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Phase-Shift Pseudopotentials and the Electron-Phonon Interaction: Theory and Results for Alkali Metals

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The electronic properties of the alkali metals are interpreted by using augmented-plane-wave (APW) pseudopotentials derived from phase-shift analyses of experimental Fermi-surface data. The APW-pseudopotential form factors are found to be consistent with the results of local-pseudopotential interpretations of the experimental data, and with the energy gaps predicted by model-potential and band-structure calculations. It is shown that the matrix elements of the electron-phonon interaction can be deduced from the empirical phase shifts. The result is a form factor for electron-phonon coupling that is very similar to the APW form factor derived from the secular equation. The form factors for electron-phonon coupling are used to estimate the electrical resistivities and electron-phonon mass enhancements of the alkali metals. The trend of resistivities within the alkali-metal series is predicted correctly, and the renormalization factors are generally consistent with the experimental data, although the strength of the electron-phonon interaction in sodium is significantly overestimated, apparently because the experimental Fermi-surface data yield no information about V_{200} and higher pseudopotential coefficients.

I. INTRODUCTION

Experimental studies have yielded precise measurements of the anisotropies of the nearly spherical Fermi surfaces of the alkali metals, and the results have been analyzed by pseudopotential potentials based on the augmented-plane-wave (APW) method of band-structure calculation to determine the partial-wave phase shifts that describe the electron-ion interaction in these metals.[1]

Pseudopotential methods are frequently used to interpret Fermi-surface data and to correlate them with the other electronic properties of metals.[2] One associates with each lattice site in the metal a weak effective potential (the pseudopotential), which is expressed in terms of suitable parameters. The Schrödinger equation is solved for the shapes of surfaces of constant energy in $\vec{k}$ space, and the parameters of the pseudopotential are adjusted to bring the computed surfaces into agreement with the experimental data. The advantage of replacing the strong ionic potential by a weak pseudopotential is that atomiclike oscillations in the wave functions are eliminated, and one can obtain rapidly convergent solutions of the Schrödinger equation by expanding each pseudo wave function as a series of plane waves, which leads to a secular equation of the form

$$\det\{[(\vec{k}+\vec{g})^2 - E(\vec{k})]\,\delta_{\vec{g}\vec{g}'} + \Gamma(\vec{k}+\vec{g},\ \vec{k}+\vec{g}\,')\} = 0\ . \qquad (1)$$

In general, the pseudopotential $\Gamma(\vec{k}, \vec{k}')$ defined in this way is nonlocal, that is, it depends on energy and on angular momentum. We shall find it convenient to characterize the nonlocal pseudopotential by its form factor $\Gamma(q)$, which is defined as the matrix element for scattering on the free-electron Fermi sphere when $q \leqslant 2k_F$, and for back scattering from a state on the sphere when $q > 2k_F$.

Recent calculations have shown that, except perhaps for sodium, the Fermi-surface distortions of the alkali metals cannot be explained in detail unless the nonlocality of the pseudopotential is taken into account. Two different methods based on band theory have been used to construct nonlocal pseudopotential for the alkali metals. One of these, in which the matrix elements are derived from the orthogonalized plane wave (OPW) secular determinant, has been used to calculate pseudopotential form factors from first principles,[3] but has not been used to interpret Fermi-surface data. The other, the phase-shift method based on the APW secular determinant, has been used to analyze experimental Fermi-surface data for all of the alkali metals.[4]

The APW pseudopotential is often written in the form

$$\Gamma_{\text{APW}}(\vec{k}, \vec{k}') = \frac{4\pi R_s^2}{\Omega}\left((E - \vec{k}\cdot\vec{k}')\,\frac{j_1(|\vec{k}-\vec{k}'|R_s)}{|\vec{k}-\vec{k}'|} + \sum_l (2l+1) P_l(\cos\theta_{\vec{k}\vec{k}'})\, j_l(kR_s)\, j_l(k'R_s)\,(u_l'/u_l)_{R_s}\right), \qquad (2)$$

where R_s is the radius of the muffin-tin sphere, and $(u_l'/u_l)_{R_s}$ is the logarithmic derivative of the radial wave function of energy E and angular momentum l, evaluated at $r=R_s$. The radial wave function is conveniently expressed in terms of partial-wave phase shifts η_l by writing

$$u_l(R_s)=j_l(\kappa R_s)-\tan\eta_l\, y_l(\kappa R_s)\ , \qquad (3)$$

where

$$\kappa=\sqrt{E}\ .$$

In a phase-shift analysis one adjusts the phase shifts η_l and the Fermi energy parameter E_{F} that appear in the APW (or Korringa-Kohn-Rostoker) secular equation in order to bring the shape of the surface of constant energy

$$E(\vec{k})=E_{\mathrm{F}}$$

into agreement with the experimental Fermi-surface data. Even though the APW secular equation depends on Γ_{APW} only for $\vec{k}$ and $\vec{k}'$ differing by a reciprocal-lattice vector, the functional form (2) gives a representation of the pseudopotential for all wave vectors. In the preceding paper[5] it was shown that a set of APW pseudopotentials can be constructed in this way, the particular pseudopotential obtained depending on the choice of the Fermi energy parameter E_{F}. Two pseudopotentials of special interest were discussed, the minimum-perturbation pseudopotential, whose form factor satisfies

$$\lim_{q\to 0}\Gamma_{\mathrm{MP}}(q)=0\ , \qquad (4)$$

and the pseudo-atom pseudopotential, for which

$$\lim_{q\to 0}\Gamma_{\mathrm{PA}}(q)=-\left(\tfrac{2}{3}E_{\mathrm{F}0}\right)\ , \qquad (5)$$

where $E_{\mathrm{F}0}$ is the Fermi energy for free electrons. The former corresponds to a model of the metal in which the ionic potentials associated with each atomic cell is regarded as neutralized by the charge distribution within that cell. The latter corresponds to a superposition of long-range overlapping ionic potentials, each screened by an extended distribution of conduction charge.

