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Pseudoatom version of the rigid-muffin-tin approximation

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The electron-phonon coupling parameter (λ) is calculated for the metals K, Al, Cu, and Nb using the rigid-muffin-tin approximation but with the Fermi energy as an adjustable parameter and phase shifts obtained by fitting the Fermi-surface dimensions. A pseudoatom muffin-tin potential is obtained by making a suitable choice of the Fermi-energy parameter. In simple metals the choice is defined in terms of the screening constraint. In transition metals an arbitrary choice (half the "band-structure" value) is suggested. For the simple metals λ changes by a factor of 3 or more over the range of Fermi energies considered but agrees well with experimental estimates at the pseudoatom value. In niobium the shift leaves the average value of λ essentially unaltered but changes the anisotropy so as to better match the experimental anisotropy. Provided the same criteria are used for determining the Fermi-energy parameter, very similar results are obtained using a scaling procedure suggested by Butler and based on the atomic-sphere approximation.

I. INTRODUCTION

The problem of calculating the properties of the electron-phonon interaction (in particular the coupling constant λ) in transition metals and transition-metal compounds was significantly simplified when Gaspari and Gyorffy[1] (GG) introduced the rigid-muffin-tin approximation. They argued that in a transition metal, where there is a d resonance near the Fermi level, the extra scattering due to displacement of an ion is dominated by the local potential of the ion and will be well represented by taking the "band-structure" muffin-tin potential, i.e., the muffin-tin form of the potential constructed for the purposes of calculating the band structure. In their derivation of the relevant formulas GG made a further approximation of spherical bands, but subsequent work[2,3] has shown that in cubic metals the nonspherical terms due to s to p or p to d scattering vanish and for d to f scattering they are rather small.

The rigid-muffin-tin approximation (RMTA) has the advantage that little computation is required over and above that for a standard band-structure calculation. Applied to transition metals it gives values of λ that are approximately correct and it is particularly useful in studying trends through the Periodic Table.[4] However, there appears to be a significant discrepancy when considering the anisotropy of λ in niobium, one of the few metals for which experimental values are available. The measured values[5] show a variation of more than 50%, by contrast the RMTA calculation of Butler, Pinski, and Allen[6] (BPA) finds only a small variation in the opposite sense. A similar result was obtained by Harmon and Sinha,[7] using an augmented-plane-wave (APW) formalism but with the same rigid-ion approximation and "band-structure" potential. They attribute the discrepancy to neglect of the Coulomb tails associated with the displaced ion which, although screened, will nevertheless couple to the neighboring ions. This effect is seen most clearly in RMT calculations of λ in simple metals[4] where λ is underestimated by factors of order 3–10. However, as Harmon and Sinha point out, including the effects of the tails and screening results in a considerably more complicated problem. A model calculation for niobium including these effects gave an acceptable anisotropy but at the expense of values of λ about 80% too large.

The formalism of the RMTA is so simple and so easily implemented that it would obviously be desirable if the effects of the screened tails could be included while retaining the muffin-tin form of the potential. Ziman[8] has introduced the concept of a pseudoatom, an atomic potential that when displaced carries with it not only the ion core, but also the correctly screened Coulomb tails. Such potentials necessarily overlap, so to retain the simple formalism of GG a muffin-tin version of a pseudoatom potential is required which models the effects of the screened tails. A clue to finding such a potential is obtained from the results of fitting measured Fermi-surface dimensions (determined usually from the de Haas-van Alphen effect) with a set of phase shifts, or equivalently logarithmic derivatives, using a muffin-tin formalism such as the APW or Korringa-Kohn-Rostoker (KKR) method.[9] Although these phase shifts describe the way the potential scatters the electrons at the Fermi energy, they do not define the potential uniquely and this ambiguity is reflected in the fact that over a wide range of energy the fit is essentially independent of the choice of Fermi energy measured with respect to the muffin-tin zero (MTZ), i.e., the flat region of energy between the muffin-tins which is chosen as the zero of energy. The choice of MTZ may therefore be considered as an arbitrary parameter which can be selected so as to reproduce most closely a muffin-tin version of the psedoatom potential. In this context, as distinct from establishing a procedure for constructing potentials from first principles, it is important to realize that the flat region of the muffin-tin potential is an artefact of the formalism and of little physical significance. Indeed, in the APW method the radius of the muffin-tin spheres can, without affecting the shape of the Fermi surface or the fitted phase shifts, be varied over a wide range to include values sufficiently large to completely eliminate the flat region. The fitted phase shifts can therefore be considered as specifying some form of model potential in which the MTZ appears only as an adjustable parameter with little or no physical significance.

