite sign so that the total correction is less than 1% of the total contribution. Calculations on other 4*d* transition metals indicate that these nonspherical corrections are generally on the order of 10% or less for the cubic elements. It is likely, however, that they will be larger for compounds.

We then take (2.25) as the basis for our calculation. If the phase shifts at the Fermi energy are known, the matrix elements, $V'_{l,l+1}$ are easily calculated from (2.12). The density-matrix coefficients $T_{ll'}^{t}$, however, must be obtained from an integral over the Fermi surface (2.18). This integral is the subject of Sec. III.

III. FERMI-ENERGY DENSITY MATRIX

In the spirit of our previous remarks we now want to evaluate Eq. (2.25) with as few computational uncertainties as possible. Some years ago Faulkner, Davis, and Joy[21] demonstrated that the (KKR) band theory technique can be used to calculate constant-energy surfaces very efficiently. In these calculations, the KKR determinant $D(E,\vec{k})$ is generated for some energy E and a number of $\vec{k}$'s along a set of directions emanating from the center of the Brillouin zone. The $\vec{k}$'s such that $D(E,\vec{k})=0$ are the radii of the constant-energy surface. The volume within the constant-energy surface gives the number of electronic states having energy less than E [i.e., the integrated density of states $M(E)$]. The Fermi energy is that energy for which $M(E)$ is equal to the number of conduction electrons per atom in bands which are not completely filled.

Typically, a transition-metal Fermi surface will consist of several sheets. These sheets usually form fairly simple surfaces, however, they may be centered about points other than the center of the Brillouin zone. In Nb, one has a hole surface centered at Γ (Fig. 1), a multiply connected surface (Fig. 2) which may be taken to be centered at *P* (in which case it is an electron surface), and a hole surface centered at *N* (Fig. 3). We found it necessary to modify the constant-energy search progarms to allow for searches emanating from points other than the zone center, in order to generate a sufficiently dense set of points over the entire Fermi surface to allow accurate evaluation of (2.18).

In addition to $M(E)$, we obtain $N(E)$ directly from each constant-energy search. For this reason the determination of the Fermi energy usually takes only two or three constant-energy searches. Thus for Nb our initial guess was $E_F=0.62$ Ry. A

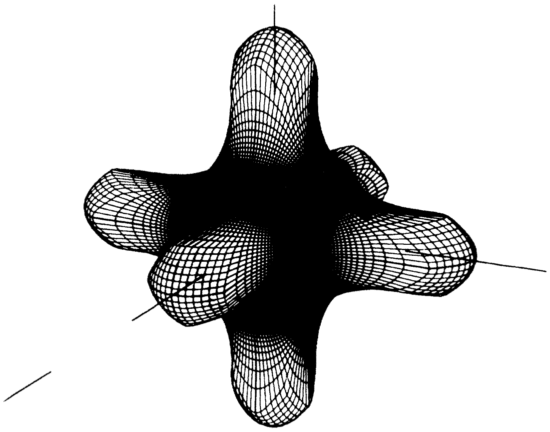

FIG. 1. Computer-generated perspective drawing of Γ centered hole jack in niobium.

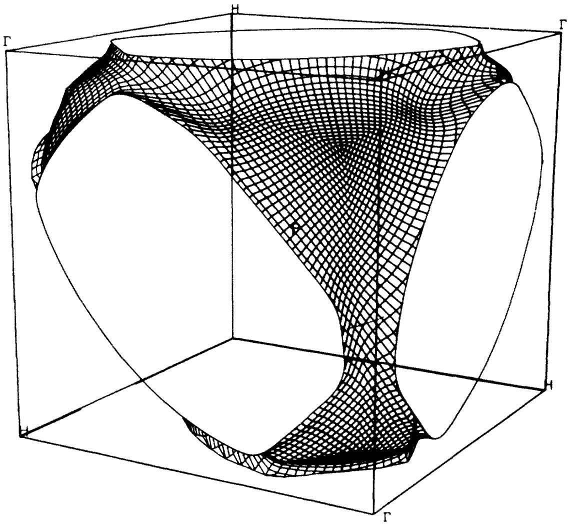

FIG. 2. Computer-generated perspective drawing of jungle-gym surface. The search was along rays centered at the point *P*.

constant-energy search at that energy yielded $M(E) = 2.4695$ states/spin and $N(E) = 11.11$ states/Ry spin. A linear extrapolation yielded $E_F = 0.623$ Ry, which was in error by only 0.000 17 Ry.

Typically, we search 561 directions in $\frac{1}{48}$th of the zone. This corresponds to 26 066 directions in the full zone. We also calculate the wave functions for each point on the surface. Typical search times range from 3 to 12 min (on an IBM 360/91), depending upon the value of l at which the KKR matrix is truncated, and whether or not prior knowledge of the Fermi surface is used to narrow the search range. The fact that this technique allows one to concentrate all of his calculational effort at one energy, combined with the numerical efficiency of the KKR method when operated in the constant-energy mode, allows us to calculate Fermi-surface properties with greater speed and accuracy than previous techniques.

We do not actually use a symmetrized KKR program as indicated in (2.17). We solve the usual KKR equation,

$$\sum_{l'm'} \Lambda_{lm,l'm'}(E,k)C_{l'm'}(E,k) = 0\,, \tag{3.1}$$

integrate over angles to obtain unsymmetrized density matrix coefficients,

$$T_{lm,l'm'} = \frac{\Omega}{(2\pi)^3} \sum_n \int d\hat{k}\, k_n^2 C_{lm}(k_n) C_{l'm'}(k_n) \Big/ (\hat{k}\cdot\nabla_k E_{k_n})\,, \tag{3.2}$$

and finally symmetrize these coefficients in a manner to be described below.