In the present paper we discuss what is known experimentally and theoretically about the electronic properties of the alkali metals in terms of phase-shift pseudopotentials. In Sec. II we compare the APW form factors with local-pseudopotential interpretations of Fermi-surface data, and with the predictions of model potential and first-principles band-structure calculations. Our results are in agreement with calculations which predict that the p-like state $N_{1'}$ lies below the s-like state N_1 in lithium and sodium, but that this ordering is reversed in the heavier alklali metals. In Sec. III we calculate the matrix elements of the electron-phonon interaction, expressing them as form factors determined by the APW phase shifts. We emphasize that the phase shifts of the pseudoatom pseudopotential, rather than those of the minimum-perturbation pseudopotential, must be used to calculate the electron-phonon interaction. The electron-phonon form factors are very similar to, but not identical with, the APW pseudo-atom form factors discussed above. This similarity is the APW analog of an identity theorem for OPW-based pseudopotentials that has been proved by Sham.[6] In Sec. IV we use the electron-phonon form factors to calculate the phonon contribution to the electrical resistivities of the alkali metals at room temperature, and the renormalization of the energy bands at the Fermi surface caused by the electron-phonon interaction. We find good qualitative agreement with the experimental data, expecially in the heavier alkali metals, although our pseudopotential calculation seems to overestimate the electron-phonon interaction in sodium. Finally, in Sec. V we summarize the results and conclusions of this work.

II. BAND-STRUCTURE PROPERTIES

In this section we compare the APW-pseudopotential form factors with the results of local-pseudopotential interpretations of experimental Fermi-surface data, and with model-potential and first-principles band-structure calculations. A qualitative comparison between the pseudo-atom form factors and model-potential form factors by Animalu and Heine,[7] and Shaw,[8] and OPW-pseudopotential form factors by Harrison,[3] has been presented in a preliminary report of this work,[9] and will not be repeated here.

Analysis of Fermi-surface data has shown that only for sodium, and perhaps lithium, is a local pseudopotential an adequate model of the electron-ion interaction. Values of the local-pseudopotential coefficients for these metals have been derived by Cohen and Heine,[2] and by Lee,[10] from Fermi-surface data. The results are reproduced in Table I, where they are compared with the corresponding back-scattering matrix elements of the APW pseudopotentials. The agreement for lithium is satisfactory, although the numerical values of the coefficients cannot be determined very accurately because of uncertainties in the experimental data. The results for sodium show that the back-scattering matrix elements derived from the APW pseudopotentials are significantly smaller than those derived from local pseudopotential analysis of Fermi-surface data. It seems that, even for sodium, nonlocality of the pseudopotential must be taken into account if accurate pseudopotential coefficients are required. The shape of the Fermi surface of sodium is dominated by the V_{110} pseudopotential

TABLE I. Comparison of back-scattering matrix elements of the APW form factors with pseudopotential coefficients derived from local-pseudopotential analysis of experimental Fermi-surface data. Energies in rydbergs.

		Li	Na
Local	$\lvert V_{110}\rvert$	0.11 (Ref. 2)	0.0165(7) (Ref. 10)
Local	$\lvert V_{200}\rvert$	0 (Ref. 2)	≤0.022 (Ref. 10)
APW	V_{110}^{PA}	+0.102(39)	+0.009
APW	V_{200}^{PA}	+0.087(80)	+0.015
APW	V_{110}^{MP}	+0.108(39)	+0.013
APW	V_{200}^{MP}	+0.064(80)	−0.008

coefficient, and the value of V_{200} is determined only within wide limits by the experimental data. Correspondingly, the V_{200} coefficients of the APW-pseudopotential form factors for sodium are not well determined by fitting the Fermi-surface data, and consequently the APW form factors for sodium are probably less accurate than those of the heavier alkali metals.

Various estimates of the back-scattering matrix elements V_{110} and V_{200} in the alkali metals are set out in Table II. The results of Cohen and Heine[11] were deduced from the *sp* splitting of the atomic spectra. The values of V_{110} calculated from the model-potential form factor of Animalu and Heine[7] include second- and higher-order corrections that were taken from earlier calculations by Heine and Abarenkov.[12] These corrections turn out to be quite important in the heavier alkali metals. No such correction has been applied to the coefficients derived from Shaw's optimized model potential.[8] Also in Table II we present values of V_{110} and V_{200} calculated from the APW pseudo-atom and minimum-perturbation form factors. These two form factors are in good agreement with one another in the structure region, and the agreement with the predictions of Cohen and Heine[11] is remarkable. The matrix elements are large and positive in lithium, and become increasingly negative in the heavier alkali metals, apparently changing sign between sodium and potassium. As we shall see, this trend is consistent also with the results of first-principles band-structure calculations.

TABLE II. Back-scattering matrix elements V_{110} and V_{200} for the alkali metals (rydbergs).

				Present work	
	(a)	(b)	(c)	(d)	(e)
			V_{110}		
Li	0.076	0.100	0.072	0.102(39)	0.108(39)
Na	0.010	0.022	0.018	0.009	0.013
K	−0.004	−0.002	0.004	−0.005	−0.005
Rb	−0.013	−0.008		−0.011	−0.013
Cs	−0.016	−0.018		−0.016	−0.019
			V_{200}		
Li		0.063	0.060	0.087(80)	0.064(80)
Na		0.009	0.014	0.015	−0.008
K		−0.005	−0.002	−0.017	−0.015
Rb		−0.008		−0.018	−0.018
Cs		−0.010		−0.020	−0.023

[a] Reference 11.

[b] Ref. 7 (but including higher-order corrections estimated from Ref. 12).

[c] Reference 8.

[d] APW-pseudo-atom form factor.

[e] APW-minimum-perturbation form factor.

TABLE III. First-principles calculations of the energy level splitting $(N_1 - N_1')$ in the alkali metals, and comparison with the back-scattering matrix elements of the APW pseudopotentials. Energies are in rydbergs. The quantum defect method is abbreviated QDM.

