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Energy Bands of Alkali Metals. II. Fermi Surface

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The Fermi energy, density of states, cyclotron effective mass, optical effective mass, and other parameters of the Fermi surfaces of the alkali metals are evaluated for the band structures calculated previously, using an interpolation formula suggested by the nearly free electron model. It is shown, however, that the nearly free electron model in its usual form based on a weak effective potential cannot provide a consistent description of the alkali band structures, and that generalization of the model to take account of the l dependence of the effective potential is necessary. The calculated Fermi surface parameters are compared with the results of recent experiments and with analyses by Cohen, Heine, Dugdale, Collins, and Ziman of earlier experimental work. The trends in the calculated values agree qualitatively with those found in experiments and with trends in the band structure inferred by these authors. This comparison lends support to the interpretation that differences in the properties of the alkali metals arise to a considerable extent from differences in their electronic structure. The calculations predict appreciable anisotropy of the cyclotron mass, the de Haas–van Alphen effect, and the linear dimensions of the Fermi surface for all of the alkali metals except sodium. Values of the parameters are found to be changed considerably by distortion of the Fermi surface from values obtained in the spherical approximation. The calculated values for the thermal effective mass, however, are significantly smaller than the experimental values, except for cesium, so that at least for the lighter metals the effect of electron-electron correlation and electron-phonon interaction appears to be to enhance the effective mass.

I. INTRODUCTION

IN an earlier paper[1] (hereafter referred to as I) we have presented the direct results of calculations of the energy bands of the five alkali metals for several values of the lattice constant. These calculations were carried out, using the quantum defect method and the Green's function method, for values of the propagation vector **k** along the [100], [111], and [110] axes within the Brillouin zone as well as at symmetry points. In the present paper we use these results and an interpolation procedure to calculate the Fermi energies of these metals and the various parameters of their Fermi surfaces. We compare the calculated values of these parameters and their trends through the alkali series with recent experimental evidence relating to the shape of the Fermi surface and with the conclusions of several recent theoretical analyses of the metals' properties.

We must first obtain a good interpolation procedure to describe the nonspherical distortions in the conduction band for energies near the Fermi energy. As we have seen in I, a power series expansion in the components of **k** is not convenient to describe this distortion. A much more successful interpolation formula is, however, suggested by the nearly free electron model of a metal,[2] although that model in its usual form does not suffice to describe the distortion of the bands which we have calculated for the alkali metals.

The nearly free electron model, which treats the effective crystal potential as weak, has recently attracted renewed interest as the basis of fruitful interpretations of features of the Fermi surfaces of a number of polyvalent metals as revealed by recent experiments.[3,4] The reasons for the model's success have been clarified by Phillips and Kleinman,[5] and by Cohen and Heine,[6] who have pointed out that while crystal potentials are not, in fact, weak, the effective pseudopotentials seen by valence electrons may be weak because the requirement that wave functions of valence states be orthogonal to those of core states has the effect of introducing a repulsive pseudopotential that partially cancels the true potential. Our calculated band structures of the alkali metals provide an opportunity for a quantitative test of the nearly free electron model as a description of the bands. As we shall show, the model in the simple form usually considered[2,4] is not successful in providing a quantitative description of the alkali band structure and fails as well in certain qualitative respects. This failing is, however, not unexpected, for the usual form of the model ignores the fact that the correct pseudopotential is different for states of different angular momentum l, as Phillips and Kleinman have noted.[5] This l dependence has been emphasized by Antončik[7] and is a consequence of exchange interaction and of the fact that the pseudopotential arises from the process of orthogonalizing a valence wave function of given l to core states of the same l. In other words, the pseudopotential is in fact not a simple potential but an operator acting differently on states of different l. Antončik[7] has given expressions for the matrix elements of such an operator; he shows that the splittings of states at symmetry points depend on the pseudopotential in a complicated way and no longer are given simply in terms of a very few Fourier coefficients of an effective crystal potential. Our test of this model against the calculated alkali band structures will thus show that even if the pseudopotential is weak for the reasons advanced by Phillips, Kleinman, Cohen, and Heine, and the band structure correspondingly close to that of a free electron, one should not expect complete con-

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

[2] See, for example, N. F. Mott and H. Jones, *Theory of the Properties of Metals and Alloys* (Oxford University Press, New York, 1936), p. 59.

[3] A. V. Gold, Phil. Trans. Roy. Soc. (London) **A251**, 85 (1958).

[4] W. A. Harrison, Phys. Rev. **118**, 1182, 1190 (1960).

[5] J. C. Phillips and L. Kleinman, Phys. Rev. **116**, 287 (1959).

[6] M. H. Cohen and V. Heine, Phys. Rev. **122**, 1821 (1961).

[7] E. Antončik, J. Phys. Chem. Solids **10**, 314 (1959).

sistency between different ways of evaluating Fourier coefficients of an effective potential from splittings at symmetry points if this is done with the usual simple formulas. The nearly free electron model may nevertheless provide a useful basis for a qualitative understanding of many features of band structures, and extended suitably to take account of an l-dependent pseudopotential it may provide an accurate quantitative description of the bands of many solids.[8]

In this paper we shall first show in Sec. II the failings of the usual form of the nearly free electron model as an interpolation procedure by comparing it with the calculated bands. We have not, however, attempted to incorporate an l-dependent pseudopotential into the model. Such a modification might well prove fruitful as an interpolation procedure for the alkali metals, as Cornwell's work[9] suggests, but it makes the model unwieldy for our present purposes in that the bands depend in a complicated way on an inconveniently large number of parameters.

The distortions in the calculated bands are nevertheless similar to those predicted by the nearly free electron model. This leads us in Sec. III to use the model to suggest the general form of an interpolation formula, but we then determine the parameters in this formula by fitting as closely as possible to the calculated points in the part of the conduction band near the Fermi energy. This procedure works quite successfully as a description of this region of the conduction band, and it is convenient for the evaluation of the parameters of the Fermi surface.

In Sec. IV the results of calculations for the Fermi surface are given, using this interpolation procedure. We obtain the Fermi energy, the density of states, the thermal, optical, and cyclotron effective masses, the various dimensions of the Fermi surface, and its surface area and extremal areas of cross section. Values of these parameters, evaluated for the distorted Fermi surface, are compared with those obtained with the spherical approximation. We also calculate the contribution to the "diffusion" component of the thermoelectric power that arises from the shape of the energy bands.

In Sec. V we discuss the comparison of our results with experimental information for the alkali metals relating to the energy band structure, and in particular with that relating to the shape of the Fermi surface. We emphasize those experiments made since Cohen and Heine[10] gave their review and interpretation of data available in 1958. We compare our results also with recent theoretical analyses by Collins and Ziman,[11,12] and by Bailyn[13] of the relation between the transport properties of these metals and the shape of the Fermi surface, and with a recent survey by Dugdale[14] of various experimental correlations that appear to relate to the Fermi surface shape. This comparison, while, in general, supporting an interpretation of the band structure which agrees with the trends revealed by our calculations, makes clear that definitive experimental evidence concerning the shape of the Fermi surface in the alkali metals does not yet exist, apart from some very recent work on potassium. We point out the desirability of various further experiments that would help to elucidate the band structure.

II. NEARLY FREE ELECTRON MODEL

We wish to find out whether the nearly free electron model in its usual simple form[2,4] can provide the basis for an accurate description of our calculated bands and for an interpolation procedure. Accordingly, in developing the model we assume that the valence electrons see a weak effective lattice potential (more strictly speaking, a pseudopotential obtained from the lattice potential by orthogonalizing valence wave functions to those of core states), and we assume that this effective potential can be approximated as a simple potential function rather than an operator.

With a weak potential, the wave function of a state of wave vector $\mathbf{k}$ in the conduction band is only slightly perturbed from a single plane wave $\exp(i\mathbf{k}\cdot\mathbf{r})$ (more precisely, a single orthogonalized plane wave—or OPW) except for states near the surface of the Brillouin zone (BZ). For these latter states the wave function is a linear combination of the plane waves $\exp(i\mathbf{k}\cdot\mathbf{r})$ and $\exp[i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}]$, where $\mathbf{K}$ is the reciprocal lattice vector pointing from the nearest face of the BZ surface to the opposite face. The energy surfaces are accordingly distorted from their unperturbed form only near the BZ surface, and here the distortion at $\mathbf{k}$ arises from interaction via a single Fourier coefficient of the lattice potential between a free electron (or OPW) state a at $\mathbf{k}$ and another such state b at $\mathbf{k}+\mathbf{K}$.