In addition, we have developed a normalization scheme which makes it unnecessary to calculate $\nabla_k E_k$ in (3.2). We find it more convenient to normalize our wave functions so that

$$\int \bar{\psi}_k^*(r)\bar{\psi}_k(r)\, d^3r = \Omega(\hat{k}\cdot\nabla_k E)^{-1}\,, \tag{3.3}$$

where the integration is over the Wigner-Seitz cell and Ω is the volume of the Wigner-Seitz cell. Bars distinguish quantities having the new normalization. This normalization costs very little in computational time and does not require calculations at another nearby energy. The details are described in the Appendix. With our new normalization, (3.2) becomes

$$T_{lm,l'm'} = (2\pi)^{-3} \sum_n \int d\hat{k}\, k_n^2 \bar{c}_{lm}(k_n)\bar{c}_{l'm'}(k_n)\,. \tag{3.4}$$

By taking advantage of the cubic symmetry of the system, the integrals Eqs. (3.2) or (3.4) can be restricted to the irreducible $\frac{1}{48}$th of the Brillouin zone. If $T^0_{lm,l'm'}$ is an unsymmetrized coefficient but with the domain of integration restricted to the irreducible $\frac{1}{48}$th of the zone, then

$$T^t_{ll'} = \frac{48}{d_t} \sum_{mm'} T^0_{lm,l'm'} Q^{ll';t}_{mm'}\,, \tag{3.5}$$

where d_t is the dimensionality of irreducible representation t. The matrices $Q^{ll';t}_{mm'}$ are listed in Table III and were obtained from the transformation matrices that relate real cubic harmonics to real spherical harmonics,

$$K^t_{l\mu}(\hat{r}) = \sum_m Y_{lm}(\hat{r}) u^{lt}_{m\mu} \tag{3.6}$$

by

$$Q^{ll',t}_{mm'} = \sum_\mu u^{lt}_{m\mu} u^{l't}_{m'\mu}\,. \tag{3.7}$$

The integration was performed using a trapezoidal scheme with Romberg refinements for the closed surfaces.

In order to calculate the density of states from a single constant-energy search one must integrate the density matrix for equal arguments over the Wigner-Seitz cell,

$$N(E) = \int_\Omega d^3r\, \rho(r,r;E) = \sum_{ll',t} T^t_{ll'}\rho^t_{ll'}\,, \tag{3.8}$$

where

$$\rho^t_{ll'} = \int r^2\, dr\, R_l(r)R_{l'}(r) \int_{\Omega_r} d\Omega_{\hat{r}}\, F^t_{ll'}(\hat{r},\hat{r})\,. \tag{3.9}$$

The angular integral in (3.9) is complicated by the fact that the limits are a function of r since the integration must be confined to the polyhedral Wigner-Seitz cell.

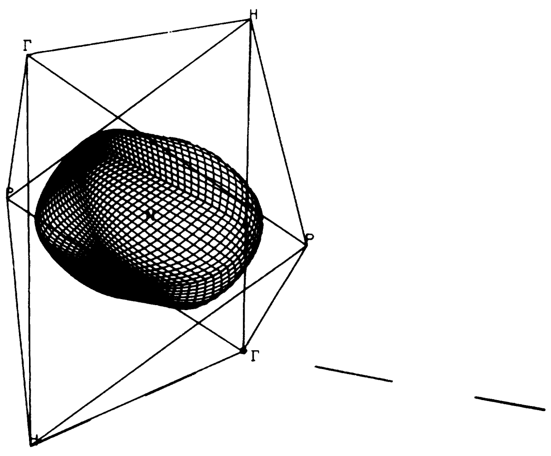

FIG. 3. Computer-generated perspective drawing of distorted ellipsoid centered at N.

TABLE III. Matrices relating symmetrized and unsymmetrized density-matrix expansion coefficients. (Blank entries are zero.)

Q^{22}, Γ_{12}

$m \diagdown m'$	−2	−1	0	1	2
−2	0				
−1		0			
0			1		
1				0	
2					1

$Q^{22}, \Gamma_{25'}$

$m \diagdown m'$	−2	−1	0	1	2
−2	1				
−1		1			
0			0		
1				1	
2					0

Q^{33}, Γ_{25}

$m \diagdown m'$	−3	−2	−1	0	1	2	3
−3	$\frac{3}{8}$		$-\frac{1}{8}\sqrt{15}$				
−2							
−1	$-\frac{1}{8}\sqrt{15}$		$\frac{5}{8}$				
0				0			
1					$\frac{5}{8}$		$\frac{1}{8}\sqrt{15}$
2						1	
3					$\frac{1}{8}\sqrt{15}$		$\frac{3}{8}$

Q^{33}, Γ_{15}

$m \diagdown m'$	−3	−2	−1	0	1	2	3
−3	$\frac{5}{8}$		$\frac{1}{8}\sqrt{15}$				
−2							
−1	$\frac{1}{8}\sqrt{15}$		$\frac{3}{8}$				
0				1			
1					$\frac{3}{8}$		$-\frac{1}{8}\sqrt{15}$
2							
3					$-\frac{1}{8}\sqrt{15}$		$\frac{5}{8}$