	Li	Na	K	Rb	Cs
OPW	0.233[a]	0.053[b]	−0.034[c]		−0.043[d]
QDM	0.219[e]	0.017[e]	−0.032[e]	−0.057[e]	−0.085[e]
APW	0.125[f]	0.029[f]	−0.027[g]	−0.054[h]	−0.069[h]
APW	0.201[i]	0.041[i]	−0.009[i]	−0.025[i]	−0.052[i]
$2V_{110}^{\mathrm{PA}}$	0.204	0.018	−0.011	−0.022	−0.032
$2V_{110}^{\mathrm{MP}}$	0.216	0.025	−0.010	−0.027	−0.039

[a] Reference 13

[b] Reference 14

[c] Reference 15

[d] Reference 16

[e] Reference 17

[f] Reference 18

[g] Reference 19

[h] Reference 20

[i] Reference 21

In the two-band approximation, the energy level splitting at N (the center of the rhombohedral face of the Brillouin zone of a bcc structure) is given by

$$(N_1 - N_{1'}) = 2V_{110}\,, \qquad (6)$$

where V_{110} is the local-pseudopotential coefficient. In sodium, V_{110} deduced from various band gaps is known to vary rather slowly with energy, and the energy level splitting at N should be close to twice the coefficient V_{110} deduced from the Fermi-surface distortions. Even though the local-pseudopotential approximation is inadequate to describe the band structures of the heavier alkali metals, the energy level splitting at N is expected to be related to the back-scattering matrix element of a nonlocal pseudopotential, approximately as in Eq. (6). Recent estimates of the level splitting in the alkali metals[13–21] are set out in Table III. The results of the various first-principles calculations vary somewhat among themselves, but are in qualitative agreement with the APW-pseudopotential analyses. In particular, they are consistent with our conclusion that the *p*-like state $N_{1'}$ is lower than the s-like state N_1 in Li and Na, whereas this ordering is reversed in K, Rb, and Cs.

It is convenient to express the APW pseudopotential in the form appropriate for scattering from a weak potential

$$\Gamma_{\mathrm{APW}}(k, k') = -\frac{4\pi}{k_F \Omega} \sum_l (2l+1) P_l(\cos\theta) \tan\delta_l \,, \tag{7}$$

where δ_l is an "effective" phase shift. Using well-known identities we can express Eq. (2) in the form of Eq. (7), with the result

$$\tan\delta_l = -k_F R_s^2 \left[j_l^2 (u_l'/u_l - j_l'/j_l) + \tfrac{1}{2} R_s (E - k_F^2)(j_l^2 - j_{l+1} j_{l-1}) \right] , \tag{8}$$

where the spherical Bessel functions j_l have the argument $k_F R_s$. In deriving Eq. (8) we have assumed that $\vec{k}$ and $\vec{k}'$ both lie on the free-electron sphere of radius k_F. The radial wave function u_l is to be evaluated at the muffin-tin radius; it can be expressed in terms of the APW phase shifts η_l by Eq. (3). In the special case $\kappa = k_F$, which corresponds to the minimum-perturbation pseudopotential, Eq. (8) reduces to

$$\tan\delta_l = \tan\eta_l (j_l/u_l) \,. \tag{9}$$

The pseudo-atom phase shifts calculated from Eq. (8) can be compared with the pseudo-atom phase shifts discussed by Meyer, Nestor, and Young,[22] as presented in Table IV. The discrepancies are greatest for lithium and cesium. Our pseudo-atom phase shifts for lithium are subject to substantial uncertainties because of uncertainties in the experimental data. Meyer *et al.* suggest that their calculated phase shifts for cesium may be rather unreliable because of a breakdown of the small-core approximation. In general, however, our results confirm their prediction of the trend of the pseudo-atom phase shifts within the alkali metal series.

III. ELECTRON-PHONON INTERACTION

In order to calculate the electron-phonon matrix element $\vec{I}(\vec{k}, \vec{k}')$, we need to know how the total potential in the crystal is altered when a single atom is displaced. This difficult problem has been discussed by many authors[23]; we note particularly a recent discussion from an APW point of view by Sinha.[24] Our point of view on this problem is very simple. We accept the argument from many-body perturbation theory that each atom carries with it rigidly an effective screened potential that is the same as the effective screened potential that determines the energy bands.[25] The problem then remains that for APW purposes, this potential has been cut into muffins, each of which contains not only the screened potential of the central atom, but also the tails of the potentials of near neighbors. Rather than attempt to invert from the muffin potentials to the actual screened potentials, we shall simple assume that the muffin potential has been chosen in such a way as to approximate most nearly the actual screened potential. This is accomplished in practice by working with the pseudo-atom phase shifts.

Within this framework, we are left with the task of calculating the matrix element of the displaced muffin potentials:

$$\hat{\epsilon} \cdot \vec{I}(\vec{k}, \vec{k}') \equiv \langle \vec{k}' | \hat{\epsilon} \cdot \vec{\nabla} V | \vec{k} \rangle \,, \tag{10}$$

where V is a single muffin potential and the states $|\vec{k}\rangle$ or $\psi_{\vec{k}}$ are APW states of the form $\exp(i\vec{k}\cdot\vec{r})$ outside the muffin-tin sphere, and smoothly matched eigenfunctions of energy E inside. Golibersuch[26] (and others earlier[27]) have shown that, by using only the assumption that $|\vec{k}\rangle$ and $|\vec{k}'\rangle$ have the same energy, Eq. (10) can be written as an integral over the surface of the muffin-tin sphere

$$\hat{\epsilon} \cdot I(\vec{k}, \vec{k}') = \frac{R_s^2}{\Omega} \int d\Omega \left[\psi_{\vec{k}'}^* \left(\frac{\partial}{\partial r} \hat{\epsilon} \cdot \nabla \psi_{\vec{k}} \right) - \left(\frac{\partial}{\partial r} \psi_{\vec{k}'}^* \right) (\hat{\epsilon} \cdot \nabla \psi_{\vec{k}}) \right]_{r = R_s} , \tag{11}$$

where the functions $\psi_{\vec{k}}$ are evaluated just inside the muffin sphere. We define the electron-phonon-interaction pseudopotential $\Gamma_{\mathrm{EP}}(\vec{k}', \vec{k})$ by

$$\vec{I}(\vec{k}, \vec{k}') = i(\vec{k}' - \vec{k}) \Gamma_{\mathrm{EP}}(\vec{k}', \vec{k}) \tag{12}$$

and proceed to express Γ_{EP} in terms of the APW phase shifts η_l.