Accordingly, the secular equation for the energy at $\mathbf{k}$ has the form

$$\begin{vmatrix} \mathcal{H}_{aa}-E & \mathcal{H}_{ab} \\ \mathcal{H}_{ab}^* & \mathcal{H}_{bb}-E \end{vmatrix} = 0, \qquad (2.1)$$

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[8] Such an extension of the model has in fact been applied recently to lithium, sodium, and potassium, by Cornwell (reference 9) as the basis of an interpolation procedure. Cornwell had fair success in adjusting his parameters to fit the energy values at symmetry points published previously by other workers. However, this fitting is not as good at all his points as we should like to see for a quantitatively accurate interpolation procedure. On the other hand, Cornwell used for sodium and potassium results given by Howarth and Jones and Callaway, the accuracy of which we have questioned in I. Thus, it remains an open question how complicated such an interpolation procedure has to be in order to reproduce to a desired degree of accuracy an accurately calculated band structure for an alkali metal.

[9] J. F. Cornwell, Proc. Roy. Soc. (London) **A261**, 551 (1961).

[10] M. H. Cohen and V. Heine, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1958), Vol. 7, p. 395

[11] J. G. Collins, Proc. Roy. Soc. (London) **A263**, 531 (1961).

[12] J. G. Collins and J. M. Ziman, Proc. Roy. Soc. (London) **A264**, 60 (1961).

[13] M. Bailyn, Phys. Rev. **120**, 381 (1960).

[14] J. S. Dugdale, Science **134**, 77 (1961).

whence the energy is given by

$$E=\tfrac{1}{2}(\mathcal{H}_{aa}+\mathcal{H}_{bb})\pm\tfrac{1}{2}[(\mathcal{H}_{aa}-\mathcal{H}_{bb})^2+4|\mathcal{H}_{ab}|^2]^{1/2} \qquad (2.2)$$

For $\mathbf{k}=(2\pi/a)(t,t,0)$ on the [110] axis $(0\leq t\leq\frac{1}{2})$ we have (in atomic units)

$$\begin{aligned}\mathcal{H}_{aa}&=V_0+(2\pi/a)^2(2/m^*)t^2,\\ \mathcal{H}_{bb}&=V_0+(2\pi/a)^2(2/m^*)(1-t)^2,\\ \mathcal{H}_{ab}&=V_1,\end{aligned} \qquad (2.3)$$

where V_1 is the Fourier coefficient of the effective lattice potential going with the first nonzero reciprocal lattice vector $\mathbf{K}_1=(2\pi/a)(\pm1,\pm1,0)$. Since $\mathcal{H}_{aa}=\mathcal{H}_{bb}$ for $t=1/2$, we find

$$E(N_1)-E(N_{1'})=2V_1, \qquad (2.4)$$

$$E(N_1)+E(N_{1'})=V_0+\tfrac{1}{2}(4\pi^2/a^2m^*). \qquad (2.5)$$

Hence from (2.2), on the [110] axis E should be given by

$$\begin{aligned}E=\tfrac{1}{2}&[E(N_1)+E(N_{1'})]\\ &-(4\pi^2/a^2m^*)[\tfrac{1}{2}-t^2-(1-t)^2]\\ &\pm\{(4\pi^2/a^2m^*)^2(1-2t)^2\\ &\qquad+(1/4)[E(N_1)-E(N_{1'})]^2\}^{1/2}.\end{aligned} \qquad (2.6)$$

On the [111] axis the $\mathbf{k}$ vector $\mathbf{k}=(2\pi/a)(t,t,t)$ is equidistant from three faces of the BZ surface. The excited free electron state that mixes with the plane wave $\exp(i\mathbf{k}\cdot\mathbf{r})$ is then the symmetric linear combination of the three plane waves obtained from $\mathbf{k}$ by Bragg reflection in each of these faces,

$$\psi_b=(1/\sqrt{3})\sum_{i=1}^{3}\exp[i(\mathbf{k}+\mathbf{K}_i)\cdot\mathbf{r}], \qquad (2.7)$$

We find accordingly

$$\begin{aligned}\mathcal{H}_{aa}&=V_0+(2\pi/a)^2(3/m^*)t^2,\\ \mathcal{H}_{bb}&=V_0+2V_1+(2\pi/a)^2(1/m^*)[t^2+2(1-t)^2],\\ \mathcal{H}_{ab}&=\sqrt{3}V_1,\end{aligned} \qquad (2.8)$$

and for $t=1/2$

$$E(P_1)-E(P_4)=4V_1. \qquad (2.9)$$

If the nearly free electron model is applicable, the same choice of V_0, V_1, and m^* (which may differ from the free electron mass since the unperturbed wave function is an OPW rather than a plane wave) should suffice with these formulas to fit the calculated bands along both the [110] and [111] axes, and similarly on the [100]. Accordingly, if we eliminate V_0 on [111] using (2.5), E should be given on the [111] axis by

$$\begin{aligned}E=\tfrac{1}{2}&[E(N_1)+E(N_{1'})]\\ &+V_1+(4\pi^2/a^2m^*)[2t^2+(1-t)^2-\tfrac{1}{2}]\\ &\pm\{[(4\pi^2/a^2m^*)(1-2t)+V_1]^2+3V_1^2\}^{1/2}.\end{aligned} \qquad (2.10)$$

With V_1 given by (2.4), we have been able to choose m^* in all of the cases we have studied such that (2.6) fits the calculated points on the [110] axis quite satisfactorily for $\frac{1}{4}\leq t\leq\frac{1}{2}$. When we have used these same parameters in (2.10), however, the resulting expression gives energy values for the [111] axis consistently lower than those calculated by the Green's function method. For lithium at the lattice constant in Fig. 1 of I, (2.10) gives a value at $t=3/8$ (roughly the Fermi energy) that is 0.017 Ry below the calculated value, and 0.015 Ry at $t=5/16$. For rubidium (Fig. 4 of I) the corresponding errors are 0.020 and 0.014, and for cesium (Fig. 5 of I) 0.051 and 0.034. While these errors are not large on an absolute scale, comparison with the figures of I shows that they alter substantially the relative positions of the energies of the [110] and [111] axes. Thus, these values would place the band on the [111] axis close to or *below* that on the [110] axis for the same $|\mathbf{k}|$, for energies at and below the Fermi energy, thus completely changing the form of the distortion of the energy surfaces.

Since the energy splittings at N and P in these cases are not small compared with the conduction bandwidth, we have calculated in second order the perturbations to the energy arising from other reciprocal lattice vectors of the form $\mathbf{K}=(2\pi/a)(\pm1,\pm1,0)$, etc., apart from the one (or three) already treated. We obtain in place of (2.3) the expression

$$\mathcal{H}_{ab}=V_1-4V_1^2(a^2m^*/4\pi^2), \qquad (2.11)$$

for $\mathcal{H}_{ab}$ at $t=1/2$, with similar corrections to $\mathcal{H}_{aa}$ and $\mathcal{H}_{bb}$, and similarly on the [111] axis. For lithium it proved impossible to solve for V_1 real (as it should be since the lattice has inversion symmetry) when $\mathcal{H}_{ab}$ in (2.11) is set equal to half the splitting at N. Thus, for lithium, either other terms in the Fourier expansion of the potential are important, or the potential is too strong for use of perturbation theory, or the simple form of the nearly free electron model is inappropriate. For rubidium and cesium, however, the improved formulas including the terms of order $V_1^2(a^2m^*/4\pi^2)$ lead to corrections in the desired direction of raising the [111] axis relative to the [110], but the error remaining is still half that found previously. Further improvement might be made if the effect of other terms in the Fourier expansion of the potential were included; these terms are not negligible, to judge from splittings of states at H, and higher states at P and N.

Thus, the nearly free electron model, in its usual simple form and with neglect of higher order perturbations, is not applicable to give a consistent description of the distortions of the energy surfaces in the conduction bands of the alkali metals except for sodium, for which the surfaces up to the Fermi energy depart negligibly from spheres. Including the effects of other reciprocal lattice vectors seems to improve the model somewhat, except for lithium, but complicates it greatly.

