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Fermi Surfaces of Potassium and Rubidium*

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Experimental data on the shapes of the Fermi surfaces of K and Rb are used to determine the first two Fourier coefficients of the effective potential in the metals for scattering at the Fermi energy. Band-structure contributions to the specific-heat masses and cyclotron masses are deduced using the empirical values of the band gaps. Addition of mass-enhancement terms arising from electron-electron and electron-phonon interactions gives fair agreement with experiment.

I. INTRODUCTION

The use of the pseudopotential approach to the study of transport properties and Fermi-surface structures of solid and liquid metals is now firmly established.[1] For many metals new and powerful techniques, such as the Heine and Abarenkov[2] model potential method, give insight into the nature and form of the effective potential experienced by conduction electrons. For the transport integrals what is required is the Fourier transform of the screened electron-ion potential. It is therefore often convenient to define the effective potential by its Fourier transform and it is more common to talk about the band gap or Fourier coefficients of a potential in a metal than to consider the real-space equivalent. For scattering of conduction electrons on the energy shell the argument of the transform runs from around zero (the plasma-scattering region) to $2k_F$ (the neighborhood of the structure region). The curve, $V(K)$ say, is a measure of the scattering probability for processes confined to the Fermi surface and involving a momentum transfer $\mathbf{K}(=\mathbf{k}-\mathbf{k}')$. Because the pseudopotential is normally defined in a plane-wave representation we can regard $V(K)$ as a form of t matrix for the scattering for a single ion in the sense that it is precisely the operator which takes an electron in a plane-wave state $\mathbf{k}$ into a different state $\mathbf{k}'$, both $\mathbf{k}$ and $\mathbf{k}'$ lying on the energy shell E_F. If $V(K)$ in the important structure region is determined from experiment then all of the most significant higher order terms are automatically included.[3]

From the definition of the potential through its Fourier transform and its use in transport-phenomena calculations the argument $2k_F$ enters as a natural physical cutoff. The $V(K)$ curves, with K running from 0 to $2k_F$ have been successfully employed in the Ziman theory[4] of the transport properties of liquid metals. For a solid metal, and particularly here for the case of the alkali series, we are led to consider the possibility of continuing the curve $V(K)$ beyond $2k_F$. Formally there is no problem in defining a Fourier transform of the Heine-Abarenkov (HA) model potential for arguments greater than $2k_F$. The physical interpretation of the continued curve is also quite straightforward: we are still concerned with scattering processes which conserve energy. The momentum transfer $(\mathbf{k}-\mathbf{k}')$ is larger than $2\mathbf{k}_F$. It therefore follows that such a scattering event must proceed with an intermediate Bragg reflection and thus the vectors of the reciprocal lattice enter into the definition of the potential. HA pointed out that even for momentum transfers less than $2\mathbf{k}_F$ intermediate states brought in through Bragg reflection could lead to small changes in the model potential. These were termed second-order processes and a quantitative study of their importance in both the model potential and in the screening function has recently been given by Animalu.[5]

To include all of the possible Bragg reflection processes in the definition of the potential for $K>2k_F$ is a formidable problem. In this paper we seek to avoid these difficulties for the cases of potassium and rubidium by appealing directly to experimental Fermi-surface data currently available for these two metals. Recent de Haas–van Alphen studies[6] of the Fermi surfaces of potassium and rubidium reveal them to be only slightly distorted from free-electron spheres. From the magnitude of the distortions, which have been mapped out with great precision, we are able to elucidate information on the first two band gaps V_{110} and V_{200}. We note that the arguments for these Fourier coefficients of the potential exceed $2k_F$ and a determination of the band gaps thus yields a guide to continuation of the $V(K)$ curve.

II. TWO-BAND MODEL

The scheme we use may be simply termed a two-band model: we consider the s and p bands only and ignore the effects of higher (and lower) bands. Without any zonal structure the Fermi surface of the alkali metals is a free-electron sphere containing one electron per atom. The presence of a single Bragg scattering plane introduced outside of such a sphere mixes in a reflected component into the otherwise single orthogo-

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[1] For a review see J. M. Ziman, Advan. Phys. **13**, 89 (1964).

[2] V. Heine and I. Abarenkov, Phil. Mag. **9**, 451 (1964).

[3] N. W. Ashcroft and L. J. Guild, Phys. Letters **14**, 23 (1965).

[4] J. M. Ziman, Phil. Mag. **6**, 1013 (1961).