$Q^{33}_{mm'}, \Gamma_{2'} = \delta_{2m}\delta_{2m'}$

Q^{31}, Γ_{15}

$m \diagdown m'$	−1	0	1
−3	$\sqrt{5/8}$		
−2			
−1	$\sqrt{3/8}$		
0		−1	
1			$\sqrt{3/8}$
2			
3			$-\sqrt{5/8}$

Fortunately, $F^t_{ll'}(\hat{r},\hat{r})$ has full cubic symmetry and can therefore be written as the sum of Kubic harmonics of the one-dimensional irreducible representation Γ_1. Thus,

$$F^t_{ll'}(\hat{r},\hat{r}) = A^{t0}_{ll'}K_0^{(1)}(\hat{r}) + A^{t4}_{ll'}K_4^{(1)}(\hat{r}) + A^{t6}_{ll'}K_6^{(1)}(\hat{r}) \,, \tag{3.10}$$

where the coefficients $A^{t,l''}_{ll'}$ are given in Table IV.

TABLE IV. Expansion of $F^t_{ll'}(\hat{r},\hat{r})$ in Γ_1 Kubic harmonics [all entries should be multiplied by $(4\pi)^{-1/2}$].

l	l'	t	$A^{t0}_{ll'}$	$A^{t4}_{ll'}$	$A^{t6}_{ll'}$
0	0	Γ_1	1	0	0
1	1	Γ_{15}	3	0	0
2	2	$\Gamma_{25'}$	3	$-2\sqrt{3/7}$	0
2	2	Γ_{12}	2	$2\sqrt{3/7}$	0
3	3	Γ_{25}	3	$-\frac{1}{11}\sqrt{21}$	$-90/11\sqrt{26}$
3	3	Γ_{15}	3	$\frac{3}{11}\sqrt{21}$	$50/11\sqrt{26}$
3	3	$\Gamma_{2'}$	1	$-\frac{2}{11}\sqrt{21}$	$40/11\sqrt{26}$
1	3	Γ_{15}	0	−2	0

The angular integrals in (3.9) are then determined in terms of three integrals

$$W^l(r) = \int_{\Omega_r} d\Omega_{\hat{r}}\, K_l^{(1)}(\hat{r}) \,, \quad l = 0, 4, 6 \,. \tag{3.11}$$

These integrals can be performed analytically for most values of r, but we found it necessary to evaluate them numerically when $\hat{r}$ is restricted to the corners of the cell. Once the functions $W^l(r)$ are known, only a set of one-dimensional integrals remain.

Our potential was generated by using the overlapping charge-density technique suggested by Mattheiss.[22] The atomic charge densities for Nb in the $4d^45s^1$ configuration were obtained from a Herman-Skillman program.[23] An exchange multiplier, α, of 1.0 was used. The lattice constant was 6.2294 a.u. We shall call this potential V_1 to distinguish it from a second potential which was made available to us by Klein and Papaconstantopoulos.[24] This potential was calculated self-consistently for $\alpha = 0.704$. The lattice constant for this potential which we shall call V_2 was 6.2486 a.u.

IV. RESULTS

Figures 1–4 show the three sheets of the Nb Fermi surface calculated for the potential V_1. We emphasize that each mesh point is generated from first principles using a maximum orbital quantum number of 3. The Fermi surface for the V_2 potential is quite similar, and drawings similar to Figs. 1–4 for this potential would hardly be distinguishable from those shown.

Table V gives, for V_1, the density-matrix expansion coefficients, and the enclosed volume for each of the three surfaces S_1 (hole jack at Γ), S_2 (multiply connected surface of Fig. 3), and S_3 (distorted ellipsoid centered at N). Also given is $\rho^t_{ll'}$ [defined in Eq. (3.9)]. We list the contribution from within the muffin tin separately in order to make contact with the augmented-plane-wave cal-

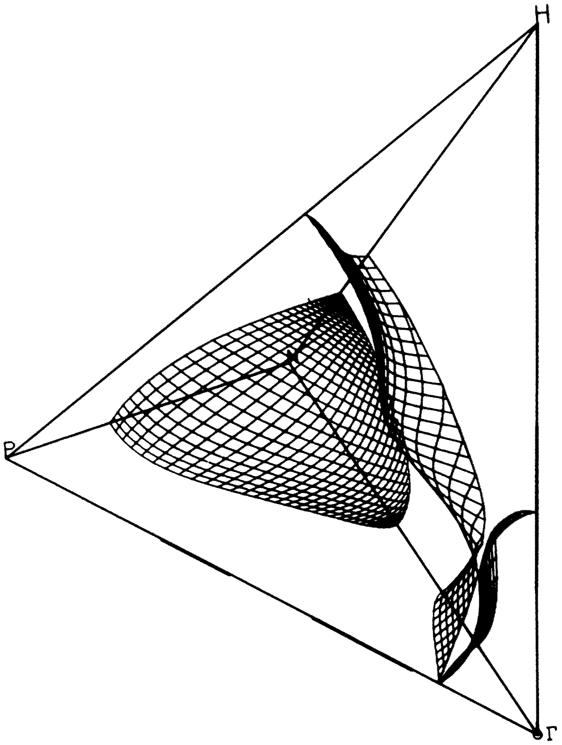

FIG. 4. Irreducible portion of Brillouin zone showing all three surfaces.

culations of Boyer *et al.*[19] The final column gives $N^t_{ll'}$, the total contribution to the density of states from a particular irreducible representation and set of orbital quantum numbers

$$N^t_{ll'} = T^t_{ll'} \rho^t_{ll'} . \tag{4.1}$$

All numbers are in program units and may be converted to atomic units by multiplying $T^t_{ll'}$ by $2\pi/a$ and $\rho^t_{ll'}$ by $(a/2\pi)^3$, where a is the lattice parameter. For V_1, $a/2\pi$ is 0.991 44.