The intent of this paper is to calculate λ within the RMTA as a function of the MTZ and to establish criteria for that choice of MTZ which corresponds to a psedoatom potential. Phase shifts obtained by fitting the Fermi surface have been used because it was felt important that the muffin-tin potential reproduce accurately the correct Fermi surface (which is used for the integrals that appear in the RMTA) and because, except for the density of states at the Fermi level and the phonon part, no other information is required to calculate λ within the RMTA. It is emphasized that fitted phase shifts provide no information on the shape of the bands away from the Fermi surface, as would be required to obtain the density of states, so *any* density of states (including the correct one) is consistent with a phase shift fit to the Fermi surface.

The examples chosen to illustrate this approach include simple metals rather than just transition metals because the connection between the choice of MTZ and the pseudoatom is most easily understood in these cases and also, if the treatment of the screened tails is successful in these cases, it will likely be a good approximation in the transition metals where the tails and the screening produce a somewhat smaller effect. Four metals are considered: potassium (typical of results in the alkali metals), aluminum as an example of nearly-free-electron-like metal where band-structure effects distort the Fermi surface and invalid single-plane-wave approximations, copper as a nonsimple metal, typical of the noble metals, and niobium as the most extensively studied example of a transition metal.

II. CHOOSING THE PSEUDOATOM MUFFIN-TIN POTENTIAL

The connection between pseudoatoms and rigid-ion potentials is most clear in the simple metals where the concept of a pseudopotential can be used. This is the basis of the work by Lee and coworkers[10–13] in the alkali metals and copper where a phase-shift pseudopotential is constructed from the parametrization of the Fermi surface. Notwithstanding the discussion above of a pseudoatom muffin-tin potential purely as a model potential, there is a connection between the range of the pseudoatom potential and the position of the MTZ. The total crystal potential can be considered as the sum of atomic potentials which overlap to an arbitrary extent. Pseudoatom potentials have appreciable overlap because, when displaced, the screened Coulomb tail which extends into the neighboring cells must also move. By contrast conventional muffin-tin potentials, constructed for a band-structure calculation, do not overlap at all and if such a muffin-tin potential is displaced, it carries with it not its own tail but the tails from the surrounding ions which should remain fixed. The flat region of the MTZ between the muffin-tin spheres has an energy defined conventionally as the average of the residual contributions from the surrounding atoms. If the radius of the muffin-tin sphere is decreased, an increased fraction of the total potential is included in the MTZ region, the energy of this region (E_{MTZ}) is lowered, and the Fermi energy measured with respect to this energy (i.e., $E_F - E_{\text{MTZ}}$) is increased. Conversely, increasing the muffin-tin radius, corresponding to a potential having more overlap, reduces the parameter $E_F - E_{\text{MTZ}}$. Because E_{MTZ} is chosen to be zero, the parameter specifying the position of the MTZ is just E_F. In terms of a multiple scattering formalism the physical significance of overlapping muffin-tin spheres is not precisely defined (although it should be noted that KKR equations can be derived for overlapping spheres,[14,15] but in terms of a pseudopotential the important parameter is the $q \to 0$ limit of the form factor $\Gamma(q)$. For the pseudopotential corresponding to a screened pseudoatom, long-range fluctuations must be screened out and

$$\Gamma(0) = -\tfrac{2}{3} E_{F0} , \qquad (1)$$

where E_{F0} is the free-electron Fermi energy, or more generally[16,17]

$$\Gamma(0) = -Z/2N(E_F) , \qquad (2)$$

where Z is the valence and $N(E_F)$ the density of states at the Fermi energy for one spin state. For free-electron behavior Lee and Heine[11] argue that

$$\Gamma(0)=E_F-E_{F0}\ . \tag{3}$$

So, turning on the pseudoatom corresponds to reducing E_F-E_{MTZ} from E_{F0} to $E_{F0}/3$. This is consistent with increasing the spatial extent of the potential to include the screened Coulomb tail. In terms of a muffin-tin model potential of fixed radius this corresponds to introducing a step at the edge of the muffin-tin sphere to represent the effects of the screened tails.

Using this approach, the procedure for constructing a pseudoatom pseudopotential is to determine phase shifts from a fit to the Fermi surface with the MTZ chosen so as to satisfy the requirements of screening as given by Eq. (2). The form factor will therefore be correct at $q=0$ and also, because the Fermi surface has been fitted, at q of the order of a reciprocal-lattice vector. Using this pseudopotential Allen and Lee[12] then constructed an electron-phonon form factor within a one-APW approximation and obtained good values for the resistivity and the mass enhancement in the alkali metals. In copper Nowak[13] retained the concept of a pseudoatom potential derived from a fit to the Fermi surface but used a multiple-APW formalism to calculate the electron-phonon matrix element and replaced the left-hand side of Eq. (2) by the Fermi-surface average of the low-q limit of the matrix element.