Let us consider the contribution of a single harmonic component of ψ to the integral (11). We write

$$\vec{I}(\vec{k}, \vec{k}') = \sum_{lm,\, l'm'} c_{l'm}^*(\vec{k}') c_{lm}(\vec{k}) \vec{I}(l'm', lm), \tag{13}$$

TABLE IV. Comparison between pseudo-atom phase shifts (in radians) calculated by Meyer *et al.* and phase shifts δ_l calculated from the APW-pseudo-atom form factors [Eq. (8)].

		δ_0	δ_1	δ_2
Li	a	0.242	0.417	0.015
	b	0.558(120)	0.329(46)	−0.016(31)
Na	a	0.582	0.284	0.026
	b	0.616(2)	0.246(1)	0.022(1)
K	a	0.535	0.212	0.078
	b	0.494(1)	0.241(1)	0.059(1)
Rb	a	0.574	0.191	0.083
	b	0.525(6)	0.223(3)	0.062(2)
Cs	a	0.445	0.122	0.149
	b	0.535(21)	0.198(7)	0.074(5)

[a] Reference 22. [b] Present work.

where we have defined

$$\psi_{\vec{k}} = \sum_{lm} c_{lm}(\vec{k})\psi_{lm}(\vec{r}) , \tag{14a}$$

$$\psi_{lm}(\vec{r}) = u_l(\vec{r})\, Y_{lm}(\hat{r}) , \tag{14b}$$

$$c_{lm}(\vec{k}) = 4\pi i^l\, Y^*_{lm}(\hat{k})\,[\,j_l(k_F R_s)/u_l(R_s)\,] , \tag{14c}$$

and the integral is defined, with no loss of generality, by taking only the z component

$$\hat{z}\cdot\vec{I}(l'm', lm) = \frac{R_s^2}{\Omega}\int d\Omega\left[\,\psi^*_{l'm'}\left(\frac{\partial}{\partial r}\,\frac{\partial}{\partial z}\,\psi_{lm}\right) - \left(\frac{\partial}{\partial r}\,\psi^*_{l'm'}\right)\left(\frac{\partial}{\partial z}\,\psi_{lm}\right)\right] . \tag{15}$$

The Wigner-Eckart theorem gives selection rules for the matrix element (15), namely, $\Delta l = \pm 1$ and $\Delta m = 0$. (The former selection rule is the basis of a paper by Hopfield.[28]) Furthermore, we can express all the integrals in terms of the $m = 0$ integrals. The result is that (15) becomes

$$\hat{z}\cdot\vec{I}(\vec{k}, \vec{k}') = (4\pi)^2 i \sum_l (j_l j_{l+1}/u_l u_{l+1}) I_z(l) \times \sum_m \{[(l+1)^2 - m^2]^{1/2}/(l+1)\}\,[\,Y^*_{l+1,m}(\hat{k})\,Y_{lm}(\hat{k}') - Y^*_{l,m}(\hat{k})\,Y_{l+1,m}(\hat{k}')\,] . \tag{16}$$

The notation $I_z(l)$ is shorthand for $\hat{z}\cdot\vec{I}(l+1, 0; l, 0)$ as defined in Eq. (15). Making successive applications of the recursion relation

$$\left[\frac{(l+1)^2 - m^2}{(2l+1)(2l+3)}\right]^{1/2} Y_{l+1,m} = \cos\theta\; Y_{l,m} - \left(\frac{l^2 - m^2}{(2l-1)(2l+1)}\right)^{1/2} Y_{l-1,m} \tag{17}$$

and the addition theorem for spherical harmonics, we obtain

$$\hat{z}\cdot\vec{I}(\vec{k}, \vec{k}') = 4\pi i(\cos\theta_{\vec{k}} - \cos\theta_{\vec{k}'})\sum_l (j_l j_{l+1}/u_l u_{l+1}) \times I_z(l)\{[(2l+1)(2l+3)]^{1/2}/(l+1)\} \times \sum_{n\leq l}(2n+1)P_n(\cos\theta_{\vec{k}\vec{k}'}) . \tag{18}$$

Using standard techniques[24,26] to evaluate the angular integral $I_z(l)$, we find

$$J_z(l) \equiv \{[(2l+1)(2l+3)]^{1/2}/(l+1)\}\, I_z(l) = (R_s^2/\Omega)\,[(u_{l+1}u_l'' - u_{l+1}'u_l') - (l/R_s)(u_{l+1}u_l' - u_{l+1}'u_l) + (l/R_s^2)u_l u_{l+1}\,] . \tag{19}$$

Using Eq. (3) and the recursion relations and Wronskians for spherical Bessel functions, Chui[29] has succeeded in reducing (19) still further (details are given in the Appendix). His result is

$$J_z(l) = (1/\Omega)(\tan\eta_l - \tan\eta_{l+1}) . \tag{20}$$

Finally, using the free-electron-sphere approximation $k = k' = k_F$, the result for the electron-phonon form factor (12) is

$$\Gamma_{\mathrm{EP}}(\vec{k}, \vec{k}') = -(4\pi/k_F\Omega)\sum_l (j_l j_{l+1}/u_l u_{l+1}) \times (\tan\eta_l - \tan\eta_{l+1})\sum_{n\leq l}(2n+1)P_n(\cos\theta) , \tag{21}$$

where the argument of the spherical Bessel functions is $k_F R_s$. It is convenient to write this expression in the form

$$\Gamma_{\mathrm{EP}}(\vec{k}, \vec{k}') = -(4\pi/k_F\Omega)\sum_l (2l+1)P_l(\cos\theta)\tan\xi_l . \tag{22}$$