Table VI gives the density-matrix expansion coefficients and wave-function integrals for the self-consistent potential (V_2). This potential was calculated for a slightly different lattice parameter so that $a/2\pi$ is 0.994 50. The agreement between the Fermi-surface properties of the two potentials is quite gratifying.

Several observations can be made from Tables V and VI. By comparing the contribution to $\rho^t_{ll'}$ from within the muffin tin to its total value, one can obtain a feeling for where in the cell the various components of the density of states are situated. For comparison, the ratio of the volume within the muffin tin to that within the full cell is 0.68. Thus the s electrons are rather uniformly distributed, the p electrons are slightly more dense in the interstitial region, the d electrons are largely confined within the muffin tin, and the f electrons are largely outside the muffin tin. The f states with $\Gamma_{2'}$ symmetry are an exception to the last statement. This is no doubt due to the fact that the $K_3^{2'}$ Kubic harmonic is proportional to xyz, and vanishes at the corners of the cell. All of this is as expected from our knowledge of the spatial variation of the radial wave functions and Kubic harmonics.

Consider now the results for the coefficients $T^t_{ll'}$. It is instructive to compare these results with those one would obtain for a single scatterer in a zero-potential medium, namely,

$$T^{t(1)}_{ll'} = \sqrt{E_F}/\pi \approx 0.25 \text{ Ry}^{1/2} . \tag{4.2}$$

Thus the s coefficient is approximately the single-scatterer value, whereas band effects enhance the p coefficient by a factor of about 3, decrease the d coefficients slightly for $\Gamma_{25'}$ and greatly for Γ_{12}, and increase the f coefficients by factors ranging from 3 to 6. These enhancements of the p and f state density were completely unanticipated in the

TABLE V. Density matrix expansion coefficients for V_1 ($E = 0.623$ Ry) (du indicates dimensionless program units).

				$T^t_{ll'}$			$\rho^t_{ll'}$		
l	l'	t	S_1	S_2	S_3	Total	Within muffin tin	Total	$N^t_{ll'}$
0	0	Γ_1	0.000 0	0.032 4	0.189 1	0.2215	1.0827	1.6549	0.367
1	1	Γ_{15}	0.005 5	0.104 8	0.610 5	0.7208	1.4026	2.5656	1.849
2	2	$\Gamma_{25'}$	0.039 4	0.124 0	0.042 0	0.2054	27.866	30.601	6.286
2	2	Γ_{12}	0.003 4	0.014 3	0.055 5	0.0732	18.580	21.366	1.564
3	3	Γ_{25}	0.190 4	0.639 2	0.814 1	1.6437	0.0561	0.1508	0.2478
3	3	Γ_{15}	0.032 7	0.560 7	0.142 2	0.7356	0.0561	0.1501	0.1104
3	3	$\Gamma_{2'}$	0.032 7	0.871 3	0.307 3	1.2113	0.0187	0.0285	0.0346
1	3	Γ_{15}	−0.012 8	−0.145 7	0.247 9	0.0894	0	(×2)(0.1985)	0.0177
Volume			0.981 07	−0.226 55	0.747 275	1.5018		Total	10.476 states/du
$E_F = 0.6228$ Ry (extrapolated)									10.298 states/Ry

TABLE VI. Density matrix expansion coefficients for V_2 ($E=0.629$ Ry) (du indicates dimensionless program units).

			$T^t_{ll'}$				$\rho^t_{ll'}$		
l	l'	t	S_1	S_2	S_3	Total	Within muffin tin	Total	$N^t_{ll'}$
0	0	Γ_1	0.0004	0.0324	0.1838	0.2166	1.0745	1.6391	0.335
1	1	Γ_{15}	0.0057	0.1069	0.6161	0.7287	1.4020	2.5524	1.860
2	2	$\Gamma_{25'}$	0.0406	0.1269	0.0432	0.2107	25.532	28.194	5.940
2	2	Γ_{12}	0.0038	0.0147	0.0570	0.0755	17.022	19.739	1.490
3	3	Γ_{25}	0.1962	0.6025	0.7817	1.5804	0.0600	0.1593	0.2518
3	3	Γ_{15}	0.0924	0.5407	0.1421	0.7752	0.0600	0.1586	0.1229
3	3	$\Gamma_{2'}$	0.0309	0.8652	0.2951	1.1912	0.0200	0.0304	0.0362
1	3	Γ_{15}	−0.0125	−0.1402	0.2505	0.0978	0	(×2)0.2021	0.0198
Volume			0.97583	−0.23104	0.74969	1.4945			10.076 states/du
$E_F=0.62954$ Ry (extrapolated)									9.966 states/Ry

semiquantitative estimates of η,[6,11] but are in agreement with the results of Klein and Papaconstantopoulos,[12] and of Boyer *et al.*[19] We believe that an understanding of this effect is a very important aspect of understanding the origin of the electron-phonon coupling in transition metals. We shall return to this question in Sec. V.