However, the electron-phonon matrix element need not be evaluated within the APW approximation. Indeed, repeating the derivation in Allen and Lee using KKR wave functions just reproduces the GG RMT formalism[18] so the results of the GG formalism can be carried over and used with the phase shifts and wave functions corresponding to a pseudoatom potential.

In lead a similar but slightly different philosophy has been used by Papaconstantopoulos, Zdetsis, and Economou.[19,20] As in other simple metals the RMTA gives values of λ approximately 50% too low. Following a suggestion of Butler they reevaluated the phase shifts of the "band-structure" potential at $E_F=E_{F0}/3$ and then renormalized the potential terms in the GG formula using the new phase shifts. This improved the calculated value of λ to 80% of the correct value. Subsequently they used an alternative procedure, a correction potential describing a screened tail was explicitly added to the muffin-tin potential with the strength of the potential chosen so as to satisfy the screening requirement [Eq. (2)]. When the contribution from this potential was added to the RMT part a good value of λ was obtained. However, this procedure can be criticized because the correction potential is used *only* to calculate λ, to which the low-q behavior of the form factor makes a substantial contribution, and was not used for calculating the Fermi-surface shape. In fact the correction potential also contributes at q of the order $2k_F$ (as is indeed apparent from Fig. 2 of Ref. 20), which implies that properties sensitive to this region of the form factor, such as the Fermi-surface shape or the resistivity, would also be changed by the correction potential. Any correction potential added to the "band-structure" muffin-tin potential to approximate a screened pseudoatom should satisfy not only the constraint of screening but also retain the correct Fermi-surface shape. Constructed in this way the total potential will be suitable for calculating not only the coupling constant λ but also other properties, such as resistivity, dependent on the electron-ion interaction.

Even for copper the screening criterion [Eq. (2)] is not well defined because of the nonlocal nature of the phase-shift form factor. In transition metals not only is the form factor nonlocal but also the derivation of Eq. (2) is suspect and indeed it is not clear what value should be chosen for the valence Z. It is nevertheless interesting to examine the general behavior of the $q=0$ form factor. Using the KKR-Z phase-shift pseudopotential this takes the form[21]

$$\Gamma^{(0)}_{\mathrm{KKR}Z}=-\frac{4\pi}{\kappa\Omega}\frac{\hbar^2}{2m}\sum_l(2l+1)\tan\eta_l'\frac{j_l^2(k_FR_s)}{j_l^2(\kappa R_s)}\ , \tag{4}$$

where $\kappa=(2mE_F/\hbar^2)^{1/2}$, Ω is the atomic volume, R_s the MT radius, and $\cot\eta_l'=[\cot\delta_l-n_l(\kappa R_s)/j_l(\kappa R_s)]$, with j_l and n_l the spherical Bessel and Neumann functions and δ_l the phase shifts. Using phase shifts specified in more detail below, this quantity is plotted in Fig. 1 for the four metals chosen as examples. In all cases R_s was chosen as the Wigner-Seitz radius and for potassium, aluminum, and copper the free-electron radius was used for k_F. For niobium two choices of k_F are shown, a minimum value of 0.25 (in units of $2\pi/a$) which is the mean radius of the octahedron and a maximum of 0.707 which passes through the center of the ellipsoids at N. Several features are apparent; for the simple metals Eq. (3) seems to be a good approximation for E_F near E_{F0} but there is an increasing deviation as E_F is decreased and it is in just this important region that there is the most difference between the KKRZ and APW form factor (cf. Ref. 11). This is attributed mainly to neglect of the higher phase shifts, for scattering with q of the order of a reciprocal-lattice vector, i.e., for describing the shape of the

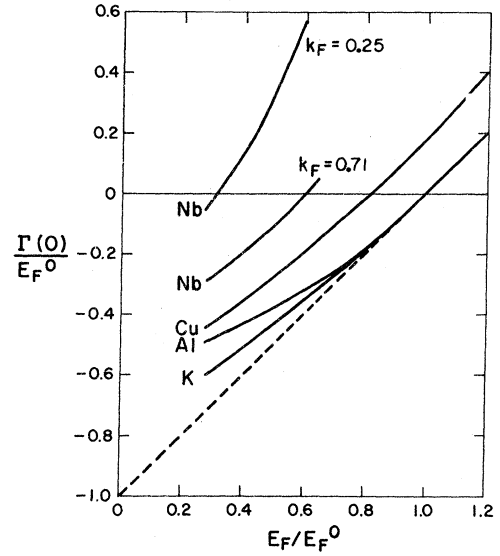

FIG. 1. The $q = 0$ limit of the KKR-Z form factor calculated on the free-electron sphere and expressed as a ratio to the free-electron Fermi energy E_{F0} (see Table I for values). For niobium, where E_{F0} has little meaning, it has been arbitrarily chosen as 1 Ry and the form factor has been calculated with two choices of k_F (given in units of 2π/lattice constant). The dotted line is the approximation $\Gamma(0) = E_F - E_{F0}$. Corresponding to the values shown in Table I the limit $\Gamma(0) = -Z/2N(E_F)$ is $-0.617\,E_{F0}$ for potassium, $-0.631E_{F0}$ for aluminum, and $-0.540E_{F0}$ for copper.