[5] A. E. O. Animalu, Phil. Mag. **11**, 379 (1965).

[6] D. Shoenberg and P. J. Stiles, Proc. Roy. Soc. (London) **A281**, 62 (1964).

nalized-plane-wave (OPW) wave function. For this combination the energy surface $E_{\mathbf{k}}=E_F$ is defined by the secular equation for the energy $E_{\mathbf{k}}$:

$$\begin{vmatrix} \mathbf{k}^2-E_{\mathbf{k}} & V_G \\ V_G & (\mathbf{k}-\mathbf{G})^2-E_{\mathbf{k}} \end{vmatrix}=0. \qquad (1)$$

In this equation V_G is the Fourier coefficient of the effective potential associated with the zone plane situated $1/2G$ away from the center of the zone. We find it convenient to work in mass independent units

$$\hbar^2/2m=2\pi/a=1,$$

and to use a zero of energy defined by $\langle\mathbf{k}|V|\mathbf{k}\rangle=0$ (see Sec. IV). From a simple second-order perturbation-theory argument[7] we anticipate the Fermi energy E_F to be shifted from the free-electron value by an amount proportional to $|V_G|^2$. In fact, for the simple two-band case we write:

$$E_F=E_F{}^0-C_G|V_G|^2. \qquad (2)$$

Now suppose we also write

$$k_F=k_F{}^0(1+\Delta(\theta)) \qquad (3)$$

representing the polar equation of the distorted surface of constant energy based on $\mathbf{G}$ as azimuth. Thus $\Delta(\theta)$ is the dilatation to the free-electron Fermi radius $k_F{}^0$. Experimentally the quantity Δ is found to be exceedingly small (of order a few parts per thousand at most), so that a simple expansion of the secular equation (1) in Δ suggests itself. Ignoring squares and higher powers of Δ we find the solution

$$\Delta(\theta)=(V_G{}^2/2E_F{}^0)\{[G^2-2k_F{}^0G\cos\theta]^{-1}-C_G\}. \qquad (4)$$

Since the Fermi surfaces of potassium and rubidium are well contained within the zone the fraction in (4) never becomes large.

The Fermi energy E_F (and the coefficient C_G) is determined very simply from the relation (3) for k_F. We find the volume enclosed by this surface and demand that it be identical to the free electron volume. With the use of (4) we obtain an explicit relation for C_G: the integration is standard and yields

$$C_G=(1/8E_F{}^0)x\ln|(1+x)/(1-x)| \qquad (5)$$

with $x=2k_F/G$. It is interesting to record here that the equation for the shift in energy (2) remains substantially accurate for values of V_G approaching the free-electron Fermi energy. [Equation (2) was tested against the energy shifts produced in a machine calculation in which the energy required to produce a volume containing one electron per atom was plotted against the band parameter V_G.]

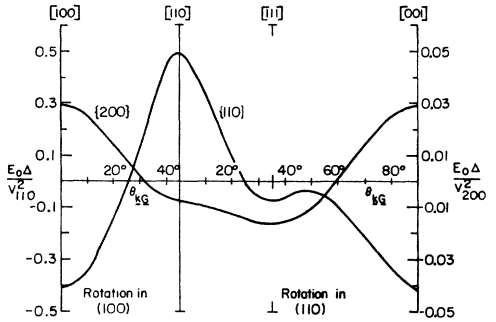

FIG. 1. Combined distortion curves for {110} planes and {200} planes as given by Eq. (8).

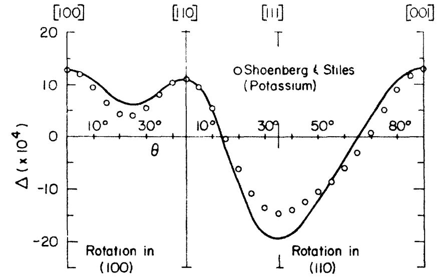

FIG. 2. The experimental deviations from sphericity in potassium (○) and the theoretical anisotropy (solid line) fitted at [100] and [110].