By manipulating (21), we find

$$\tan\xi_l = \frac{j_l j_{l+1}}{u_l u_{l+1}}\tan\eta_l + \sum_{n=l+1}^{\infty}\frac{j_n}{u_n}\left(\frac{j_{n+1}}{u_{n+1}} - \frac{j_{n-1}}{u_{n-1}}\right)\tan\eta_n . \tag{23}$$

Our expressions (22) and (23) for the form factor of the electron-phonon interaction cannot be reduced to those given earlier [(7) and (8)] for the form factor of the APW pseudopotential. However, we have evaluated the two form factors numerically, using the APW phase shifts obtained by analyzing the Fermi-surface data for each of the alkali metals. In each case we have adjusted the Fermi energy parameter to set $\lim_{q\to 0}\Gamma(q) = -(\frac{2}{3}E_{\mathrm{F0}})$ as discussed by Lee and Heine.[5] Our results are given in Figs. (1) and (2), and the corresponding phase shifts ξ_l are given in Table V. The APW form factors are a very good approximation to the electron-phonon form factors in all the alkali metals, although there are small discrepancies for K, Rb, and Cs in the region $q \simeq 2k_F$.

It is not accidental that Γ_{EP} and Γ_{APW} are very

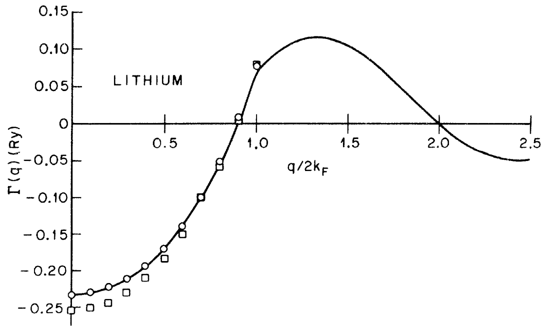

FIG. 1. The solid line is the APW-pseudo-atom form factor for lithium. The squares represent the electron-phonon form factor calculated from the same values of η_l, whereas the circles give the electron-phonon form factors calculated from a set of η_l's chosen to make the $q = 0$ limit equal to $-\frac{2}{3}E_{F0}$.

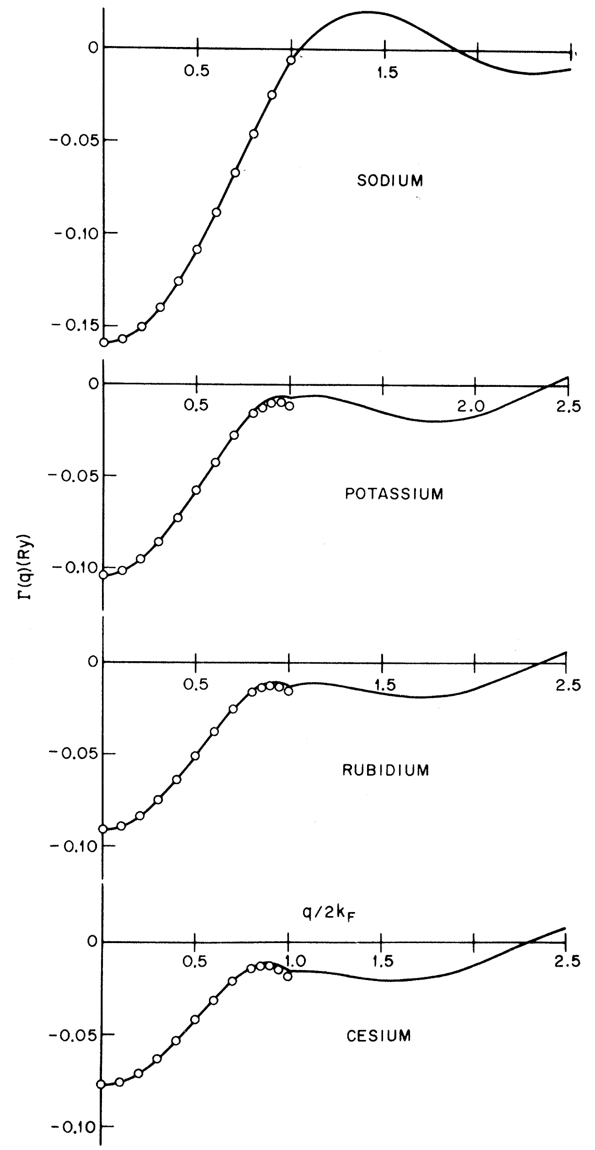

FIG. 2. Form factors for the alkali metals. Lithium is illustrated separately in Fig. 1. The solid line is the APW form factor and the circles are the EP form factor, as in Fig. 1.

similar. Sham[6] demonstrated that the matrix element $\vec{I}(\vec{k}, \vec{k}')$ of Eq. (10) is invariant under the replacement of real wave functions by OPW pseudo wave functions, and the real potential by the OPW pseudopotential, provided that the states $|\vec{k}\rangle$ and $|\vec{k}'\rangle$ are exact eigenstates of the same energy. Sham's arguments have been generalized by Austin, Heine, and Sham[30] and by one of the authors[31] to include a broad class of pseudopotentials, including, in principle, the APW pseudopotential. Thus Γ_{EP} and Γ_{APW} would have been identical if the single APW states used in constructing the form factors had been exact eigenstates. The close similarity of Γ_{EP} and Γ_{APW} arises from the fact that a single APW is a good approximate eigenfunction for an alkali metal.