Fermi surface, contributions from the higher phase shifts essentially cancel and can be absorbed into the low l phase shifts but at $q = 0$ the contributions all add coherently and, because the term $j_l^2(\kappa R_s)$ varies essentially as κ^{2l}, become increasingly important as κ is reduced. In this context it is probably relevant that $l_{\max}$ was 3 for potassium but in aluminum, where the deviation is larger, it was only 2. For this reason it is suggested that using the expression

$$E_F - E_{F^0} = -Z/2N(E_F) \tag{5}$$

is a better approximation than either the KKRZ or APW form factor. For both the simple metals considered, although this is quite close to the choice of $E_F = E_{F^0}/3$, it gives values of λ that are significantly different (see below).

For copper $\Gamma(0)$ varies over the Fermi surface but using Eq. (5) [with the value of $N(E_F)$ from Table I] fixes the choice of E_F at 0.24 Ry, rather close to the value of 0.27 Ry obtained by Nowak on the basis of the $q = 0$ limit of the electron-phonon matrix element. For niobium, however, this criterion is obviously useless because neither E_{F^0} nor Z are well defined. At the "band-structure" value of E_F, of order 0.65 Ry, $\Gamma(0)$ is positive for all values of k_F which would correspond to a negative value of Z. It is reasonable to suppose that Z is positive, if only slightly, because electrons move off the atoms when they are brought together in the solid, so the pseudoatom choice of E_F is presumably less than the band-structure value. It is suggested that the somewhat arbitrary choice of half the band-structure value (say 0.32 Ry in Nb) will not be too much in error though this may need to be reviewed in light of the calculated values of λ. In copper this value (~0.29 Ry) is close to the value deduced from Eq. (5).

It is emphasized that the value of $N(E_F)$ used in the criterion given by Eq. (5) and also used in the RMTA [see Eq. (7) below] is *not* determined from the phase-shift parametrization of the Fermi surface and does not change as the MTZ is moved. In terms of an *ab initio* KKR hand-structure calculation the density of states depends on the structure constants and also on the gradient with respect to energy of the phase shifts. This latter quantity is entirely undetermined by the procedure of fitting the Fermi surface and conversely *any* value of $N(E_F)$ can be made consistent with the parametrized Fermi surface. The view taken here is that a reliable value of $N(E_F)$ (unenhanced) be chosen and the values used are listed in Table I. These represent average values based on band-structure calculations[22-25] and experimental estimates from cyclotron masses[25-28] or electronic specific-heat coefficients[29] and measured values of λ[30-33].

III. CALCULATION OF λ

The electron-phonon coupling parameter λ is calculated using the RMT expression

$$\lambda = \eta / M\langle\omega^2\rangle\,, \tag{6}$$

where M is the ionic mass, $\langle\omega^2\rangle$ an average phonon frequency squared, and the electronic factor η is given by[3]

$$\eta = 2N(E_F)^{-1}\Bigg(\sum_{l=0,1,2}(l+1)V_{l,l+1}^2\,\overline{T}_{ll}\overline{T}_{l+1,l+1} + \tfrac{3}{35}V_{23}^2\Delta T_{22}\Delta T_{33} - \tfrac{12}{5}\sqrt{\tfrac{3}{7}}\,V_{12}V_{23}\Delta T_{22}T_{13}^{15}\Bigg), \tag{7}$$

TABLE I. Parameters used in rigid-muffin-tin calculation. The pseudoatom value of E_F is defined by $E_{F0}-Z/2N(E_F)$. Sources are given in the text.

	E_{F0} (Ry)	$N(E_F)$ (states/Ry atom spin)	$\langle\omega^2\rangle^{1/2}$ (K)	Pseudoatom value of E_F	λ (Expt.)
K	0.1559	5.20	74	0.0597	0.15
Al	0.8641	2.75	305	0.319	0.45
Cu	0.5202	1.78	245	0.239	0.13
Nb		9.84	196		

where $V_{l,l+1} = \sin(\delta_l - \delta_{l+1})$ and

$$\bar{T}_{00} = T^{1}_{00},\ \bar{T}_{11} = T^{15}_{11},\ \bar{T}_{22} = (3T^{25'}_{22} + 2T^{12}_{22})/5,$$

$$\bar{T}_{33} = (3T^{25}_{33} + 3T^{15}_{33} + T^{2'}_{33})/7,\ \Delta T_{22} = T^{25'}_{22} - T^{12}_{22},$$