A serious drawback to use of the usual form of the nearly free electron model to give even a very approxi-

TABLE I. First Fourier coefficient V_1 of effective potential, as obtained from splittings of states at N, P, and H from Eqs. (2.4), (2.9), and (2.12) of text. (Energies in rydbergs.)

	Li	Na	K	Rb	Cs
a (au)	6.65	8.11	10.05	10.74	11.46
$V_1(N)$	+0.101	+0.008	−0.016	−0.028	−0.042
$V_1(P)$	+0.076	+0.018	+0.020	+0.018	+0.024
$V_1(H)$	+0.052	+0.026	+0.039	+0.038	+0.047

mate description of the energy bands in the alkalies is the model's failure to account consistently for the calculated splittings of the states at N, P, and H. Equations (2.4) and (2.9) give two formulas for V_1, and in the same approximation for the lowest states at H we obtain a third,

$$6V_1=E(H_1)-E(H_{12}). \tag{2.12}$$

In Table I are listed the different values for V_1 obtained from these three formulas for each metal from the calculated points. Evidently the three values for each metal differ not only in magnitude, but for potassium, rubidium, and cesium also in sign.[15] The discrepancies are evidently too large to be remedied by going to higher order perturbation theory.

As we have mentioned elsewhere,[16] this striking failure of the nearly free electron model is not surprising when we consider that the pseudopotential actually should depend on the angular momentum l of the state under study.[5,7] Such dependence invalidates Eqs. (2.4), (2.9), and (2.12), since the energy of an s state like H_1 depends on the Fourier coefficients of the s pseudopotential, that of a d state like H_{12} on those of the d pseudopotential. States like N_1, $N_{1'}$, or P_4 that are mixtures of functions of different l have energies depending on complicated averages of the Fourier coefficients for different $\mathbf{K}$ of the pseudopotentials for the different l, as Antončík[7] has shown. Since these pseudopotentials are largely independent, the splittings in Eqs. (2.4), (2.9), and (2.12) depend in fact on a number of independent parameters instead of a single V_1. The price of generalizing the nearly free electron model to include an l-dependent potential is thus to introduce more independent parameters than can be determined from the splittings at a few symmetry points. Such a generalization might provide a useful interpretation of the alkali metal band structures as Cornwell[9] has suggested; we have not, however, investigated this possibility. We can conclude in any case that attempts to interpret calculated or experimental band structures in terms of the nearly free electron model and a simple effective potential will usually yield inconsistencies.

III. INTERPOLATION PROCEDURE FOR CALCULATED BANDS

Notwithstanding the inadequacies of the usual form of the nearly free electron model, this model does predict correctly that the constant energy surfaces in the conduction band of the alkali metals are nearly spherical but bulge in the [110] directions toward the zone faces. We, therefore, use this model to suggest the general form of an interpolation formula, but we choose values for parameters in this formula to give as accurate a description as possible of the conduction band alone, with little regard for higher bands. Fitted to our calculated energies on the symmetry axes, this formula provides an approximate interpolation to arbitrary directions of $\mathbf{k}$ within the zone and permits evaluation of the changes in Fermi energy, density of states and other parameters of the Fermi surface caused by the nonspherical distortions.

In the nearly free electron model, if the energy gap at the zone face is small, the distortion of the energy surfaces in the direction of one zone face arises primarily from interaction with the $\mathbf{K}$ vector associated with that face. We denote by $(2\pi/a)(1/\sqrt{2}-u)$ the component of $\mathbf{k}$ along the normal to the nearest face, and by $(2\pi/a)w$ the magnitude of the projection of $\mathbf{k}$ on that face. Then, from Eq. (2.2), the nearly free electron model leads to an expression for the energy of the conduction band near that face of the form

$$E(\mathbf{k})=\lambda w^2+f(u), \tag{3.1}$$

where $f(u)$ is given by Eq. (2.6). The distortion in the direction of one face thus has axial symmetry about the normal to that face, and the energy varies quadratically in the component of $\mathbf{k}$ parallel to that face, the coefficient λ being the same as for the undistorted surface. The surfaces of constant energy thus comprise twelve axially symmetric bulges—one for each zone face—seated on a spherical base. If the bulges are small they do not overlap each other appreciably and may be treated independently, as for example in calculating the amount by which the bulges change the density of states or the cyclotron mass.

We use this same description of the distorted surface as the basis of an interpolation procedure for our calculated bands. For the spherical base on which the bulges are seated we use the constant energy surfaces as calculated from the spherical approximation of Sec. IV of I. To describe each bulge we use Eq. (3.1), with

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[15] The fact that the order of the states P_1 and P_4, and H_1 and H_{12} is for K, Rb, and Cs the reverse of that to be expected in the nearly free electron model from the order of the states N_1 and $N_{1'}$ does not imply that the energy gap between the first and second bands necessarily vanishes at some intermediate point along the lines D and G on the BZ face connecting N with P and H, respectively. From the character tables of Bouckaert, Smoluchowski, and Wigner [Phys. Rev. **50**, 58 (1936)] it can be shown that the representations of the group of $\mathbf{k}$ along D and G that are compatible with N_1 and $N_{1'}$ are both compatible with P_4 and with both H_{15} and H_{12}. Since P_4 is below P_1 for all the alkalies, and the lowest state at H is either H_{15} or H_{12}, it follows that for all the alkalies the gap between the first and second bands at N must shrink to zero at both P and H. It could vanish at an arbitrary intermediate point along D or G (or elsewhere on the zone face), but this is not required by the topology of the bands. The first two bands will stick together also along the edge F of the zone wherever F_3 lies below F_1.

[16] F. S. Ham, in *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1960), p. 9.

TABLE II. Parameters in an interpolation formula [Eq. (3.2) of text] for energies of the conduction band of the alkali metals along the [110] axis for $\frac{1}{4} \leqslant t \leqslant \frac{1}{2}$, where $\mathbf{k} = (2\pi/a)(t,t,0)$. (Energies in rydbergs, a and $\mathbf{k}$ in atomic units.) (Sodium is omitted because the spherical approximation suffices for an accurate description of the conduction band in this metal.)

	a	$E(N)$	V_1	ξ	ω
Lithium	5.338	−0.3888	+0.2176	+1.15104	+2.14415
	6.651	−0.4115	+0.1008	+0.74724	+1.08003
	8.109	−0.4017	+0.0386	+0.51114	+0.52926
Potassium	8.109	−0.2649	−0.06095	−0.05304	+0.27392
	10.049	−0.2943	−0.01610	+0.27494	+0.26487
	11.458	−0.3055	−0.01345	+0.26488	+0.17918
Rubidium	9.053	−0.2861	−0.0718	−0.24483	+0.12718
	10.742	−0.2958	−0.0285	+0.18744	+0.19583
	12.575	−0.3019	−0.0203	+0.21553	+0.12848
Cesium	10.049	−0.2970	[a]	[a]	[a]
	11.458	−0.2958	−0.04245	+0.02193	+0.10019
	13.348	−0.2917	−0.02490	+0.14319	+0.08697

[a] For this case we use $f(u) = E(N) + \alpha u^2 + \beta u^4$, with $\alpha = -0.3475$, $\beta = -1.0667$.

$f(u)$ chosen to fit our calculated energies along the [110] axis. In practice we have used the expression

$$f(u) = E(N) + |V_1| + \xi u^2 - (\omega u^2 + V_1^2)^{1/2}. \tag{3.2}$$

Here $E(N)$ is the energy of the lower state at N, $|V_1|$ is half the energy gap at N, and ξ and ω are chosen so that (3.2) gives correctly our calculated energies at the points with $t = 1/4$ and $3/8$, where $\mathbf{k} = (2\pi/a)(t,t,0)$. Values of these parameters are listed in Table II.