We can generalize (2) and (4) to cover the cases of two or more Bragg reflection planes enclosing the free-electron sphere. For instance, with zone planes at $\pm1/2\mathbf{G}$, expansion of a third-order secular determinant gives

$$\Delta(\theta)=(V_G{}^2/E_F{}^0)\{[G^2-4E_F{}^0\cos^2\theta]^{-1}-C_G\} \qquad (6)$$

which indicates that in this approximation the deviations from sphericity are simply additive. (Note that θ is again measured from the reciprocal lattice vector G.) In conjunction with (6) we also find that to first order in Δ the energy shifts (per zone plane introduced) are additive. Similarly, for any number of Bragg-plane pairs we have the results

$$E_F=E_F{}^0-\sum_{G\ \text{pairs}}2C_GV_G{}^2 \qquad (7)$$

and for the distortion along the direction $\mathbf{k}$

$$\Delta_{\mathbf{k}}=\sum(V_G{}^2/E_F{}^0)\{[G^2-4E_F{}^0\cos^2\theta_{\mathbf{kG}}]^{-1}-C_G\}, \qquad (8)$$

where $\theta_{\mathbf{kG}}$ is the angle between $\mathbf{k}$ and the reciprocal lattice vectors taken in the sum.

It is important to note that the total distortion in a given direction $\mathbf{k}$ is the combination of the extension of the Fermi radius towards the nearest Bragg plane superimposed upon a slight decrease due to all of the others. To illustrate, if we consider the {110} set of zone planes, a bulge along a chosen [110] direction associated with a selected (110) plane is actually sitting on a slight hollow which is the combined distortion of the remaining eleven {110} planes. This effect leads to somewhat higher Fourier coefficients than might be expected.

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[7] N. W. Ashcroft, Phil. Mag. 8, 2055 (1963).

TABLE I. Energies in electron volts.

	$\lvert V_{110}\rvert$	$\lvert V_{200}\rvert$	$\lvert V_{110}\rvert$ (Alone)	$V_{110}{}^{N}$ (Ham[a])	$V_{200}{}^{H}$	V_{110} (HA)	$\left(\frac{dV_{200}}{dE}\right)_{E_F}$	$\left(\frac{dV_{200}}{dE}\right)_{E_F}$	$\left(\frac{dV_{000}}{dE}\right)_{E_F}$
K	0.23	1.16	0.17	−0.24	−0.33	−0.054±0.068	0.014	0.030	0.12
Rb	0.43	1.43	0.40	−0.37	−0.58	−0.19 ±0.05	0.008	0.041	0.15

[a] The values of V_{200} are deduced from the splittings at H (see text). Note that V_{200} and V_{110} in Ham's calculation pertain to the energies at H and N, respectively, whereas our values listed here are deduced for scattering at an energy E_F.

Typical curves of (8) for sums over {110} and {200} planes are drawn out in Fig. 1. Comparisons with plots of actual distortions found in potassium and rubidium (Figs. 2 and 3) indicate that the observed deviations from sphericity arise from a weighted superposition of the {110} and {200} curves. The quantitative agreement shown in Figs. 2 and 3 is a result of assigning to $\lvert V_{110}\rvert$ and $\lvert V_{200}\rvert$ the values given in Table I. Distortions from inclusion of higher sets of zone planes ({211}, {220}, etc.) are small, largely isotropic and alter very little the curves of Figs. 2 and 3.

The agreement between (8) and the experimental points of Shoenberg and Stiles is reasonable. What is clearly demonstrated is the importance of including the effects of the (200) band gaps (see Sec. III). It is possible, of course, to fit a 110 curve to the principal ⟨110⟩ distortion but the overall agreement with the experimental points is poor as can be readily inferred from Figs. 1, 2, and 3. For the purposes of comparison we give this value of $\lvert V_{110}\rvert$ in Table I.

III. THE BAND GAP

From the values of the parameters listed in Table I it appears that $\lvert V_{110}\rvert$ deduced from Fermi surface data is in better agreement with Ham's[8] calculated values than with the estimates given by Heine and Abarenkov. We note that our values of $\lvert V_{110}\rvert$ are deduced for scattering on the Fermi surface and it follows that the energy-dependent band gaps determined here pertain to the choice $E=E_F$. Ham's values for V_{110} (as listed in Table I) are derived from the band splitting at N and therefore properly relate to the choice $E=E_N$. We make a similar distinction between the V_{200} parameters gleaned from Ham's work and the V_{200} parameters found here. Let us consider the symmetry point H. In the free electron approximation the lowest level is sixfold degenerate at energy E_H. Under the action of the crystal potential these levels split into a triply degenerate, doubly degenerate and singlet levels; viz.,

$$H_{15}=E_H-V_{200}\qquad\text{(triple)},$$
$$H_{12}=E_H+V_{200}-2V_{110}\qquad\text{(double)},$$
$$H_{1}=E_H+V_{200}+4V_{110}\qquad\text{(single)}.$$

It follows that $V_{200}=\frac{1}{6}(H_1+2H_{12}-3H_{15})$ and the values quoted in Table I are calculated from this relation using Ham's tabulated values. These parameters are appropriate to an energy $E=E_H$; our values are appropriate to $E=E_F$.