and

$$\Delta T_{33} = T^{25}_{33} - 3T^{15}_{33} + 2T^{2'}_{33}\ .$$

The density matrix coefficients $T^{t}_{ll'}$ are conveniently calculated as (κ/π) $(\mathrm{Im}\chi_{LL'}/\sin^2\delta_l)$, where $\chi_{LL'}$ is the Brillouin-zone integral of the reciprocal KKR matrix. For potassium the integrals were performed using the special directions technique[34] and for the other metals the tetrahedron technique was employed[35] using 32, 768 basic tetrahedra in the irreducible $\frac{1}{48}$th of the Brillouin zone for Al and Cu, 4096 tetrahedra for Nb. Quadratic interpolation and an extrapolation procedure were also used. It should be noted that except for the density of states $N(E_F)$ and the phonon part $M\langle\omega^2\rangle$, all terms in λ are determined without adjustment by a phase-shift parametrization of the Fermi surface; so, provided the same values of $N(E_F)$ and $\langle\omega^2\rangle$ are used, the variation of λ as a function of the MTZ will depend only on the fit to the Fermi surface with an error dependent on the quality of the fit. Because the intent of this paper is to study this variation rather than attempt a best *a priori* calculation, $N(E_F)$ and $\langle\omega^2\rangle$ will be considered as parameters to be obtained from accurate, convenient sources. The value of $N(E_F)$ listed in Table I are discussed above. The average phonon frequency $\langle\omega^2\rangle^{1/2}$ given in Table I is defined by[3]

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

For potassium, published values[36] of $\alpha^2F(\omega)$ have been integrated approximately, for aluminum and copper the approximation $\langle\frac{1}{2}\theta_D^2\rangle$ has been used, where θ_D is the Debye temperature deduced from electronic specific-heat measurements[29] and for niobium the value is taken from BPA.[6]

IV. RESULTS

Potassium. The phase shifts used in the parametrization were interpolated from published values[10,11] using formulas due to Andersen.[9] The calculated values of λ shown in Fig. 2 vary by a factor of at least 20 over the range considered. At $E_F = 0.159$ Ry, the band-structure value, the present calculation finds $\lambda = 0.02$ compared with the simple RMT calculation[4] which obtained $\lambda = 0.04$. The discrepancy can be traced to the calculated phase shifts being approximately 40% larger than the corresponding fitted values. At the value of E_F that satisfies the screening limit (see Table I), λ is 0.17 which may be compared with 0.18 calculated by Allen and Lee[15] using 1 APW, a value of ~0.15 deduced from measured effective masses[26] and (0.13 ± .03) deduced from point-contact tunneling.[30] In view of the extreme variation of the calculated values of λ as the MTZ is changed, the agreement is quite gratifying.

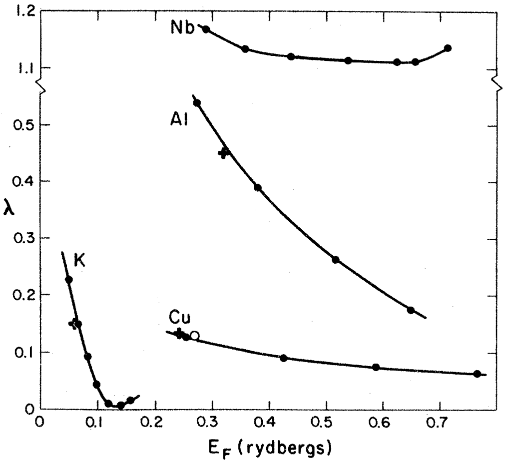

FIG. 2. Values of the electron-phonon coupling constant λ calculated using the RMTA for various choices of the Fermi-energy parameter. The open circle shows the results of Nowak (Ref. 13) and the crosses indicate the experimental values of λ and pseudoatom value of E_F.

Aluminum. For values of the Fermi-energy parameter between approximately 0.25 and 0.7 Ry, a KKR phase-shift parametrization[37] with $l_{\max} = 2$ provided a good fit to the Fermi-surface data with an rms error of less than 0.4%. The calculated values of λ are shown in Fig. 2, computational errors are estimated to be less than 2%, and errors from neglect of the $l = 3$ phase shifts are estimated, in the worst case, to be less than 10%. As in potassium, the most obvious feature is the variation of λ over the range of energy used. At $E_F = 0.618$ Ry, the present calculation finds $\lambda = 0.19$, compared with the RMT calculation using a self-consistent muffin-tin potential[4] which gave $\lambda = 0.13$ using $l_{\max} = 3$ (0.12 with $l_{\max} = 2$). The discrepancy can be traced to the p and d-phase shifts; the term $\sin^2(\delta_1 - \delta_2)$ is approximately 80% larger for the phase shifts derived from the fit to the Fermi surface than for those derived from the calculated potential. Experimental estimates of λ are about 0.44 from effective masses[27] and 0.5 ± 0.1 from tunneling data.[31] This may be compared with the calculated value, at $E_F = 0.32$ Ry, of 0.46 which shows a very satisfactory agreement.