It is important in our interpolation procedure to preserve the quadratic dependence of the energy on w even when the energy in the spherical approximation is not a simple quadratic function of k. This approximation greatly simplifies subsequent calculations. In particular, in computing the density of states $n(E)$ per unit volume and unit energy range,

$$n(E) = \frac{1}{4\pi^3} \int_{S(E)} \frac{dS}{|\nabla_k E|}, \tag{3.3}$$

if $E(\mathbf{k})$ is given by (3.1), then we have the simple result noted by Jones[17] that, whatever the form of $f(u)$, the contribution to $n(E)$ of the part of the constant energy surface cut off by the planes $u = u_1$ and $u = u_2 > u_1$ is simply

$$\Delta n(E) = (4\pi^2\lambda)^{-1}(2\pi/a)^3(u_2 - u_1). \tag{3.4}$$

Furthermore, the surface area of the part of a sphere of radius $k = (2\pi/a)z$ cut off by these planes is $(2\pi z)(2\pi/a)^2(u_2 - u_1)$. In the spherical approximation the contribution to the density of states from this portion of the sphere of energy E is, therefore,

$$\Delta n_s(E) = (2\pi/a)^2 z (2\pi^2)^{-1} [(dE_s/dk)_{E_s=E}]^{-1}(u_2 - u_1), \tag{3.5}$$

where (dE_s/dk) is evaluated at the energy E. Comparing this expression with (3.4), we see that the bulge increases the density of states at energy E above that given in the spherical approximation for the sphere of the same energy by an amount proportional to the distance the bulge protrudes beyond the sphere, if λ in (3.1) is chosen as

$$\lambda = (2\pi/a)(2z)^{-1}(dE_s/dk)_{E_s=E}. \tag{3.6}$$

This choice of λ is in fact suggested as follows by the nearly free electron model. In that model the effect of the Bragg reflection is to change the dependence of $E(\mathbf{k})$ on u while leaving the dependence on w unchanged. For the calculated energy bands, if we consider the spherical approximation to give the undistorted surface, we should therefore keep the same dependence on w for the distorted surface. Let $\mathbf{k}_0$ be a point on the [110] axis, and $\mathbf{k}$ a nearby point with the same component parallel to the axis, so that

$$\begin{gathered} \mathbf{k}^2 - \mathbf{k}_0^2 = k_\perp^2 = (2\pi/a)^2 w^2, \\ \text{or} \\ |\mathbf{k}| - |\mathbf{k}_0| \cong (2\pi/a) w^2/2z. \end{gathered} \tag{3.7}$$

In the spherical approximation $E_s(\mathbf{k})$ is a function of $|\mathbf{k}|$ only, so that

$$E_s(\mathbf{k}) \cong E_s(\mathbf{k}_0) + (|\mathbf{k}| - |\mathbf{k}_0|)\partial E_s(k_0)/\partial k,$$

or from (3.7)

$$E_s(\mathbf{k}) \cong E_s(k_0) + (2\pi/a) w^2 (2z)^{-1} \partial E_s(k_0)/\partial k. \tag{3.8}$$

The coefficient of w^2 here is just λ as given by (3.6). Thus we make this choice of λ (which is therefore a slowly-varying function of the energy E) for use in our interpolation formula (3.1) to describe the surface of energy E. In terms of the coefficients of Table VI of I, we obtain from Eq. (3.6)

$$\lambda(E) = (2\pi/a)^2[E_2 + 2E_4 z^2 (2\pi/a)^2]. \tag{3.9}$$

We ignore the energy variation of λ in forming the gradient of E as given by (3.1) with respect to $\mathbf{k}$.

Summing over the twelve bulges, we find then that with this interpolation procedure the density of states for the distorted surface is increased over that for the surface of the same energy in the spherical approximation by an amount

$$n(E) - n_s(E) = [3/\pi^2\lambda(E)](2\pi/a)^3 \Delta u, \tag{3.10}$$

where

$$\Delta u = (1/\sqrt{2}) - z - u_m. \tag{3.11}$$

Here $z = (a/2\pi)k$, and $u_m = [\frac{1}{2}\sqrt{2} - (a/2\pi)k_m]$, k being the radius of the sphere of energy E, and k_m the length of the k vector to the extremity of the bulge on the distorted surface of energy E. If the distorted surface contacts the zone face, u_m is zero. For the sphere

$$n_s(E) = (2\pi^2\lambda)^{-1}(2\pi/\mathrm{a})^3 z. \tag{3.12}$$

In subsequent sections we shall show how this interpolation procedure may be used to compute the Fermi energy, the area of the Fermi surface and its

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[17] H. Jones, Phil. Mag. 43, 105 (1952).

TABLE III. Calculated Fermi energy E_F and thermal effective mass (m_t/m_0) of the alkali metals for several values of the lattice constant a. E_{FS} and $(m_t/m_0)_s$ are values calculated from the spherical approximation; $E(N)$ is the energy of the lower state at N. (Energies in rydbergs; a in atomic units.)

	a	E_{FS}	E_F	$E(N)$	$(m_t/m_0)_s$	(m_t/m_0)
Lithium	5.338	−0.365	−0.402	−0.389	1.55	2.41
	6.651	−0.422	−0.433	−0.412	1.32	1.64
	8.109	−0.429	−0.431	−0.402	1.20	1.29
Sodium	6.651	−0.296	−0.296	−0.219	1.04	1.04
	8.109	−0.369	−0.369	−0.308	1.00	1.00
	10.049	−0.383	−0.383	−0.349	1.00	1.00
Potassium	8.109	−0.251	−0.270	−0.265	1.27	1.91
	10.049	−0.320	−0.322	−0.294	1.01	1.07
	11.458	−0.327	−0.328	−0.306	0.98	1.02
Rubidium	9.053	−0.255	−0.283	−0.286	1.20	2.47
	10.742	−0.305	−0.310	−0.296	0.99	1.18
	12.575	−0.313	−0.315	−0.302	0.96	1.08
Cesium	10.049	−0.248	−0.285	−0.297	1.36	2.62
	11.458	−0.285	−0.298	−0.296	1.06	1.75
	13.348	−0.294	−0.299	−0.292	0.98	1.26

cross sections, and the various effective masses, for the nonspherical conduction band.

Our interpolation procedure is quite similar to the "eight cone" model used by Ziman[18] in analyzing the properties of the noble metals. Both treat each bulge separately, using a local energy variation of the form (3.1), and both assume that in the regions between the bulges the surfaces are nearly enough spherical so that complications from the overlap of different bulges may be ignored. Ziman's work is, however, based directly on the usual form of the nearly free electron model, while our procedure is designed primarily to interpolate between the calculated results on symmetry axes and has to take account of the fact that the "undistorted" bands in the spherical approximation are not simply quadratic in k.

The assumption that the bulges may be treated independently and that they have axial symmetry is clearly accurate only when the distortions are small. When the distortion is sufficient to cause the Fermi surface of the alkalies to touch the zone faces, there is appreciable overlap between different bulges, and the accuracy of this approximation is questionable. Since our calculated bands show no contact for any of the alkalies except cesium at lattice constants near the equilibrium value, this assumption should be quite accurate for most of our present work. We shall use this assumption even when contact occurs, since a better calculation would pose formidable difficulties without changing the qualitative behavior of the results.

IV. FERMI SURFACE

A. Fermi Energy

We have evaluated the Fermi energy by obtaining from (3.10) as a function of energy the difference in density of states between the distorted energy surfaces and the bands in the spherical approximation, and then integrating this difference numerically. This yields the increase in volume of the distorted surface of energy E over that of the sphere of the same energy. The Fermi energy E_F is then the energy of the surface containing one electron per atom (including spin degeneracy). These results are given in Table III, along with the Fermi energy in the spherical approximation E_{FS}, and the energy $E(N)$ of the lower state at N. The Fermi surface contacts the zone face if $E_F > E_N$. For sodium the bands are so little distorted that we have used only the spherical approximation to obtain E_F.

In Table IV the same quantities are listed for the equilibrium lattice constants at 0°K, using Barrett's values[19] as an approximation to the latter. E_{FS} is obtained from the parameters of Table VII of I and from $E(\Gamma_1)$ in Table II of I. The difference $E_F - E_{FS}$ was found by interpolation from Table III.

The Fermi surface of cesium is thus found from the calculations to barely miss contact with the zone face at the 0°K equilibrium lattice constant. Contact occurs at a 2% reduction in lattice constant below the equilibrium value, and the area of contact increases rapidly as the lattice constant is decreased further. For all the other alkali metals, the distortion at equilibrium is not nearly enough to cause contact. For rubidium our calculations indicate that contact occurs for $a/a_0 \cong 0.9$, while for the others contact is not found within the range of a we have used.