It is clear that the empirical magnitudes for V_{200} are considerably in excess of the results listed by Ham. Examination of the experimental distortion data shows that the deduced magnitude of the V_{200}'s are not unexpected. In potassium the distortion along ⟨100⟩ is actually larger than that observed along ⟨100⟩, and this implies a large gap on the (200) face which is far less effective in producing distortions to the Fermi sphere than the much closer (110) face. Likewise in rubidium; if the {110} planes were acting alone the distortions at ⟨110⟩ would be -80×10^{-4}, but what is observed is -23×10^{-4} and a substantial (200) band gap is required to bridge the difference.

Naturally Eq. (8) does not permit us to determine the sign of V_{110} or V_{200}: we elect to make them all negative for the following reasons. First, this choice of sign gives the best fit in a determination of the effective masses [Sec. IV, Eq. (11)]. Second, the V_{110} match better with Ham's values. The differences between Ham's V_{200} and ours may be regarded as a core-shift effect.[9] To assign positive values to V_{200} requires an exceedingly large change. Third, choosing both to be negative ensures a fairly smooth continuation of the model potential $V(K)$ curves for potassium and rubidium.[10] These curves, together with those for lithium, sodium and cesium are shown in Fig. 4. As we have chosen to work in mass-independent and lattice-

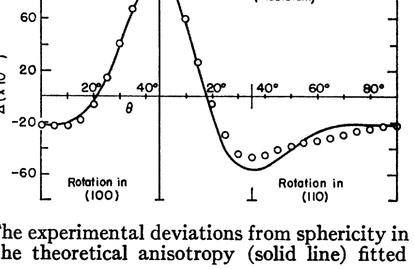

FIG. 3. The experimental deviations from sphericity in rubidium (O) and the theoretical anisotropy (solid line) fitted at [100] and [110].

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[8] F. S. Ham, Phys. Rev. **128**, 82, 2524 (1962).

[9] For a discussion of core shifts and pseudopotentials, see P. J. Lin and J. C. Phillips (to be published).

[10] Lorna J. Sundström, private communication, and Phil. Mag. **11**, 657 (1965).

TABLE II. Effective masses for the alkali metals. $(\delta m/m)_{e\text{-}e}$ is taken from Rice (Ref. 12) using a linear extrapolation. The errors attached to K and Rb are estimated to cover both extrapolation and the neglect of higher order terms. The errors attached to $(\delta m/m)_{e\text{-}p}$ cover umklapp corrections and the form of potential (see text).

	$(\delta m/m)_{e\text{-}e}$	$(\delta m/m)_{e\text{-}p}$	β	$(m^*/m)_{\mathrm{Total}}$	$(m^*/m)_{\mathrm{CR}}$ [b]	$(m^*/m)_{\mathrm{SH}}$
Li	0.03	0.34	0.24[a]	...	...	2.19[c]
Na	0.06	0.18	0.01[a]	...	1.24	1.25[c]
K	0.11±0.05	0.15±0.01	0.05	1.18±0.06	1.21	1.23[d]
Rb	0.13±0.07	0.17±0.02	0.21	1.38±0.09	...	1.36[c]
Cs	0.15	0.18	0.34[a]	...	...	1.63[c]

[a] These values of β are deduced from $(m^*/m)_{\mathrm{SH}}$.
[b] C. C. Grimes and A. F. Kip, Phys. Rev. **132**, 1991 (1963).
[c] Reference 10 and D. L. Martin, Phys. Rev. **124**, 438 (1961).
[d] J. D. Filby and D. L. Martin, Proc. Roy. Soc. (London) **A284**, 83 (1965).

constant independent units the differences in the potential are best displayed by normalizing the curves to $\frac{2}{3}E_F$ (where $-\frac{2}{3}E_F$ is the long-wavelength limit of the screened electron-ion potential). In the plasma region (small K) the curves are almost inseparable, which is not unexpected. Only in the region of large K, where core effects are increasingly important, is there a noticeable divergence.