Copper. There exist several phase-shift parametrizations of the Fermi surface of copper. For convenience the results of Shaw, Ketterson, and Windmiller[38] which have been parametrized using Andersen's formula[9] are used. At a Fermi energy of 0.598 Ry where, except for the f-phase shift which is unimportant in this context, the fitted and calculated phase shifts are in good agreement, the calculation agrees well with the RMT calculation in Ref. 4. At 0.27 Ry the calculated value of λ (0.126) is in good agreement with the APW calculation of Nowak (0.12 ± 0.02) and at $E_F = 0.24$ Ry, the pseudoatom choice, $\lambda = 0.13$.

Experimental estimates of λ include values of 0.11 deduced from cyclotron-mass data,[28] 0.13 ± 0.03 deduced from proximity-effect tunneling data,[31] and 0.16 deduced from superconducting alloys.[32] The calculated value of λ is not as strong a function of the Fermi-energy parameter as for potassium and aluminum, but there is a change of about a factor of two between the values calculated using the band-structure and pseudoatom choices of MTZ. In the former case, approximately equal contributions to λ comes from the p-d and d-f terms; in the latter case approximately 80% comes from the p-d term and the d-f term is the smallest (see also Table II).

Niobium. The Fermi surface of niobium has been parametrized by Crabtree *et al.*[5] Their best fit, at a Fermi-energy parameter of 0.683 Ry, required a crystal field splitting of the $l = 2$ phase shifts. From this fit 18 radius vectors were calculated (6 on each of the 3 sheets of Fermi surface) and used to derive further phase-shift parameters as a function of Fermi energy. Over a range of 0.29 to 0.65 Ry the radii could be fitted with an rms error of less than 2%, outside this range the quality of fit deteriorated rapidly with energy. The calculation reproduced published values[3] of T_{ll}^{t} to about 2% and at $E_F = 0.623$ the calculated value of λ agrees with BPA.[6] In BPA the phase shifts were also adjusted, independently, to fit the shape of the Fermi surface, so the agreement gives some confidence in the whole computational procedure.

The calculated values of λ, Fig. 2, are only weakly dependent on the choice of MTZ. Comparison with experimental values is not easy. The results of tunneling experiments are somewhat controversial[39] but a recent analysis of Al:Nb data[33] suggests that the calculated value of $\lambda \sim 1.12$ is not unreasonable although with an acceptable choice of the McMillan μ^* this leads to an overestimate of the superconducting transition temperature. This value is, however, significantly lower than the average of 1.33 deduced by comparing a band structure adjusted to fit the Fermi surface with de Haas–van Alphen cyclotron masses or with the electronic specific heat.[5] An explanation of the discrepancy has been advanced by Rietschel and Winter.[40] They suggest that the measured enhancement factor of 1.33 includes a contribution of about 0.21 from paramagnons which *enhances* the measured cyclotron masses and electronic specific heat but *depresses* the superconducting transition temperature.

While this provides a reasonable explanation of the average value of λ it does not explain the measured anisotropy. Experimentally, the ellipsoids are found to have the lowest enhancement factor (1.1) and the octahedron the largest (1.7) while BPA and the present calculation find a very small anisotropy in the reverse sense. Average values of η^s were, therefore, obtained for each sheet of Fermi surface using a expression of the form

$$\eta^s = \frac{1}{N_s(E_F)} \sum_l (l+1)(\bar{T}^s_{ll}\bar{T}_{l+1,l+1} + \bar{T}_{ll}\bar{T}^s_{l+1,l+1})V^2_{l,l+1}$$

$$+ \text{ corresponding nonspherical terms,}$$

where the density matrix is decomposed into contributions $\bar{T}^s_{ll}$ from each sheet of the surface and $N_s(E_F)$ is the density of states for each sheet with values taken from BPA. Calculated values of η_s are shown in Fig. 3.