B. Density of States and Thermal Effective Mass

The full density-of-states curve for lithium for $a = 6.65$ a.u. is plotted in Fig. 1, being typical of that for bands with appreciable distortion. The smooth curve represents the spherical approximation, $n_s(E)$, as given by (3.12), while the peaked curve gives $n(E)$ for the distorted surface. The peak occurs at the energy of the

TABLE IV. Fermi energy and thermal effective mass of the alkali metals for equilibrium lattice constant at 0°K. E_{FS} and $(m_t/m_0)_s$ denote the values obtained in the spherical approximation with the parameters of Tables II and VII of I, and E_F and (m_t/m_0) the values for the distorted surface, obtained by interpolation from Table III. $E(N)$ is the energy of the lower state at N. (Energies in rydbergs, lattice constant in angstroms and in atomic units.)

	Li	Na	K	Rb	Cs
a_0 (Å)	3.491	4.225	5.225	5.585	6.045
a_0 (a.u.)	6.597	7.984	9.874	10.555	11.424
E_{FS}	−0.420	−0.367	−0.318	−0.302	−0.284
E_F	−0.431	−0.367	−0.320	−0.308	−0.297
$E(N)$	−0.412	−0.302	−0.293	−0.295	−0.296
$(m_t/m_0)_s$	1.32	1.00	1.02	0.99	1.06
(m_t/m_0)	1.66	1.00	1.09	1.21	1.76

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[18] J. M. Ziman, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1961), Vol. 10, p. 1.

[19] C. S. Barrett, Acta Cryst. **9**, 671 (1956). We use Barrett's values for the lattice constant at 5°K for all the metals except lithium, for which we use his value at 78°K.

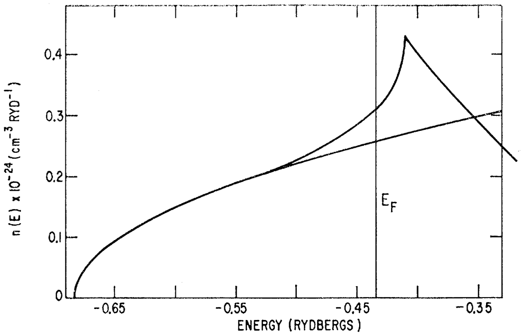

FIG. 1. Density-of-states curve for lithium, $a=6.65$ au. The smooth curve represents the spherical approximation, the peaked curve the correct band structure including the nonspherical distortion. E_F is the Fermi energy for the correct band structure.

lower state at N ($N_{1'}$ for lithium) and has a vertical tangent on its low-energy side.

It is convenient to describe the density of states at the Fermi energy in terms of a "thermal effective mass" m_t defined[20] by

$$m_t/m_0=n(E_F)/n_0(E_{F0}), \tag{4.1}$$

where m_0 is the free-electron mass, and $n_0(E_{F0})$ is the density of states at the Fermi surface of a gas of free noninteracting electrons of the same density as that of the conduction electrons in the metal. In atomic units, m_t/m_0 is given by

$$\frac{m_t}{m_0}=\frac{2\pi^2}{k_F}n(E_F)=\frac{1}{2\pi k_F}\int_{S(E_F)}\frac{dS}{|\nabla_k E|}, \tag{4.2}$$

where k_F is the radius of the Fermi surface in the spherical approximation (*not* the radius of the spherical base of the actual Fermi surface).

The thermal effective mass is determined experimentally by the ratio of the electronic heat capacity of a metal to that calculated for a free-electron gas of the same density (without electron-electron or electron-phonon interaction). Thus, m_t calculated from our energy bands using (4.2) represents an approximation to this experimental value when no correction is made for electron-electron and electron-phonon interactions.

Our calculated values of m_t/m_0 are given in Table III. For comparison we also give the value of the thermal mass given by the spherical approximation,

$$(m_t/m_0)_s=(E_2+2k_F^2E_4)^{-1}. \tag{4.3}$$

From the difference between (m_t/m_0) and $(m_t/m_0)_s$ we see that the distortion of the band causes an appreciable increase in the thermal effective mass.

C. Optical Effective Mass

The optical effective mass m_a is defined from the average inverse effective mass of the conduction electrons[20] (in cgs units)

$$m_a^{-1}=(4\pi^3N\hbar^2)^{-1}\int d^3k\,\tfrac{1}{3}\nabla_k^2E, \tag{4.4}$$

where N is the number of electrons per unit volume, and the integral is over the occupied part of the band. This mass determines the coefficient

$$\omega_a^2=4\pi Ne^2/m_a, \tag{4.5}$$

of the term $(-\omega_a^2/\omega^2)$ in the real part of the dielectric constant of a cubic metal at angular frequency ω (infinite relaxation time). This term determines the rate of change with frequency of the real part of the dielectric constant at frequencies well below the interband absorption edge.

For an alkali metal, we have on transforming to atomic units and using Gauss's theorem

$$\frac{m_a}{m_0}=6\left(\frac{2\pi}{a}\right)^3\left[\int_{S(E_F)}dS\,|\nabla_kE|\right]^{-1}, \tag{4.6}$$

so that, as Cohen has shown,[20] m_a is inversely proportional to the average velocity at the Fermi surface.

For the distorted energy bands we use our interpolation procedure, Eqs. (3.1) and (3.2), with $\lambda(E_F)$ given by (3.6), to describe the energy surfaces for $E\cong E_F$ over one of the bulges. The contribution to the integral $\int dS|\nabla_kE|$ from one bulge in the Fermi surface between its extremity at u_m and the plane $u=u_2$ is then given by

$$\left(\frac{2\pi}{a}\right)^3\frac{\pi}{\lambda(E_F)}\int_{u_m}^{u_2}|\nabla_kE|^2du.$$

We denote by Δ_a the difference

$$\Delta_a=\left(\frac{2\pi}{a}\right)^2\left[\int_{u_m}^{u_2}|\nabla_kE|^2du-\int_{1/\sqrt{2}-z}^{u_2}|\nabla_kE_s|^2du\right], \tag{4.7}$$

where the latter integral is over the spherical cap cut off by the plane $u=u_2$ from the sphere of radius $k=(2\pi/a)z$ and energy $E_S=E_F$ in the spherical approximation. This sphere forms the spherical base on which the bulges in the Fermi surface are seated. If the plane $u=u_2$ is chosen to cut the Fermi surface in the region where the bulge merges with the base, Δ_a represents the increment by which one bulge increases the value of the integral over the value given for the spherical base by the spherical approximation. Since there are twelve bulges, we obtain finally for (4.6)

$$\frac{m_a}{m_0}=\left(\frac{2\pi}{a}\right)^2\left(\frac{3\lambda(E_F)}{\pi}\right)\frac{1}{4[\lambda(E_F)]^2z^3+6\Delta_a}. \tag{4.8}$$

We note that the reduced radius z of the spherical base of the Fermi surface is less than z_F, the reduced radius of the Fermi surface in the spherical approximation. In the latter approximation $\Delta_a=0$, and since $(4\pi z_F^3/3)=1$

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[20] M. H. Cohen, Phil. Mag. 3, 762 (1958).

TABLE V. Calculated parameters of the Fermi surfaces of the alkali metals at the lattice constant a indicated: thermal mass m_t, optical mass m_a, cyclotron mass m_c, area A of extremal cross section of the Fermi surface, surface area S of the Fermi surface, radius k of the Fermi surface in various directions, and parameters ξ_1 and ξ_{1s} relating to the "diffusion" component of the thermoelectric power. Subscripts indicate the direction appropriate to k, or the direction of the normal to the plane of cross section or to that of the cyclotron orbit. S_0 and A_0 denote the corresponding areas of a spherical Fermi surface, and k_F its radius.