IV. CALCULATION OF λ AND ρ

In this section we present calculations of the electron-phonon mass-enhancement parameter λ and the phonon resistivity ρ from the electron-phonon form factor $\Gamma_{EP}(q)$ defined in Sec. III.

Rigorous formulas for λ and ρ are[32]

$$\lambda = N(0)\langle\langle |M_{\vec{k}\vec{k}'}|^2/\hbar\omega_{\vec{q}}\rangle\rangle \quad , \tag{24}$$

$$\rho = (3\pi k_B T/\hbar n e^2)\langle\langle |M_{\vec{k}\vec{k}'}|^2(\vec{v}_k - \vec{v}_{k'})^2 \times N_{\vec{q}}(N_{\vec{q}}+1)\hbar\omega_{\vec{q}}\rangle\rangle/\langle v_k^2\rangle^2 \ , \tag{25}$$

where $M_{\vec{k}\vec{k}'}$ is the matrix element for scattering from a state $\vec{k}$ to a state $\vec{k}'$, both on the Fermi surface (FS) by phonons of frequency $\omega_{\vec{q}}$ (where $\vec{q}$ is the momentum transfer $\vec{k}' - \vec{k}$ reduced to the first Brillouin zone). A summation over all allowed phonon modes is implied in all our equations. The density of states at the Fermi energy $N(0)$ should not be renormalized by the electron-phonon interaction; n is the carrier density, $N_{\vec{q}}$ is the Bose distribution function, and $\vec{v}_k = \nabla_k \epsilon_k/\hbar$ is the velocity associated with the electron state $\vec{k}$. The ⟨⟩ indicate that the term inside is to be averaged over the FS according to the rule

$$\langle A_{\vec{k}}\rangle = \frac{\int_{FS} dS_{\vec{k}} A_{\vec{k}} |v_k|^{-1}}{\int_{FS} dS_{\vec{k}} |v_{\vec{k}}|^{-1}} \quad . \tag{26}$$

[The double brackets in Eqs. (24) and (25) imply that both states $\vec{k}$ and $\vec{k}'$ are so averaged.] Equation (24) is exact in perturbation theory[33] to order $(m/M)^{1/2}$, the square root of the electron-to-ion mass ratio. Equation (25) assumes that phonons are in equilibrium, and results from a variational trial function[27] $\varphi_{\vec{k}} = \text{const} \times \vec{v}_k \cdot \vec{E}$ for the deviation of the electron distribution from equilibrium in the presence of a field $\vec{E}$. Calculations of both λ and ρ based on Eq. (24) and (25) have appeared frequently. For a detail of the present method and a review of much of the previous work on λ, see Allen and Cohen.[34] For calculations of ρ see, for example, Dynes and Carbotte.[35]

For the alkali metals it is a very good approximation to take the Fermi surfaces as spherical and the wave functions on the Fermi surfaces as single APW's. In this approximation, the matrix element reduces to

$$M_{\vec{k}\vec{k}'} = i(\hbar/2M\omega_q)^{1/2}\,\hat{\epsilon}_q \cdot (\vec{k}' - \vec{k})\,\Gamma_{EP}(\vec{k}' - \vec{k}) \ , \tag{27}$$

where M is the ionic mass and $\hat{\epsilon}_q$ is the phonon polarization vector. The calculation of λ and ρ is now straightforward, provided that the phonon dispersion relations and polarizations are known.

TABLE V. Phase shifts ξ_l that enter in the expression [Eq. (22)] for the form factor of the electron-phonon interaction.

	ξ_0	ξ_1	ξ_2
Li	0.544(120)	0.339(50)	−0.018(30)
Na	0.615(2)	0.246(1)	0.022(1)
K	0.511(1)	0.228(1)	0.063(1)
Rb	0.536(6)	0.213(3)	0.066(2)
Cs	0.534(20)	0.205(10)	0.071(5)

The dispersion relations for all the alkali metals except Cs have been measured along symmetry directions by inelastic neutron scattering.[36] The most accurate procedure is to calculate ω_q and $\hat{\epsilon}_q$ from a model dynamical matrix adjusted to fit the experimental data. However, experience[34] has shown that ω_q can be replaced by a spherically averaged frequency $\omega(|\vec{q}|)$ without significantly reducing the (necessarily limited) accuracy of calculations of λ and ρ. We therefore have used a spherical model for ω_q, constructed by averaging $(1/\omega_q^2)$ as obtained from data along symmetry directions, or for cesium, from Ho's[37] pseudopotential calculation. The polarizations $\hat{\epsilon}_q$ are assumed to be either pure longitudinal or pure transverse. There is no coupling via transverse phonons unless $\vec{k}' - \vec{k}$ lies outside the first Brillouin zone (Umklapp process.)

The density of states $N(0)$ and the Fermi velocity v_F are approximated by free-electron values. Band-structure effects in the alkali metals increase $N(0)$ to a value $N_B(0) = m_B N(0)$, where m_B is a dimensionless measure of the band mass at the Fermi level relative to the free electron mass. Correspondingly v_F is reduced to a value v_F/m_B. We have set m_B equal to unity because the band masses of the alkali metals are at present unknown. One method of estimating m_B is to divide the phonon renormalized density of states determined from the low-temperature electronic-specific-heat coefficient γ, by the phonon-enhancement factor $1+\lambda$. However, we are not sufficiently confident of current information about λ and γ to follow this approach. Ham's[17] first-principle calculations of m_B have been accepted for many years and are probably as reliable as any; however, they are not completely consistent with what is known about γ and λ. The available evidence suggests that for Na, K, and perhaps Rb, the value of m_B is close to unity, whereas for Li and Cs, m_B is somewhat larger. When more reliable values of m_B are available our results for λ and ρ can be corrected by multiplying by factors of m_B and m_B^2, respectively.