It is apparent that as E_F is reduced from the band-structure value the anisotropy of η moves closer to that measured. In particular, the ellipsoids are reduced from having the largest value of η^s to the lowest. Using (anisotropic) values of $\langle\omega^2\rangle$ taken from BPA, the average values of λ_s at our pseudoatom choice of E_F (0.32 Ry) are 0.99, 1.25, and 1.27 for the ellip-

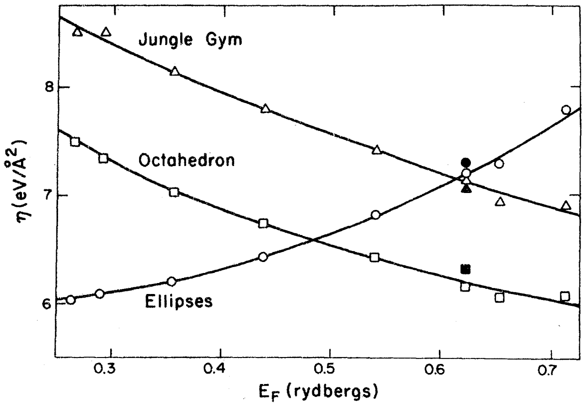

FIG. 3. Values of the electronic factor η averaged over each of the three sheets of Fermi surface in niobium. The solid symbols are the values calculated in Ref. 4.

soids, the octahedron, and the jungle gym, respectively, compared with experimental values of 1.10, 1.71, and 1.43. If an isotropic paramagnon contribution of 0.20 is added to all values the agreement with experiment, although not perfect, is substantially better than for the simple RMT calculation.

V. DISCUSSION

In the four examples considered the results show clearly that modifying the RMTA by shifting the MTZ to produce a pseudoatom muffin-tin potential produces a marked improvement in the agreement with experiment. It is also interesting to note that in the case of potassium and aluminum there is a significant difference between the values of λ calculated at the same Fermi energy with phase shifts obtained from a self-consistent band-structure potential and with phase shifts fitted to the Fermi surface.

For simple metals and copper the criterion of setting

$$E_F - E_{F^0} = -Z/2N(E_F)$$

appears to be quite satisfactory, and for niobium and copper the somewhat arbitrary choice of half the band-structure value would appear to be reasonable. In fact, for the reasons given by Gaspari and Gyorffy, the basic RMTA provides a reasonable average value for the electron-phonon interaction and the changes to the anisotropy produced by shifting the MTZ are a relatively small portion (~25%) of the total value of λ (see Table II).

The results presented above can be compared with those obtained using the procedure suggested by Butler[41] in which he argues that a muffin-tin form of pseudoatom potential can be constructed by using the atomic sphere approximation (ASA). Andersen[9] has pointed out that the logarithmic derivatives of the wave functions, evaluated at the Wigner-Seitz radius, are approximately independent of the choice of MTZ and can therefore be used to obtain new phase shifts δ_l^* at any new Fermi energy E_F^*. Butler then noted that new wave-function coefficients T_{ll}^{t*} can be obtained by setting

$$T_{ll}^{t*} = T_{ll}^{t}(E_F)(R_l/R_l^*)^2 ,$$

where

$$R_l = j_l(\sqrt{E_F}R_{\mathrm{WS}})\cos(\delta_l) - n_l(\sqrt{E_F}R_{\mathrm{WS}})\sin(\delta_l)$$

and

$$R_l^* = j_l(\sqrt{E_F}^*R_{\mathrm{WS}})\cos(\delta_l^*) - n_l(\sqrt{E_F}^*R_{\mathrm{WS}})\sin(\delta_l^*) .$$

In practice the results of phase-shift parametrizations of Fermi surfaces show that "focusing" radii exist and are indeed close to R_{WS}, e.g., for the metals considered here the maximum deviation, in copper,[38] is about 15%.

This approach has been applied here using both the focusing radii and the Wigner-Seitz radii and the results, shown in Table II, are compared with those from the fitting procedure. The phase shifts and values of T_{ll}^t are taken from the fit near a band-structure choice of E_F which is used as the basis of the calculation, and E_F^* is chosen near the pseudoatom value. The nonspherical correction terms have been ignored (with little error in the calculated value of λ) and the various contributions from the *s-p*, *p-d*, and *d-f* scattering terms are shown separately as an indication of the extent to which the electron-phonon interaction exhibits anisotropy over the Fermi surface. In all four cases the ASA values agree rather well

TABLE II. Values of λ and angular momentum decomposition calculated using the RMTA (neglecting nonspherical terms) for values of E_F near the "band-structure" value and near the pseudoatom value. "Fit" denotes phase shifts and density matrix coefficients T_{ll}^t derived from a Fermi-surface fit. Scaled values of T_{ll}^{t*} are derived using Butler's procedure with either "focusing" radii (i.e., with the same phase shift as for the fit at the same value of E_F) or with Wigner-Seitz radii. Values of $N(E_F)$, $\langle\omega^2\rangle$, and experimental values of λ are taken from Table I except for lead where all parameters are taken from Ref. 19.