	Lithium	Sodium	Potassium	Rubidium	Cesium
a (a.u.)	6.651	8.109	10.049	10.742	11.458
m_t/m_0	1.64	1.00	1.07	1.18	1.75
$(m_t/m_0)_s$	1.32	1.00	1.01	0.99	1.06
m_a/m_0	1.45	1.00	1.02	1.06	1.29
m_t/m_a	1.13	1.00	1.06	1.11	1.36
$m_{c[110]}/m_0$	1.48	1.00	1.035	1.07	1.46
$m_{c[100]}/m_0$	1.65	1.00	1.063	1.16	1.92
$m_{c[111]}/m_0$	1.82	1.00	1.092	1.25	2.38
$A_{[110]}/A_0$	0.976	1.00	0.995	0.979	0.94
$A_{[100]}/A_0$	0.993	1.00	1.001	0.996	0.99
$A_{[111]}/A_0$	1.011	1.00	1.007	1.013	1.04
S/S_0	1.06	1.00	1.03	1.06	1.12
$(S/S_0)^2$	1.11	1.00	1.06	1.13	1.25
$k_{[110]}/k_F$	1.023	1.00	1.007	1.018	1.08
$k_{[100]}/k_F$	0.973	1.00	0.994	0.980	0.94
$k_{[111]}/k_F$	0.983	1.00	0.994	0.980	0.94
ξ_1	+0.92	+1.46	+1.15	+0.70	−0.32
ξ_{1s}	+1.98	+1.46	+1.35	+1.24	+1.13

for a body-centered cubic lattice, we have

$$(m_a/m_0)_s=(2\pi/a)^2[\lambda(E_F)]^{-1}, \tag{4.9}$$

a result identical with the corresponding expression (4.3) for the thermal mass.

We have calculated Δ_a by integrating numerically the first integral in (4.7), using (3.1), (3.2) and Table II to plot $|\nabla_k E|^2$ as a function of u. We chose u_2 such that the area of the spherical cap was about one-twelfth the area of the sphere. Both w and $|\nabla_k E|^2$, as obtained from (3.1), where found at $u=u_2$ to be reasonably close to their values for the spherical base, and before integrating we made a smooth interpolation to make this agreement precise. While this procedure obviously has some inaccuracy, improving it would be difficult and the results for m_a/m_0 appear reliable within several percent provided the distortion is not so large that appreciable contact occurs.

The resulting values for m_a/m_0 are given in Table V. We have done these integrations for each alkali metal for only that value of the lattice constant in Table III which is nearest the equilibrium value. The small change in m_a/m_0 produced by shifting to the equilibrium lattice constant can be estimated from the corresponding change in the thermal mass (Table IV).

D. Cyclotron Mass

The cyclotron resonance frequency[21] is given (in cgs units) by

$$\omega_c=\frac{2\pi eH}{\hbar c}\left[\oint\frac{dk}{v_\perp}\right]^{-1}, \tag{4.10}$$

where the line integral is taken around an orbit defined by the intersection of the Fermi surface with a plane perpendicular to the magnetic field $\mathbf{H}$, and $v_\perp$ is the component of electron velocity perpendicular to $\mathbf{H}$. We will consider only extremal orbits when $\mathbf{H}$ lies along the [110], [100], and [111] directions. Then for an alkali metal with a simply connected Fermi surface these orbits pass directly over two, four, and six of the bulges, respectively, as sketched in Fig. 2. For the first two of these orbits $\nabla_k E$ is required by symmetry to be perpendicular to $\mathbf{H}$, and for the [111] extremal orbits the same is true in the approximation of treating each bulge separately and assuming each to be azimuthally symmetric. Then, on comparing (4.10) with the free-electron resonance frequency eH/m_0c, we obtain for these orbits the expression for the cyclotron mass m_c (in atomic units)

$$\frac{m_c}{m_0}=\frac{1}{\pi}\oint\frac{dk}{|\nabla_k E|}. \tag{4.11}$$

Using our interpolation procedures, with the same approximations used in deriving the expression (4.8) for the optical mass, we obtain from (4.11) for the contribution of a single bulge to m_c/m_0

$$\left(\frac{2\pi}{a}\right)^2\frac{1}{\pi\lambda(E_F)}\int_{u_m}^{u_2}\frac{du}{|w(E_F)|}. \tag{4.12}$$

Since $\int|w|^{-1}du$ for a spherical surface is simply the angle subtended by the arc at the center of the sphere, we obtain finally for our three extremal orbits

$$\frac{m_c}{m_0}=\left(\frac{2\pi}{a}\right)^2\frac{1}{\lambda(E_F)}\left(1+\frac{n\Delta_c}{2\pi}\right), \tag{4.13}$$

where n is the number of bulges that the orbit passes directly over, and Δ_c is the amount by which the integral $\int|w|^{-1}du$ over a single bulge exceeds the angle which this segment of the orbit subtends at the center

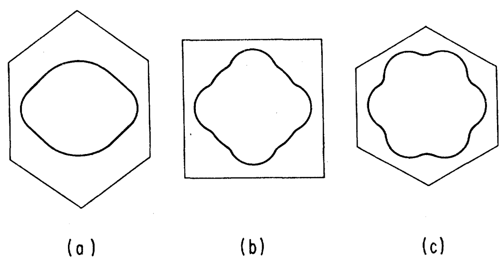
(a) (b) (c)

FIG. 2. Extremal cyclotron orbits in $\mathbf{k}$ space for a simply connected Fermi surface in a body-centered cubic lattice. The direction of the magnetic field $\mathbf{H}$ is parallel to (a) [110], (b) [100], (c) [111]. These orbits pass, respectively, over two, four, and six of the bulges in the Fermi surface towards the [110] faces of the Brillouin zone.

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[21] M. Ya Azbel' and E. A. Kaner, J. Exptl. Theoret. Phys. (U.S.S.R.) **32**, 896 (1956) [translation: Soviet Phys.—JETP **5**, 730 (1957)].

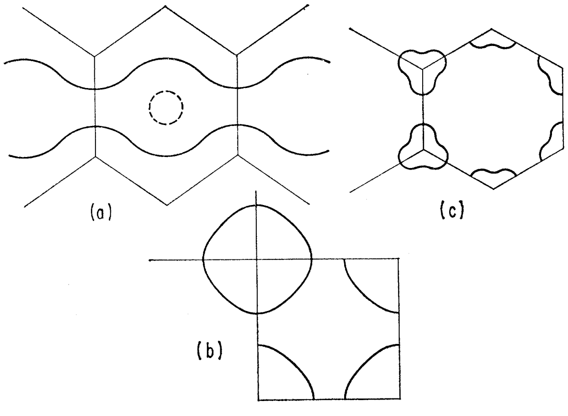

FIG. 3. Extremal cyclotron orbits in **k** space for a multiply connected Fermi surface in a body-centered cubic lattice. The direction of the magnetic field **H** is parallel to (a) [110], (b) [100], (c) [111]. In (a) are shown both the open orbits and the neck orbit.

of the Fermi surface. The values calculated from our energy bands for these extremal orbits are given in Table V, where a subscript on m_c indicates the direction of **H** thus: $m_{c[110]}$. We see that our calculations predict an appreciable anisotropy in m_c/m_0 for all the alkalies except sodium, with $m_{c[110]}<m_{c[100]}<m_{c[111]}$ if contact does not occur.

The cyclotron masses of these extremal orbits are quite sensitive to the degree of distortion of the Fermi surface, and unlike the thermal and optical masses (or the cyclotron masses of adjacent orbits) they become infinite when the Fermi surface just touches the zone face, since $w(E_F)$ in (4.12) is then proportional to u for small u ($u_m=0$). We calculated above that at the equilibrium lattice constant for 0°K the Fermi surface of cesium nearly touches the zone face, so that we cannot safely estimate these equilibrium cyclotron masses for cesium from Table V. They should be larger than the values in Table V and should be very sensitive to the orientation of **H**. For the other alkalies the change in m_c/m_0 from the lattice constant of Table V to the equilibrium value should be similar to that for the thermal mass (Table IV).

When the energy bands are sufficiently distorted that the Fermi surface contacts the zone face, the character of these extremal cyclotron orbtis is altered substantially, as shown in Fig. 3. With **H** in the [110] direction, the extremal orbits of Fig. 2 become open orbits, while a new orbit around the "neck" appears. In the approximation of our interpolation procedure (which is of uncertain accuracy for so much distortion), the cyclotron mass for this neck orbit is given simply as

$$m_{cn}/m_0=(2\pi/a)^2[\lambda(E_F)]^{-1}. \qquad (4.14)$$

For **H** along [111], the extremal orbit for the simply connected Fermi surface now becomes two separate orbits, each comprising only three of the six arcs in Fig. 3(c) and corresponding to resonance of a hole rather than of an electron. For **H** in [100], the orbit comprises the same arcs as for the simply connected Fermi surface but now represents hole resonance.