The total Fermi-energy density of states for potential V_1 (allowing for the 0.17 mRy error in estimating the Fermi energy) is 10.34 states of 1 spin/Ry. The corresponding number for the V_2 potential is 10.10. The agreement of these two numbers is encouraging, however, the experimentally predicted density of states, using a value of 7.8 mJ/mole (°K)^2 (Ref. 25) for the low-temperature specific heat and an enhancement factor ($1+\lambda$) of 1.82 is 12.35 states/(Ry spin). We are not sure how one should rationalize this discrepancy. We note that Mattheiss obtained $N(E_F)=9.89$ states/(Ry spin),[22] and Elyashar and Koelling obtained 9.95 states/(Ry spin).[26]

Table VII lists the phase shifts and matrix elements $V'_{l,l+1}$ for the two potentials. We note that in Eq. (2.12) the expression $\sin(\delta_l-\delta_{l+1})$ includes a singular contribution to $V'_{l,l+1}$ which arises from the discontinuity in the potential at the muffin-tin radius. We believe that this contribution should be included in the rigid muffin-tin picture because it approximates the effect of extending the potential continuously into the interstitial region.

Table VIII lists the contributions to η which arise from the five terms in Eq. (2.25). The first three terms are included in the original formula of Gaspari and Gyorffy. The last two terms arise from treating the nonspherical nature of the energy bands correctly. The nonspherical terms are surprisingly small. Calculations which we have performed on other transition metals indicate that the nonspherical corrections to the Gaspari-Gyorffy formula tend to be less than 10% for the cubic elements. This is, however, not a general result, since we have shown that certain combinations of the density-matrix coefficients can lead to very large nonspherical corrections. If one assumes, however, that $T^{(25')}_{22}-T^{(12)}_{22}$ is of the same order as $\overline{T}_{22}$, and that $T^{(25)}_{33}-3T^{(15)}_{33}+2T^{(2')}_{33}$ is likewise of the same order of magnitude as $\overline{T}_{33}$, we can see that the third term dominates the fourth, due to the factor of $\frac{1}{35}$ in the fourth term. The fifth term tends to be small for a different reason. Contributions to $T^{(15)}_{13}$ are not positive definite so that some portions of the Fermi surface may give contributions which cancel against contributions from other portions. The near cancellations between the fourth and fifth terms seems to be a peculiarity of Nb.

The calculated values for η are 7.06 eV/Å^2 for potential V_1 and 7.26 eV/Å^2 for potential V_2. Our value for η is only slightly lower than the value (7.39) quoted by Boyer *et al.*[19] for the same potential. The small difference is not due to the nonspherical terms but to differences in estimating the Fermi energy and in calculating the angular momentum decomposition of the density of states. It should be noted that the calculations for Nb must be done very carefully. Had we used a Fermi energy of 0.62 Ry for V_1 (lower than the true E_F by

TABLE VII. Phase shifts at the Fermi energy and rigid muffin-tin matrix elements for potentials V_1 and V_2.

	$\delta_l(V_1)$	$\delta_l(V_2)$
0	−0.84848	−0.85300
1	−0.30804	−0.31922
2	1.2019	1.1794
3	0.00583	0.00666
	$V'_{l,l+1}(V_1)$	$V'_{l,l+1}(V_2)$
0	−0.51451	−0.50879
1	−0.99815	−0.99397
2	0.93059	0.92182

TABLE VIII. Contributions to η in (eV/Å^2) for potentials V_1 and V_2.

	V_1	V_2
sp	0.4059	0.4029
pd	2.1036	2.2392
df (spherical)	4.5390	4.6448
df (nonspherical)	0.1752	0.1590
p-d-f	−0.1656	−0.1884
Total	7.0581	7.2575

only 3 mRy), η would have been about 10% higher.

Once η is known, λ may be determined from (2.5) if $\langle\omega^2\rangle$ [(2.6)] is known. Tunneling measurements of $\alpha^2F(\omega)$ have been performed only recently for Nb, and the results are still very controversial.[27] Several authors, however, have estimated $\langle\omega^2\rangle$. McMillan[10] obtained $\langle\omega^2\rangle^{1/2} = 230\,^\circ\mathrm{K}$ by taking the mean of the transverse and longitudinal peaks in the phonon density of states. Allen and Dynes[16] obtained $\langle\omega^2\rangle^{1/2} = 183\,^\circ\mathrm{K}$ by assuming α^2 to be constant in (2.4). Foulkes and Gomersall[28] obtained $\langle\omega^2\rangle^{1/2} = 152\,^\circ\mathrm{K}$ by means of an approximation which takes α^2 to be proportional to ω^{-1}.

We are inclined to accept the Allen and Dynes value, since their estimate is quite good for Ta, where tunneling data is available. The Foulkes-Gomersall and Allen-Dynes estimates for $\langle\omega^2\rangle^{1/2}$ are quite close for V, Ta, Mo, and W. The larger discrepancy for Nb may be due to the anomalous behavior of the long-wavelength TA modes. The McMillan estimates are higher by 20% to 30%. Use of $\langle\omega^2\rangle^{1/2} = 183\,^\circ\mathrm{K}$ and $\eta = 7.1$ eV/Å^2 in (2.5) yields $\lambda = 1.28$, which may be compared with empirical values ranging from[3] 0.82 to[5] 0.95.