	E_F (Ry)	Method	λ *s-p*	*p-d*	*d-f*	Total
Potassium	0.155	fit	0.010	0.001		0.01
	0.057	fit	0.098	0.082		0.18
	0.057	R_{focus}	0.069	0.060		0.13
	0.057	R_{WS}	0.141	0.059		0.20
		expt				0.15
Aluminum	0.653	fit	0.014	0.164		0.18
	0.328	fit	0.008	0.455		0.46
	0.328	R_{focus}	0.008	0.356		0.36
	0.328	R_{WS}	0.001	0.508		0.51
		expt				0.45
Copper	0.588	fit	0.002	0.039	0.021	0.06
	0.255	fit	0.019	0.095	0.011	0.13
	0.255	R_{focus}	0.013	0.069	0.008	0.09
	0.255	R_{WS}	0.030	0.087	0.016	0.13
		expt				0.13
Niobium	0.623	fit	0.026	0.321	0.763	1.11
	0.323	fit	0.001	0.062	1.082	1.14
	0.323	R_{focus}	0.001	0.051	0.955	1.01
	0.323	R_{WS}	0.000	0.058	1.049	1.11
		expt				1.12
Lead	0.365	BS	0.096	0.740	0.000	0.84
	0.119	R_{WS}	0.011	1.505	0.016	1.53
		expt				1.55

with the result obtained from a Fermi-surface fit at the same Fermi energy. Using the focusing radii, i.e., with the fitted phase shifts but scaled values of T^{t*}_{ll}, leads to values of λ of order 10% different. Comparison of the angular momentum decomposition shows that agreement between the two methods of calculation is best in the transition metals (niobium and copper) and worst in the simplest metal (potassium). It is also quite apparent in the transition metals that though the average value of λ changes by a relatively small amount as the MTZ is shifted from the band-structure value to the pseudoatom value the relative contribution of the various angular momentum components changes quite markedly.

The approach of Butler was also applied to the case of lead using the band-structure values quoted by Papaconstantopoulous *et al.*[19] The criterion of setting $-Z/2N(E_F)=E_F-E_{F0}$ fixes $E_F{}^*$ at 0.119 Ry which yields a calculated value of $\lambda=1.53$ using the ASA version of Butler's theory. This is in good agreement with the quoted experimental value of 1.55. It should be noted that using the alternative criterion of $E_F{}^*=E_{F0}/3$ gives λ about 20% low, a result following the same trend as those in Fig. 2.

It is possible to get an idea of how properties calculated using the RMTA are affected by moving the MTZ to the pseudoatom value from the band-structure value. In all metals it appears that the relative contribution of the various angular momentum components will be changed and any property sensitive to the anisotropy of the electron-phonon interaction will therefore be modified. Two obvious examples are the anisotropy of λ, as is indeed observed in Nb, and the anisotropy of the low-temperature electron-phonon scattering rate (see, e.g., the calculation of Nowak which uses essentially the same procedure). As another example, in niobium there is a strong coupling to [100] and [110] phonons that can be traced to transitions between fairly localized regions of the Fermi surface[6] so the strength of this coupling will be modified when the MTZ is shifted.

In simple metals, the value of λ is dominated by the low-q part of the pseudopotential which changes markedly as E_F is reduced, and this is reflected in a large change of λ. There will also be a large change in the low-temperature scattering rate and resistivity but the high-temperature resistivity which is more uniform Fermi-surface average will be much less effected. In transition metals the highly nonlocal nature of the pseudopotential explains why λ is only weakly affected but the low-temperature resistivity should still be changed and indeed the simple RMTA tends to give an incorrect value for the resistivity at low temperatures although it is approximately correct at high temperatures.[42]

VI. CONCLUSIONS

Using several examples it has been demonstrated that a rigid-muffin-tin version of a pseudoatom potential can be constructed which yields accurate (within 10%) values of the electron-phonon coupling parameter. In simple metals the value of λ is rather sensitive to the choice of the Fermi-energy parameter and so the criterion used for making that choice, i.e., to take

$$E_F-E_{F0}=-Z/2N(E_F)\ ,$$

is confirmed rather sensitively. In transition metals this criterion cannot be used, if only because the values of Z and E_{F0} are not well defined, but the average value of λ is much less sensitive to the value of E_F and the choice of one half of the band-structure value appears to be satisfactory. In the intermediate case of copper the two criteria are rather closely equivalent.

When the pseudoatom choice of E_F has been established the phase shifts and wave-function coefficients can be established in two ways, by fitting the experimentally determined shape of the Fermi surface with a KKR calculation or by using the approach suggested by Butler and based on the atomic-sphere approximation. In simple metals the two approaches give slightly different results but in transition metals they appear to be essentially equivalent. Either technique can be applied, not only to the calculation of the coupling constant λ and its anisotropy over the Fermi surface, but to any property involving the electron-phonon matrix element and they can be used with parameters obtained either by fitting the Fermi surface or from *ab initio* band-structure calculations. Although the exact value for the choice of muffin-tin zero is sometimes slightly arbitrary, the modified form of the RMTA *always* gives values that are in better agreement with experiment than those obtained using the simple RMTA.

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