To illustrate this situation when contact occurs, we have calculated cyclotron masses for cesium with $a=10.049$ a.u. although the accuracy of the interpolation is rather poor in this case. The Fermi energy exceeds $E(N_1)$ by $=0.012$ Ry (Table III), and the neck radius $w_n=(a/2\pi)k_n$ is 0.17. For the neck mass we find $m_{cn}/m_0=1.00$, while for the hole orbits $|m_{c[100]}/m_0|=1.82$, and $|m_{c[111]}/m_0|=1.01$, both these latter values being considerably smaller than they would be if the neck radius were not so large. Thus, with contact, hole orbits appear, and the anisotropy of the cyclotron mass is altered from that for the simply connected Fermi surface.

E. Extremal Area of Cross Section of Fermi Surface

The extremal area of cross section A of the Fermi surface determines the period of the de Haas-van Alphen effect.[22] For **H** along [100], [110], and [111] we may calculate easily from our interpolation procedure the amount by which each bulge in the Fermi surface increases this area over that of the cross section of the spherical base

$$\Delta_A=2\left(\frac{2\pi}{a}\right)^2\left[\int_{u_m}^{u_2}|w(E_F)|\,du-\int_{1/\sqrt{2}-z}^{u_2}|w_s(E_F)|\,du\right]. \qquad (4.15)$$

The ratio of A to that of the free-electron sphere $A_0=(2\pi/a)^2\pi z_F{}^2$ is then for a simply connected Fermi surface

$$A/A_0=(z^2/z_F{}^2)[1+(n\Delta_A/\pi z^2)], \qquad (4.16)$$

n being the number of bulges passed over by the extremal orbit.

Calculated values of A/A_0 are given in Table V, where the subscript on A indicates the direction of **H**. There is evidently a small anisotropy predicted for all the alkalies except sodium, with $A_{[110]}<A_{[100]}<A_{[111]}$. This amounts to only about 1% for potassium, 3 to 4% for lithium and rubidium, and about 10% for cesium. The values of Table V should be increased slightly in going to the lattice constant for 0°K.

If contact occurs, the interesting cross section for **H** in [110] is that of the neck, A_n, while for **H** in [100] or [111] it is that of the orbit around the corner of the zone as sketched in the extended zone scheme of Fig. 3. These areas should be very different, with $A_n<A_{[111]}<A_{[100]}$. As an example, from our results for cesium with $a=10.049$ au, we find $(a/2\pi)^2A_n\cong0.10$, $(a/2\pi)^2A_{[111]}\cong0.18$, and $(a/2\pi)^2A_{[100]}\cong0.78$.

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[22] L. Onsager, Phil. Mag. 43, 1006 (1952).

F. Dimensions and Surface Area of Fermi Surface

The ratio of the radius of the distorted Fermi surface to that of the free-electron sphere, k_F, is given for the [110], [100], and [111] directions in Table V at the lattice constants indicated. These values were obtained by interpolating to the Fermi energy between the calculated points along each axis. Only for lithium at these lattice constants was there a significant difference between [100] and [111] axes at E_F. Decreasing the lattice constant to the 0°K value would increase only slightly the amount by which these ratios depart from unity. At a lattice constant for cesium 2% smaller than the 0°K value, the ratio $k_{[110]}/k_F$ would be increased to 1.14, since the Fermi surface then barely touches the zone face.

The surface area of the Fermi surface is increased by a single bulge by an amount

$$\Delta_S=\left(\frac{2\pi}{a}\right)^3\frac{\pi}{\lambda(E_F)}\left[\int_{u_m}^{u_2}|\nabla_kE|du-\int_{1/\sqrt{2}-z}^{u_2}|\nabla_kE_S|du\right], \quad (4.17)$$

over that of the spherical base, when we use our interpolation procedure. The ratio of the total area S to that of the free-electron sphere S_0 is therefore

$$S/S_0=(z^2/z_F^2)[1+(3\Delta_S/\pi z^2)]. \quad (4.18)$$

Values of this ratio calculated with the usual approximations are listed in Table V. These values are evidently not accurate to better than several percent, for S/S_0 should be increased over unity by an amount proportional for small distortion to the square of the degree of distortion, as represented, say, by $[(k_{[110]}/k_F)-1]$.

Cohen[20] has shown that the ratio of the thermal and optical masses should satisfy the inequality

$$m_t/m_a>(S/S_0)^2, \quad (4.19)$$

and thus be greater than unity if the Fermi surface is simply connected (since S/S_0 can be <1 only if contact occurs). Table V shows that our computed values indeed satisfy this inequality, except that the tabulated values of S/S_0 for potassium and rubidium are slightly too high, as is evident also from the discussion of the previous paragraph when we compare the distortion for these metals with that of lithium and cesium.

G. "Diffusion" Component of Thermoelectric Power

If a relaxation time $\tau(\mathbf{k})$ exists, the "diffusion" component of the thermoelectric power[23] of a metal is given by

$$S_{\text{diff}}=-(\pi^2k^2T/3|e|E_{F0})\xi, \quad (4.20)$$

where k is Boltzmann's constant, T is the absolute temperature, $|e|$ is the magnitude of the electron charge, E_{F0} is the free-electron Fermi energy appropriate to an electron density equal to that of conduction electrons in the metal, and ξ is a number given by

$$\xi=E_{F0}\frac{d}{dE}\ln\left[\int_{S(E_F)}v\tau(\mathbf{k})dS\right], \quad (4.21)$$

v being the electron velocity.

If $\tau(\mathbf{k})$ is a function only of energy, we can take it from under the integral. Taking the derivative explicitly, we then obtain

$$\xi=E_{F0}\left\{\int_{S(E_F)}[\nabla_k^2E/|\nabla_kE|]dS\bigg/\int_{S(E_F)}|\nabla_kE|dS\right\}+\frac{E_{F0}}{\tau}\left(\frac{d\tau}{dE}\right)_{E_F}. \quad (4.22)$$

Calling the first term ξ_1, we see that for a distorted Fermi surface the integral in the denominator of this term is the same as that determining the optical effective mass in (4.6). With our interpolation procedure, the contribution to the integral in the numerator from one bulge is given simply by

$$\left(\frac{2\pi}{a}\right)\pi\int_{u_m}^{u_2}\left[4+\frac{1}{\lambda(E_F)}\frac{d^2f}{du^2}\right]du,$$

which can be integrated immediately. Taking the contribution to this result at the limit of integration u_2 to be given by the spherical approximation, we obtain for ξ_1 on summing over the twelve bulges

$$\xi_1=2\pi z_F^2\left(\frac{m_a}{m_0}\right)\left\{\frac{E_2+(10/3)k^2E_4}{E_2+2k^2E_4}z+4[(1/\sqrt{2})-z-u_m]-2z-\frac{1}{\lambda(E_F)}\frac{df(u_m)}{du}\right\}. \quad (4.23)$$

If the spherical approximation held at the Fermi surface, ξ_1 would have the value ξ_{1S} given by the first term in the bracketed expression above, the other terms vanishing since then $u_m=(1/\sqrt{2})-z_F$ and $df_s(u_m)/du=-2\lambda(E_F)z_F$.

The calculated values of ξ_1 and ξ_{1S} are listed in Table V. Obviously ξ_1 is very sensitive to the degree of distortion of the Fermi surface, largely because $|df(u_m)/du|$ in (4.23) falls rapidly with increasing distortion from the value $2\lambda(E_F)z_F$ for a spherical surface to zero when contact occurs. We find that ξ_1 is negative (that is, this contribution to the thermoelectric power is *positive*) for cesium already at the lattice constant of Table V; when contact occurs for a 2% decrease in lattice constant we estimate $\xi_1\cong-1.0$. Similarly, we

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[23] See reference 2, p. 310.

estimate that if our Fermi surface for lithium were distorted enough to barely make contact, again ξ_1 would be roughly -1.0. The free-electron value for ξ_1 is $+3/2$.

Very similar results were obtained by Ziman[18] in a similar treatment of the thermoelectric power of the noble metals, except that his values for ξ_1 remained positive for a monovalent metal whatever the degree of distortion. This difference arises primarily because we have twelve bulges in the Fermi surface for the body-centered cubic lattice in place of eight for the face-centered. It also appears that our interpolation procedure, taking approximate account of the k^4 term in the spherical approximation to the bands, leads to slightly lower values for ξ_1 for a given distortion than we would obtain following Ziman and using the nearly free electron model in a straightforward way.