V. CONCLUSIONS AND DISCUSSION

We have generalized the Gaspari-Gyorffy formula for η by taking into account the nonspherical nature of the energy bands. We find the nonspherical corrections to be negligible for Nb.

We have calculated the Fermi-energy density matrix very carefully for Nb. We find (in agreement with earlier calculations[19]) large enhancements of the p- and f-state densities above the single scatterer or free-electron estimates.

Using rigid muffin-tin matrix elements, we have calculated η and λ for Nb. It appears that the predicted value for λ is about 50% higher than the empirical value. This may be due to one or more of the following:

(i) $\langle\omega^2\rangle^{1/2} = 183\,^\circ\mathrm{K}$ may be too low. Assumption of the McMillan value (230 °K) yields $\lambda = 0.81$, which is in excellent agreement with the empirical value.

(ii) The empirical value of λ may be too low. If one uses $\mu^* = 0.2$ rather than $\mu^* = 0.13$ in McMillan's equation relating T_c and λ, one obtains $\lambda = 1.19$. This value for λ is (perhaps coincidentally) just the value needed to bring the band-theory density of states into agreement with the low-temperature specific heat.

(iii) The rigid muffin-tin electron-phonon matrix elements may be too large. A 20% reduction in $V'_{l,l+1}$ due to screening (beyond that already included in the rigid muffin-tin approximation) does not seem unreasonable.

We believe that (iii) is the most likely source of the disagreement between theory and experiment. In this regard the recent calculation of Boyer *et al.*[19] on Ta is relevant. They find the calculated λ to be larger than the empirical value by about 40%. In this case, $\langle\omega^2\rangle$ and μ^* are known from tunneling measurements. Since we do not expect the nonspherical terms to be much more important than in Nb, we conclude tentatively by a process of elimination that the rigid muffin-tin matrix elements are probably too large for Nb and Ta.

Leaving aside the problem of the matrix elements, let us consider the other quantities which determine η, namely, the density-matrix coefficients $T^{t}_{ll'}$. We consider the enhancement of the p and f coefficients above their values for the free-electron approximation or single scatterer approximation to be of crucial importance. If we had set $\overline{T}_{33}$ and $\overline{T}_{11}$ equal to their single-scatterer values we would have obtained $\eta \sim 2.2$ eV/Å^2. The effect on η of the p- and f-state density enhancements is to increase η by a factor greater than 3.

The p and f enhancements also indicate that the usual picture of a transition-metal density of states in which one has a relatively smooth flat "*s* contribution" with a superimposed peaky-*d* density of states is not adequate for understanding superconductivity. Reality is quite different. The non-*d* contributions to the density of states are much larger than the free-electron or single-scatterer model would predict. In addition, they are not smoothly varying. Table IX gives the density-matrix coefficients for the V_1 potential at an energy 3 mRy below the Fermi energy. It is probably not surprising that the total density of states is higher by 8% since the Fermi energy in Nb falls just above a narrow peak in the density of states. The point which we wish to emphasize, however, is that all of the contributions to the density of states are changing rapidly. In fact it would not be a bad approximation to say that the various contributions are varying at roughly the same rate.

In order to understand this behavior of the non-*d*

TABLE IX. Density-matrix expansion coefficients (V_1 potential) $E=0.62$ Ry.

l	l'	t	$T_{ll'}$ (total)	$\rho^t_{ll'}$ (total)	$N^t_{ll'}$	$N^t_{ll'}(0.62)/N^t_{ll'}(0.623)$
0	0	Γ_1	0.2443	1.659	0.4053	1.10
1	1	Γ_{15}	0.7804	2.563	2.000	1.08
2	2	$\Gamma_{25'}$	0.2199	30.53	6.714	1.07
2	2	Γ_{12}	0.0815	21.33	1.738	1.11
3	3	Γ_{25}	1.844	0.1489	0.274	1.11
3	3	Γ_{15}	0.7719	0.1482	0.114	1.03
3	3	$\Gamma_{2'}$	1.369	0.0282	0.039	1.13
1	3	Γ_{15}	0.0962	0.1974(×2)	0.019	1.07
Volume			1.4695		11.30 states/du 11.11 states/Ry	

components of the density of states it is important to remember that we have defined the angular momentum decomposition in such a way that all of the r-dependent state density $[\rho(r,r,E_F)]$ within a given Wigner-Seitz cell is expanded about the center of *that* cell. Thus the d orbitals centered about neighboring sites which extend into the central cell will contribute to the non-d density of states. This observation allows us to make a qualitative connection between the Gaspari-Gyorffy formula for η which for transition metals involves matrix elements between d and f or d and p orbitals, all on the same site, and the tight-binding formula for η which involves matrix elements between two d orbitals on neighboring sites.[29,30]

Generally for the transition metals, a high value of η is to be expected when in addition to having a sizeable $l=2$ phase shift, the Fermi-energy density of states is high, and when there is a substantial overlap of the d wave function from one cell to its neighbors. Moreover, the enhancement of η will be proportional to the amount of p- or f-like symmetry these overlapping d orbitals yield when expanded about the center of the cell at the origin.