Five of the curves shown in Fig. 4 (Li to Cs) incorporate local first order screening of the electron-ion interaction. A sixth, due to Animalu[5] is given for Li. This includes a small correction for the nonlocal nature of the screening function and gives a small shift in the case of this particular metal. Nonlocal screening corrections to $V(K)$ for the other alkali metals are small and are neglected here. Note that the form factor for Li_1 beyond $2k_F$ is a model potential continuation.

Being empirical or experimental values, the band gaps deduced here already include the most important higher order terms. They lie on a curve which may be regarded as a continuation of the form factor for momentum transfers in excess of $2k_F$. V_{110} and V_{200} are shown as crosses on Fig. 4. The circles are the corresponding values found by Ham and the squares indicate the HA-model potential values (V_{110} only).

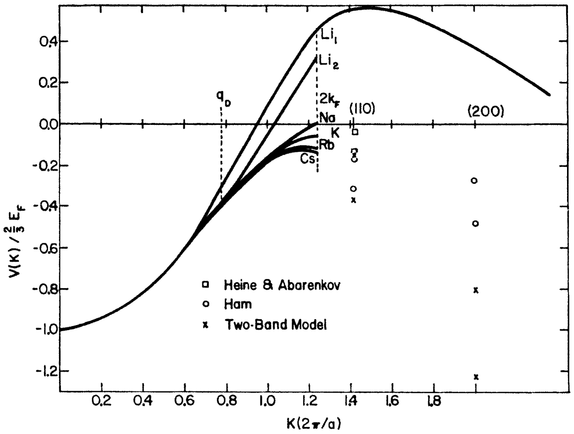

FIG. 4. Pseudopotential form factors for the alkali metals and the principal band gaps for K and Rb. In the three sets displayed the upper point refers to K and the lower to Rb. The curves in the range $0<K<2k_F$ are HA-model potentials taken from the work of Sundström (Ref. 10) (all normalized to $\frac{2}{3}E_F$).

IV. EFFECTIVE MASS

The total observed effective mass (thermal, cyclotron resonance, de Haas–van Alphen, etc.) has contributions from three major sources, viz., electron-electron interactions ($\delta m_{e\text{-}e}$), electron-lattice interactions ($\delta m_{e\text{-}p}$), and band structure[11] (δm_{BS}). In a sense, the latter can be further subdivided into a part arising from the shift in the band minimum when the valence-electron energy is shifted and a part which expresses the effect of distortions to the Fermi surface by the pseudopotential. The latter is well known and is normally evaluated by computing $\int_S dS(|\nabla_{\mathbf{k}}E|)^{-1}$ over a constant energy surface S. The former is less well-known and represents a correction due to the energy dependence of the pseudopotential.

Quantitative estimates of the effect of Coulomb interactions on the electron mass have been carried out by Rice[12] working in the Hubbard approximation. In Table II we give the results taken from Rice's (m^*/m) versus electron-separation curve. The figures for K, Rb, and Cs are taken from an extrapolated part of the (almost linear) low density region of the curve. This may introduce some uncertainties in addition to those arising from higher order corrections. In any case, the Coulomb effects are quite small and can be accounted for in terms of the opposing roles exhibited by the wave number and frequency dependence of the dielectric function.[13]

From the fact that the geometry of the alkali metal Fermi surfaces are nearly all identical (certainly from the point of view of evaluating transport integrals) we may obtain an estimate of the electron-phonon enhancement of the electron mass. A calculation of the electron-phonon mass has been completed for sodium,[11] and we use similarity arguments to proceed to the remaining alkali metals.

To second order in the effective electron-phonon matrix element $g_{\mathbf{k}-\mathbf{k}'}$ the phonon-induced effective mass

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[11] N. W. Ashcroft and J. W. Wilkins, Phys. Letters **14**, 285 (1965).

[12] T. M. Rice, Ann. Phys. (N. Y.) **31**, 100 (1965).