Our results have also been influenced by our setting $m_B = 1$ in that the form factors themselves have been constructed to approach $-N(0)^{-1}$ as q approaches zero. If we had instead used the (unknown) band density of states $-N_B(0)^{-1}$, this would have altered the shape of $\Gamma(q)$, multiplying it by a factor m_B^{-1} at $q=0$ but by a factor much closer to unity in the region $q \approx 2k_F$. The values of λ and ρ are more sensitive to q near $2k_F$ then q near zero, so this alteration of $\Gamma(q)$ is likely to reduce λ and ρ by a factor closer to unity than m_B^{-2}, but probably still significant.

In Table VI we present our values of λ using both the form factors Γ_{APW} and Γ_{EP}; the values obtained from Γ_{APW} are included to illustrate the sensitivity of λ to small changes in Γ in the region near $q = 2k_F$. Also collected in the same table are values of λ calculated by several other authors.[38–42] These other calculations differ from ours both in the choice of the pseudopotential form factors and in the parametrization of the phonon spectra. To illustrate the effect of the latter, we also show values of λ that we have calculated using our model of the phonon spectra, but using the form factors of the original authors. These results demonstrate that our model tends to yield slightly larger values of λ.

TABLE VI. Various calculations of λ for alkali metals are summarized here; in all cases the numbers have been rescaled to a free-electron choice of $N(0)$. The abbreviation HA is for the Heine-Abarenkov model potential (Ref. 12); SS is for the Schneider-Stoll empirical potential fit to phonon data (Ref. 38); APW and EP are for the form factors Γ_{APW} and Γ_{EP} defined in this paper.

	Potential	Li	Na	K	Rb	Cs
Animalu *et al.*[a]	HA	0.08	0.13 0.15[b]	0.15	0.17	0.13
Janak[c]	HA		0.13	0.12		
Robinson[d]	HA	0.38	0.11	0.11	0.12	0.11
Allen and Cohen[e]	HA	0.39	0.15	0.14	0.14	0.12
Schneider *et al.*[f]	SS	0.24	0.18	0.12	0.11	0.10
Present calculation[g]	SS	0.28	0.23	0.17	0.16	0.13
Present calculation	APW	0.57	0.39	0.15	0.18	0.19
Present calculation	EP	0.62	0.38	0.18	0.21	0.21

[a] Reference 39. These numbers are obtained from theoretical dispersion curves, *not* adjusted to experiment; pure longitudinal and transverse polarization is assumed. The theoretical $\omega(q)$ for Li is too high, which explains the small value found for λ.

[b] Same as a except experimental dispersion curves were used.

[c] Reference 40. Spherical dispersion curves were used as in the present calculation; two OPW matrix elements were also tried, and agreed with the one OPW results.

[d] Reference 41. Phonon spectra were obtained from a force-constant fit to the neutron data.

[e] Reference 34. The method is the same as in the present calculation.

[f] Reference 42. Phonon spectra were calculated from a pseudopotential constructed to agree with neutron data. The same pseudopotential is used to calculate λ.

[g] The present method, but using the form factors of f.

TABLE VII. Mass enhancement λ and resistivity ρ calculated from Γ_{EP}.

	λ	ρ(295 K) $\mu\Omega$ cm (theor.)	ρ(295 K) $\mu\Omega$ cm (expt.)[a]
Li	0.62	11.8	9.3
Na	0.38	10.5	4.8
K	0.18	9.0	7.2
Rb	0.21	16.3	12.5
Cs	0.21	23.5	20.0

[a] The experimental values of ρ are taken from G. T. Meaden, *Electrical Resistivities of Metals* (Plenum, New York, 1965).

In Table VII we present the values of λ and ρ calculated from the form factors Γ_{EP}. Except for sodium, the resistivities are in satisfactory agreement with the experimental results. The trend within the alkali series is given correctly, but the absolute resistivities are overestimated by a nearly uniform 20%, which is comparable with the uncertainty ascribable to our parametrization of the phonon spectra. However, the sodium results are anomalously large by about a factor of 2, and this must be ascribed to an error in the form factor Γ_{EP}. As emphasized above, the form factor for sodium is perhaps the least accurate of all the alkali metals in the important region $q \approx 2k_F$ because the shape of the Fermi surface gives no information about V_{200} and higher pseudopotential coefficients.

Our calculations provide further support to the suggestion[34,42] that in lithium λ is quite large. Since m_B is probably quite a bit larger than unity, it seems likely that our calculated value ($\lambda = 0.62$) is too large. However, it is hard to escape the conclusion that λ for lithium should be larger than for the other alkali metals.

One must then reconcile this with the experimental observation that lithium remains nonsuperconducting down to temperatures in the millidegree range.[43] The simplest hypothesis is that the Coulomb repulsion μ^* (see McMillan's paper[44] for the relationship between superconductivity and λ and μ^*) is anomalously large. However, a large value of m_B would only partially explain a large value of μ^*.[34] Another possibility is that lithium has a significant exchange enhancement, which might explain both the large liquid-lithium spin susceptibility[45] and the absence of superconductivity.[46] It would be most helpful in resolving the puzzles in lithium if the specific-heat coefficient γ were remeasured and the band density of states recomputed. For the latter purpose, optical data would be very helpful.

V. CONCLUSIONS

We have shown that the APW pseudopotential form factors derived from experimental Fermi-surface data and presented in the preceding paper[5] are consistent with what is known about the energy-band structures of the alkali metals. We have described a model of the electron-phonon interaction based on the displacement of rigid pseudoatom pseudopotentials. This approach leads to generally satisfactory results for the electron-phonon renormalizations and phonon resistivities of the alkali metals, although it overestimates the electron-phonon interaction in sodium.

The phase-shift pseudopotentials serve to correlate what is known about the Fermi surfaces, band structures, and electron-phonon interaction in the alkali metals. For these metals the analysis is relatively simple because the Fermi surfaces are very nearly spherical and lie entirely within the first Brillouin zone. Nevertheless, the method described here can be applied directly to correlate the electronic properties of other nontransition metals, and may well prove capable of generalization to apply also to the noble and transition metals.