APPENDIX: RESIDUE NORMALIZATION OF KKR WAVE FUNCTIONS

Our normalization technique is based on the singular behavior of the k-dependent crystal Green's function $G_k(r,r';E)$, as the energy E approaches the band-structure value E_{nk} (n is a band index and k is in the reduced zone). In terms of Bloch wave functions ψ_{nk}, we define G_k as

$$G_k(r,r';E)=\sum_n \psi_{nk}(r)\psi^*_{nk}(r')(E-E_{nk})^{-1}\,, \qquad \text{(A1)}$$

where E is understood to have an infinitesimal positive imaginary part, and the wave functions are assumed to be normalized to unity over the Wigner-Seitz cell. Evidently the normalized wave functions are displayed in the residue of G_k at one of its poles

$$\lim_{E\to E_{nk}} (E-E_{nk})G_k(r,r';E)=\psi_{nk}(r)\psi^*_{nk}(r')\,. \qquad \text{(A2)}$$

The wave functions ψ_{nk} are determined (except for a normalization constant $\alpha(n,k)$ by the KKR equations

$$\psi_{nk}(\vec{r})=\alpha(n,k)\sum_{lm} i^l c^0_{lm}(nk)R_l(r)Y_{lm}(\hat{r})\,, \qquad \text{(A3)}$$

$$\sum_{l'm'}(t_l^{-1}\delta_{ll'}\delta_{mm'}-A^0_{lm,l'm'})c_{l'm'}(nk)=0\,. \qquad \text{(A4)}$$

Here c^0_{lm} is an unnormalized wave-function coefficient. For definitness we choose the initial normalization so that $c^0_{l_0m_0}=1$ for some l_0 and m_0. It can be shown that expressions similar to (A3) and (A4) determine G_k,

$$G_{\vec{k}}(\vec{r},\vec{r}\,';E)=\sum_{LL'}[A_{LL'}(\vec{k},E)R_l(r)R_{l'}(r')+\delta_{LL'}R_l(r_<)S_l(r_>)] \times(\sin\delta_l\sin\delta_{l'})^{-1}Y_L(\hat{r})Y_{L'}(\hat{r}')\,, \qquad \text{(A5)}$$

where $R_l(r)$ is the regular solution to the radial Schrödinger equation and $S_l(r)$ is an irregular solution, R_l and S_l are normalized so that

$$\left.\begin{aligned} &R_l(r)\to\cos\delta_l j_l(\sqrt{E}r)-\sin\delta_l n_l(\sqrt{E}r)\\ &S_l(r)\to\sin\delta_l j_l(\sqrt{E}r)\end{aligned}\right\} r>r_{\text{mt}}\,. \qquad \text{(A6)}$$

In (A5) we have used L for the pair l,m. The matrix $A_{LL'}$ is the inverse of the KKR matrix occurring in (A4),

$$A_{LL'}=[(t^{-1}-A^0)^{-1}]_{LL'}\,. \qquad \text{(A7)}$$

Substitution of (A3) and (A5) into (A2) yields

$$\alpha^2(nk)c_L(n,k)c_{L'}(n,k)\,i^{l-l'} =\lim_{E\to E_{nk}}(E-E_{nk})A_{LL'}(k,E)(\sin\delta_l\sin\delta_{l'})^{-1}\,. \qquad \text{(A8)}$$

Recalling that c_{L_0} was chosen to be unity, we have

$$\alpha^2(nk) = \lim_{E\to E_{nk}} (E - E_{nk}) A_{L_0L_0}(k,E)/\sin^2\delta_{l_0} . \quad \text{(A9)}$$

The quantity $A_{L_0L_0}$ is a diagonal element of the inverse of the KKR matrix and is therefore expressible as the ratio of two determinants

$$A_{L_0L_0}(k,E) = D_{L_0}(k,E)/D(k,E) . \quad \text{(A10)}$$

Here, $D(k,E)$ is the determinant of the KKR matrix

$$D(k,E) = \mathrm{Det}\,|t^{-1} - A^0| \quad \text{(A11)}$$

and D_{L_0} is the minor of the (L_0, L_0) element of the KKR matrix

$$D_{L_0}(k,E) = \min[t_{l_0}^{-1} - A^0_{L_0L_0}(k,E)] , \quad \text{(A12)}$$

i.e., it is the determinant with the L_0th row and column deleted.

Since $D(k,E)$ goes continuously through zero as E approaches E_{nk}, we may write

$$D(k,E) \to (E - E_{nk}) D'_E(k, E_{nk}) , \quad \text{(A13)}$$

where D' is the energy derivative of the KKR matrix at its zero,

$$D'_E(k, E_{nk}) = \left.\frac{\partial D(k,E)}{\partial E}\right|_{E=E_{nk}} . \quad \text{(A14)}$$

Thus the normalization constant is given by

$$\sin^2\delta_{l_0}\alpha^2(nk) = D_{L_0}(k, E_{nk})/D'_E(k,E) . \quad \text{(A15)}$$

The advantage of this normalization scheme is that the quantities D_{L_0} and D'_E are readily obtained during the normal course of locating the energy bands and calculating the unnormalized wave-function coefficients. In a typical band-structure calculation, the determinant of the KKR matrix is evaluated for a sequence of trial energies at a fixed k. When a change of sign indicates that a band energy has been crossed, an iteration procedure is initiated to converge to the root. D' can therefore be obtained directly as a first difference. In addition, the minor D_{L_0} is usually generated in solving the homogeneous system (A4), since the usual way of solving a homogeneous system of this type is to set one C equal to unity, thereby generating a reduced inhomogeneous system. The determinant of this reduced system is then generated in solving for the remainder of the coefficients.