[13] For some comment on this point, see Ref. 9.

may be written

$$\left(\frac{\delta m^*}{m}\right)_{e\text{-}p}=\rho_{\mathrm{BS}}\int\frac{d\Omega_{\mathbf{k}'}}{4\pi}\frac{d\Omega_{\mathbf{k}}}{4\pi}\frac{|g_{\mathbf{k}-\mathbf{k}'}|^2}{\hbar\omega_{\mathbf{k}-\mathbf{k}'}},\tag{9}$$

where the angular integrations are taken over the Fermi surface. In (9) ρ_{BS} is just the band-structure density of states to be considered next. If we use the rigid ion approximation to give us $g_{\mathbf{k}-\mathbf{k}'}$ and assume that the phonon dispersion curves ($\omega_{\mathbf{q}}$ versus q) in the alkali series are isometric, we find:

$$\frac{(\delta m^*/m)_{e\text{-}p}{}^{\mathrm{Alk}}}{(\delta m^*/m)_{e\text{-}p}{}^{\mathrm{Na}}}=\frac{(E_F{}^2)^{\mathrm{Alk}}}{(E_F{}^2)^{\mathrm{Na}}}\times\frac{(\omega_M{}^2)^{\mathrm{Na}}}{(\omega_M{}^2)^{\mathrm{Alk}}}\times\frac{M^{\mathrm{Na}}}{M^{\mathrm{Alk}}}\times\frac{(m_{\mathrm{BS}}{}^*)^{\mathrm{Alk}}}{(m_{\mathrm{BS}}{}^*)^{\mathrm{Na}}}.\tag{10}$$

Here ω_m represents the maximum phonon frequency propagated in the metal and M is the ion mass. The factor which cancels from the above ratio is purely geometrical and depends only on the class of crystal structure and the shape of the Fermi surface and hence is common to each metal. To make this completely tenable we must also assume that the pseudopotentials of the metals (normalized to $\frac{2}{3}E_F$) are identical. This is apparently well satisfied for K less than q_D (the Debye cutoff) as can be seen from Fig. 4. In Na the bulk of the contribution to the phonon-induced mass comes from normal processes ($K=|\mathbf{k}-\mathbf{k}'|<q_D$). Only 20% or so of $(\delta m^*/m)_{e\text{-}p}$ results from umklapp contributions. In this region $(i\cdot e|(\mathbf{k}'-\mathbf{k})\,\mathrm{Mod}\,\mathbf{G}|<q_D)$ the pseudopotential varies somewhat from metal to metal and the results calculated from (10) shown in Table II include a small correction for these differences. At present only in sodium have the phonon dispersion curves been measured so that the values of the ω_M ratios have been deduced from elastic-constant data.[14]

To obtain a reliable estimate of the band structure effective mass it is necessary to know the energy dependence of the pseudopotential. In the formulation of Sec. I, the expression for the distortions to the Fermi surface were deduced from a second-order secular equation whose diagonal elements contained the energy zero $\langle\mathbf{k}|V|\mathbf{k}\rangle$. The presence of this term implies that in addition to the usual density-of-states factor arising from deviations from sphericity[15] there are additional contributions arising from the energy dependence of V (both explicitly and through variations in $|\mathbf{k}\rangle$ via the relation $E=k^2$). The same is true of the band gaps V_G. There is no difficulty (in principle) in evaluating this dependence: one method might be to go straight to the OPW formulation for the potential and evaluate the energy derivative of the repulsive term

$$\sum_c(E-E_c)b_{\mathbf{k}c}{}^*b_{\mathbf{k}'c},$$

but to do this a knowledge of the overlap function $b_{\mathbf{k}c}$ $(\sim\int e^{i\mathbf{k}\cdot\mathbf{r}}\phi_c(\mathbf{r})d^3\mathbf{r})$ is required and this, in turn, implies we know the energies E_c and wave functions ϕ_c for the core electrons.

A more direct method is to use a model form for the potential which accounts for both the angular and energy dependences implicity in the pseudopotential. The model potential of Heine and Abarenkov provides this information. In their approach the bare-electron-ion interaction is represented by a system of square wells for the short range behavior, augmented by a Coulomb potential for the long-range part. The strengths of the square wells (indexed by l and representing the cancelled potential in the OPW method) are determined by matching the energy levels they produce to the spectroscopic series for the free atoms. The values for these parameters appropriate to the solid are found by extrapolating or interpolating the curve of strength against energy to the Fermi energy. (It follows that the potential is specifically defined at the energy $E=E_F$.) We are primarily concerned with the slope of the curve and this quantity is not sensitive to interpolation errors to the same degree as the strength parameter.

For our purposes we require $(dV_G/dE)_{E_F}$ and $(dV_{000}/dE)_{E_F}$.[16] The values of $(dV_G/dE)_{E_F}$ listed in Table I are small and of little consequence to the calculation of the band structure effective mass. Also presented in the table are values for $(dV_{000}/dE)E_F$: these differ slightly from those given by HA and the discrepancy is due to a contribution arising from the change in k_F accompanying any change in E_F.