Note added in proof. More recent calculations suggest that the discrepancies for Na result from convergence difficulties in fitting the Fermi-surface data.[47]

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APPENDIX

The following is Chui's method[29] for deriving Eq. (20). Consider the expression

$$Q_l(a, b) \equiv \left[(a_l'' b_{l+1} - a_l' b_{l+1}') - (l/x)(a_l' b_{l+1} - a_l b_{l+1}') + (l/x^2) a_l b_{l+1} \right], \quad \text{(A1)}$$

where a_l and b_l are functions of x and the primes denote differentiation with respect to x (rather than r as previously). When a and b are both set equal to the radial function u [as in Eq. (3)], then Q_l equals $J_z(l)$ as given in Eq. (19) to within constant factors. We wish to prove that

$$Q_l(u, u) = (1/x^2)(\tan\eta_l - \tan\eta_{l+1}), \quad \text{(A2)}$$

which then allows Eq. (20) to be deduced from Eq. (19). We can expand $Q_l(u, u)$ in terms of Bessel functions j_l and y_l

$$Q_l(u,u) = Q_l(j,j) - \tan\eta_l\, Q_l(y,j) - \tan\eta_{l+1}\, Q_l(j,y) + \tan\eta_l \tan\eta_{l+1}\, Q_l(y,y)\,. \qquad \text{(A3)}$$

We now drive an expression for $Q_l(a, b)$ that is valid provided a_l and b_l satisfy the recursion relations

$$f_l' = \left(\frac{l}{2l+1}\right) f_{l-1} - \left(\frac{l+1}{2l+1}\right) f_{l+1}\,, \qquad \text{(A4)}$$

$$\left(\frac{1}{2l+1}\right) f_{l-1} - \frac{1}{x} f_l = -\left(\frac{1}{2l+1}\right) f_{l+1}\,. \qquad \text{(A5)}$$

These recursion relations are in fact satisfied by j_l and y_l but not by u_l. We use relation (A4) to reduce a_l'' and a_l' in the first term in Eq. (A1). The result can be expressed as

$$Q_l(a,b) = \frac{l}{x}\,[a_l, b_{l+1}] - \frac{1}{2l+1}\,[a_{l-1}, b_{l+1}] + \left(\frac{l+1}{2l+1}\right)[a_{l+1}, b_{l+1}] + \frac{l}{x^2}\, a_l b_{l+1}\,, \qquad \text{(A6)}$$

where the brackets denote a Wronskian. We use (A5) to reduce a_l and a_{l-1} in (A6), which gives

$$Q_l(a,b) = [a_{l+1}, b_{l+1}]\,. \qquad \text{(A7)}$$

The Wronskians of spherical Bessel functions are

$$[j,j] = [y,y] = 0$$

and

$$[j,y] = -[y,j] = (1/x^2) \qquad \text{(A8)}$$

and (A2) follows immediately from (A3) and (A8).

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Electron-Phonon Coupling and Pseudopotentials: The Mass Enhancements of the Noble Metals

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The first-principles form factors of Harrison and Moriarty (HM) and the empirical form factors of Fong and Cohen (FC) are investigated as a starting point for calculations of electron-phonon (EP) coupling in noble metals. A compact representation of Harrison's pseudopotential method for transition metals is presented. A theorem by Sham on the use of orthogonalized-plane-wave–based pseudopotentials for EP matrix elements is expressed in operator language and generalized to include a wide class of pseudopotentials, including Harrison's. With the underlying principles justified, single-plane-wave calculations of the EP mass enhancement and resistivity are presented. The FC form factors give results that are more nearly consistent with experimental knowledge than the HM form factors. The discrepancy is traced to the sign and magnitude of the d-wave interaction.

I. INTRODUCTION

There has been much recent interest[1-3] in the effect of electron-phonon (EP) interactions on the electronic properties of the noble metals. Because the Fermi-surface (FS) states contain relatively little d character, it is tempting to use for the noble metals the approximations that have been so successful for the nontransition metals.[4]

As a theoretical step in this direction, Harrison[5] has extended the orthogonalized-plane-wave (OPW) approach of Phillips and Kleinman (PK),[6] giving an energy- and angular-momentum-dependent pseudopotential with an $l=2$ resonance in the region of the d bands. From Harrison's formulation Moriarty[7] has calculated first-principles values of the form factor appropriate to scattering on the Fermi surface. We shall refer to these as the Harrison-Moriarty (HM) form factors. They differ from nontransition-metal form factors in having a hump due to the repulsive interaction above the $l=2$ resonance.

As an empirical step in the same direction, Fong and Cohen[8] have succeeded in adjusting a nonlocal model potential that reproduces experimental features of the band structure of copper, using a secular equation of 140 plane waves. Their model potential consisted of a local potential similar in shape and magnitude to nontransition-metal form factors, and a nonlocal d-wave term that is large in the region of the d bands, but very small for scattering between plane waves of wave vector equal to k_F. This d-wave term is attractive throughout phase space for elastic scattering, so the form factor looks rather different from that of HM. Preliminary results of similar calculations for silver and gold have been supplied.[9] The resulting form factors will be referred to as Fong-Cohen (FC) form factors.

The principal advantage of a pseudopotential formulation of energy bands is the possibility of using the pseudopotential to calculate other properties of the metal [such as electron-phonon (EP) coupling] in low-order perturbation theory. In this paper, such a calculation is attempted in the lowest order of approximation by using single plane waves as pseudo wave functions and neglecting the distortion of the Fermi surface from a sphere. Section III presents values of the mass enhancement λ and resistivity ρ that are determined by EP scattering on the Fermi surface. This type of calculation has been shown to be quite successful for nontransition metals. The application of these techniques to noble metals raises several questions. First is the question of whether in principle a pseudopotential that determines band structures is directly applicable to the EP problem. This question is explored in detail in Sec. II, where compact formulations are presented in operator language of Harrison's pseudopotential scheme and of Sham's theorem[10] on the use of pseudopotentials for EP coupling. The question is answered in the affirma-