This technique has an additional advantage in a constant-energy search where one searches along a ray in k space holding E constant. In this case the easily obtainable quantity is

$$D'_k(k_n, E) = \left(\frac{dD(k,E)}{dk}\right)_{k=k_n(E)} , \quad \text{(A16)}$$

where $k_n(E)$ is a value of the magnitude of $\vec{k}$ along this ray for which $E_{n,k}$ is equal to E. Now

$$D'_k = D'_E(\hat{k}\cdot\nabla_k E) . \quad \text{(A17)}$$

So that if we define $\bar{\alpha}(n,k)$ by

$$\sin^2\delta_{l_0}\bar{\alpha}^2(n,k) = D_{L_0}(k_n, E)/D'_k , \quad \text{(A18)}$$

and use $\bar{\alpha}(n,k)$ as our normalization constant rather than $\alpha(n,k)$, then our wave functions will be normalized so that

$$\int_\Omega d^3r\,\psi_k^*(r)\psi_k(r) = (\hat{k}\cdot\nabla_k E)^{-1} , \quad \text{(A19)}$$

which is most convenient for calculating the density of states and density matrix. Equation (A19) is equivalent to (3.3) if we set $\bar{\psi}_k = \sqrt{\Omega}\,\psi_k$, where Ω is the volume of the Wigner-Seitz cell.

It is interesting to note that the density of states using (A19) can be obtained from the KKR equations evaluated at one energy. The energy derivatives of the phase shifts do not enter explicitly. They do enter implicitly, however, through the r-space integrals in (A19). It should be recalled that

$$\int_0^{r_{\mathrm{mt}}} R_l^2(r)\,r^2\,\mathrm{d}r = -\left(R_l^2 r^2 \frac{d\gamma_l}{dE}\right)_{r=r_{\mathrm{mt}}} , \quad \text{(A20)}$$

where $\gamma_l(E)$ is the logarithmic derivative of R_l. $d\gamma_l(E)/dE$ depends upon the energy derivatives of $\delta_l(E)$.

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[1] J. Bardeen, Phys. Rev. 52, 688 (1937).

[2] L. J. Sham and J. M. Ziman, Solid State Phys. 15, 221 (1963).

[3] D. J. Scalapino, in *Superconductivity*, edited by R. D. Parks (Dekker, New York, 1969), Vol. I. p. 449.

[4] G. Gladstone, M. A. Jensen, and J. R. Schrieffer, in Ref. 3, Vol. II, p. 655.

[5] R. Evans, D. A. Greenwood, and P. Lloyd, Phys. Lett. A 35, 57 (1971).

[6] G. D. Gaspari and B. L. Gyorffy, Phys. Rev. Lett. 28, 801 (1972).

[7] G. Niklasson, A Sjölander, and K. S. Singwi, Phys. Rev. B 11, 113 (1975).

[8] J. Yamashita and S. Asano, Prog. Theor. Phys. 50, 1110 (1973); 51, 317 (1974).

[9] W. L. McMillan and J. M. Rowell, in Ref. 3.

[10] W. L. McMillan, Phys. Rev. 167, 331 (1968).

[11] J. J. Hopfield, Phys. Rev. 186, 443 (1969).

[12] B. M. Klein and D. A. Papaconstantopoulos, Phys. Rev.

Lett. 32, 1193 (1974).

[13] B. M. Klein and D. A. Papaconstantopoulos, in the Proceeings of the Conference on Low Lying Vibrational Modes and Their Relationship to Superconductivity, San Juan, Puerto Rico, 1975 (unpublished).

[14] D. A. Papaconstantopoulos and B. M. Klein, Phys. Rev. Lett. 35, 110 (1975).

[15] A. A. Abrikosov, L. P. Gorkov, and I. Ye. Dzyaloshinskii, *Quantum Field Theory Methods in Statistical Physics* (Pergamon, New York, 1965).

[16] P. B. Allen and R. C. Dynes, Phys. Rev. B 12, 905 (1975).

[17] P. Morel and P. W. Anderson, Phys. Rev. 125, 1263 (1962).

[18] W. John, J. Phys. F 3, L231 (1973).

[19] L. L. Boyer, B. M. Klein, and D. A. Papaconstantopoulos, in Ref. 13.

[20] F. C. bon der Lage and H. A. Bethe, Phys. Rev. 71, 612 (1947).

[21] J. S. Faulkner, H. L. Davis, and H. W. Joy, Phys. Rev. 161, 656 (1967).

[22] L. F. Mattheiss, Phys. Rev. B 1, 373 (1970).

[23] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, New Jersey, 1963).

[24] B. M. Klein and D. A. Papaconstantopoulos (private communication).

[25] C. C. Koch, J. O. Scarbrough and D. M. Kroeger, Phys. Rev. B 9, 888 (1974), and references therein. There is some uncertainty as to how one should extract γ from the low-temperature specific-heat data. Values of γ ranging from 7.5 to 7.93 $\mathrm{mJ/mole\,°K^2}$ seem possible.

[26] N. Elyashar and D. D. Koelling (private communication).

[27] J. Bostock, V. Diadiuk, W. N. Cheung, K. H. Lo, R. M. Rose, and M. L. A. MacVicar, Phys. Rev. Lett. 36, 603 (1976).

[28] I. F. Foulkes and I. R. Gomersall, J. Phys. F 5, 153 (1975).

[29] J. Appel and W. Kohn, Phys. Rev. B 4, 2162 (1971).

[30] A. Birnboim and H. Gutfreund, Phys. Rev. B 12, 2682 (1975).