In terms of an arbitrary energy scale, we may write

$$E_F=E_F{}^0+V_{000}-\sum_{G\text{ pairs}}2C_GV_G{}^2$$

and it follows that the band-structure effective mass may be written

$$\left(\frac{m^*}{m}\right)_{\mathrm{BS}}=\left\{1+\left(\frac{dV_{000}}{dE}\right)_{E_F}-\beta\right\}^{-1},$$

with

$$\beta=\sum_{G\text{ pairs}}2\left[V_G{}^2\left(\frac{dC_G}{dE}\right)_{E_F}+2V_GC_G\left(\frac{dV_G}{dE}\right)_{E_F}\right],\tag{11}$$

which is evaluated using the parameters listed in Table I. The values of β for potassium and rubidium are given in Table II. The total effective mass, also presented in Table II, is appropriate to a density-of-states factor involving an average over the entire Fermi surface as is given, for example, by the low-temperature electronic specific heat. Neglecting the anisotropy of the electron-phonon interaction, or more accurately, neglecting the resulting anisotropy where this quantity is integrated around a central cyclotron orbit, the cyclotron mass is

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[14] Y. P. Varshni and F. J. Bloore, Phys. Rev. **129**, 115 (1963).

[15] H. Jones, Proc. Phys. Soc. (London) 49, 250 (1937).

[16] I am grateful to Dr. V. Heine for allowing me to use unpublished data.

TABLE III. Energies in electron volts.

	$\lvert V_{110} \rvert$	V_{110} (Ham)	Δ_{110}
Li	1.3	1.37	1.3×10^{-2}
Na	0.18	0.11	5×10^{-4}
Cs	0.50	-0.57	2×10^{-2}

equal in this approximation to the specific-heat mass.[17] The agreement between the calculated and experimental masses is reasonable and indicates the need for further data on the remaining alkali metals.

Fermi-surface mapping for Li, Na, and Cs is as yet very incomplete. In the case of Li and Na complications arise through the tendency of these metals to undergo a martensitic transformation into the hcp phase at low temperatures. Some indication of the size of the first band gap in these metals may be obtained by using the specific-heat effective masses and working back through the corresponding β's. These are marked with an "a" in Table II. Ignoring contributions from V_{200} for the moment we find values for $\lvert V_{110} \rvert$ as listed in Table III. We have compared them with Ham's calculated values and the agreement is satisfactory. The distortions along the [110] direction can be evaluated with the aid of (6) and they are listed in Table III. In Li some comparison may be made with dimension obtained from position annihilation experiments.[18] These give a dimension corresponding to $\Delta_{110}\sim0.03$, in some disagreement with our figure but confirming as we do that there is likely to be no contact of the Fermi surface with the nearest zone boundary (assuming we are dealing with the bcc phase). Shoenberg and Stiles are able to give an upper limit on the distortions to the Fermi surface in sodium of about 5×10^{-4}, in good agreement with our rough figure. There is no data of sufficient accuracy in Cs with which to compare the dimension obtained here. The effect of including a set of (200) planes does not alter significantly the value of the V_{110} band gap. For example, in Rb the ratio V_{200}/V_{111} has the value 3.3. If we use the same ratio in Cs the effect is merely to lower V_{110} to 0.42 eV.

Finally, using the band gaps and parameters listed in Tables I–III we may readily determine the Fermi energy (as measured from the band minimum) and hence evaluate the minimum energies required for direct and indirect (e.g., phonon assisted) interband transitions. In K and Rb these are 1.43, 0.89 and 1.16, 0.99 eV respectively. Using the estimates of the band gaps given in Table III the corresponding values for the metals Li, Na and Cs are 5.3, 4.3; 2.05, 1.14; and 1.64, 1.36 eV respectively.

ACKNOWLEDGMENTS

The author wishes to thank Dr. D. Shoenberg, Dr. V. Heine, and Professor J. C. Phillips for valuable discussions.

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[17] S. Nakajima and M. Watabe, Progr. Theor. Phys. (Kyoto) **30**, 772 (1963).

[18] J. J. Donaghy, A. T. Stewart, J. H. Kusmiss, and D. M. Rockmore, Proceedings of the 9th International Conference on Low Temperature Physics, Columbus, Ohio, 1964 (to be published).