V. DISCUSSION AND COMPARISON WITH EXPERIMENT

In comparing our calculated energy bands with experiment, we emphasize that it is the trends through the series of the alkali metals which we expect the calculations to predict correctly, rather than the precise value of any parameter for a given metal. Accordingly the following discussion is arranged so that each experimental property that is directly related to our calculated band structure is discussed under one subheading for the whole alkali series.

Cohen and Heine[10] have given an excellent survey of the experimental information available in 1958 that is relevant to an attempt to deduce from experiment the shape of the Fermi surface and other features of the energy band structure of the alkali metals. Their review covered the magnetoresistance, the Knight shift, the thermoelectric power, the ratio of electrical and thermal resistivities at low temperature, the soft x-ray emission, and the variation with pressure of the electrical resistivity and Knight shift. They showed that these experimental results were all more or less consistent with a monotonic trend in the band structure. According to this trend, the Fermi surface of lithium was quite anisotropic and probably in contact with the zone face, with the p state at N below the s state; the Fermi surface of sodium was very nearly spherical; and for potassium, rubidium, and cesium the anisotropy increased in that order, with the s state at N increasingly farther below the p state. This trend, as we have seen, is the same as that found in our calculations, with the exception that we do not find sufficient Fermi surface distortion for lithium to cause contact.

Since 1958, further experimental data have become available, and several authors have given detailed analyses of different aspects of these data. We will review these below as they pertain to our calculations. Of especial interest, Collins and Ziman[11,12] have studied the electrical and thermal resistivities and the phonon drag component of the thermoelectric power on the basis of a model in which differences in these properties between the five alkali metals are attributed to differences in their electronic structure, and in particular to differences in the shape of the Fermi surface. Assuming similar lattice spectra for all the alkali metals and taking account of the dependence of phonon umklapp scattering on the shape of the Fermi surface, they show that the observed magnitude and temperature variation of these properties are generally consistent with our calculated trend in the band structures. Indeed they estimate values for the band gap at N which are remarkably close to our calculated values given in Table II of I. However, they show that the observed behavior of these properties is also consistent with the opposite trend, with the s state at N below the p state for lithium, and above it for potassium, rubidium, and cesium, so that they can not deduce a unique model on this basis.

On the other hand, in another extensive study of the transport properties of the alkali metals, Bailyn[13] has emphasized the extreme anisotropy of the phonon spectrum of these metals.[24] He has shown that the umklapp processes dominate the normal phonon scattering processes in the electrical resistivity above a few degrees Kelvin and that transverse modes of not especially short q make the dominant contribution to umklapp scattering. Assuming spherical Fermi surfaces, he finds he can obtain the observed transport properties of the alkali metals by a suitable choice of the effective Debye temperatures for various parts of the phonon spectrum and of the matrix elements for the various scattering processes. Thus, Bailyn's work shows that changes in the phonon spectrum and in the matrix elements can have the same effect on the transport properties as distortions of the Fermi surface. His conclusion that the important phonons have moderately long q implies that the transport properties should not in fact be especially sensitive to distortions in the Fermi surface. Bailyn does not attempt to provide a realistic calculation for any of the alkali metals, but his work shows that without more accurate knowledge of the phonon spectrum of the alkali metals than is at present available one does not know with any confidence how much of the differences in the observed transport properties can be ascribed to differences in the degree of distortion of the Fermi surface.

Brooks[25] has shown that the Knight shift of lithium and its pressure variation may be accounted for without assuming a distorted Fermi surface, because the p character of the wave function increases sufficiently rapidly with decreasing lattice constant even in the spherical approximation.

Thus, each of the properties of the alkali metals analyzed by Cohen and Heine and by Collins and Ziman

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[24] The phonon spectrum of sodium has very recently been determined by the method of neutron spectrometry and this anisotropy confirmed. [A. D. B. Woods, B. N. Brockhouse, R. H. March, and R. Bowers, Proc. Phys. Soc. (London) **79**, 440 (1962)].

[25] H. Brooks (unpublished); see remark in Appendix of reference 10).

except perhaps for the soft x-ray emission of Li, the interpretation of which is uncertain (see below), could be accounted for without assuming a distorted Fermi surface. There remains, obviously, a great need for definitive experiments on the shape of the Fermi surface for these metals. Nevertheless, despite these warnings that other effects *can* be equally important, the fact that the available experimental data on the alkali metals are on the whole consistent with a definite trend in the distortion of the Fermi surface which agrees with our calculated trend gives considerable support to Cohen, Heine, Collins, and Ziman's interpretation that much of the difference between these metals can be traced to differences in the shape of their Fermi surfaces. Similar conclusions about the trend in the shape of the Fermi surface have been reached by Dugdale[14] on the basis of a number of suggestive experimental correlations, discussed below.

A. Electronic Specific Heat

Recent measurements of the electronic component of the low temperature specific heat $C_e = \gamma T$ by Martin[26] for lithium and sodium and by Lien and Phillips[27] for potassium, rubidium, and cesium for the first time provide a complete set of values for all of the alkali metals. In units of (mJ)/(g atom °K^2), the measured values for γ are for Li, Na, K, Rb, and Cs, respectively, 1.63, 1.38, 2.13, 2.59, and 3.63. Using Barrett's values[19] for the lattice constants, we obtain from these results the experimental values 2.19, 1.27, 1.28, 1.36, and 1.63, respectively, for the ratio m_t/m_0 of the thermal effective, mass m_t to the free-electron mass m_0. The values for lithium and sodium, however, are for samples which have in part undergone a martensitic transformation from the body-centered cubic to an hexagonal close-packed phase. In his work on sodium, Martin[26] partially inhibited this transformation by a thermal cycling procedure; from a small increase in the observed γ he estimated that γ for the bcc phase was slightly higher than for the hcp phase but that the difference was almost certainly less than 20%.[28,29] Since the original samples contained more or less equal amounts of the two phases, we conclude that m_t/m_0 for the bcc phase of sodium might be as large as 1.4. For lithium the situation is less clear. Martin suggests that γ may be about 20% higher in the hcp phase than in the bcc phase; if so, and if 50% of the sample transformed, then m_t/m_0 for bcc lithium is about 2.0.

Comparing the experimental values of (m_t/m_0) (without making the uncertain correction for the martensitic transformation) with our calculated ones in Table III and IV, we see that the trends agree at the equilibrium lattice constant: Sodium and potassium have the smallest values, and lithium and cesium the largest. However, the calculated value for cesium exceeds that for lithium, the opposite of what is observed, and except for cesium the calculated values are too small.

We expect the calculated thermal masses to differ from the observed values, however, because we have made no attempt to include electron-electron correlation or electron-phonon interaction in the calculations. Indeed, if the difference between the calculated and experimental values is ascribed primarily to these effects we obtain a measure of their importance. Such a comparison suggests that these effects increase the thermal mass of lithium and sodium by some 20 to 40% but that the increase becomes smaller in the sequence sodium, potassium, rubidium, cesium and may actually become a negative correction of some 10% to the thermal mass of cesium. Alternatively, of course, the calculations may predict too large a distortion of the Fermi surface for the heavier alkali metals and thereby overestimate their thermal mass. This would be the case if, for example, our treatment of the exchange-correlation hole places the p state at N an electron volt or so too high relative to the s state, as Cohen and Heine have suggested.[10]

Theoretical estimates of the effects of correlation and electron-phonon interaction at realistic metallic densities are at the present time not at all satisfactory. Quinn and Ferrell[30] have estimated that correlation may decrease the thermal mass by some 5% at such densities, while DuBois' results[31] indicate an increase. Fletcher and Larson,[32] extending the Bohm-Pines theory, found an increase of some 30 to 50% for all the alkali metals. For the electron-phonon interaction Quinn and Ferrell[30] estimated roughly a 25% enhancement of the thermal mass for all the alkali metals from the normal phonon processes, and Quinn[33] found that umklapp processes make an additional comparable increase which seems to increase with increasing lattice constant.

An interesting feature of Quinn and Ferrell's result[30] is that the electron-phonon enhancement in the thermal mass due to normal phonon processes is proportional to the dimensionless constant introduced by Fröhlich[34] in

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[26] D. L. Martin, Phys. Rev. **124**, 438 (1961); Proc. Roy. Soc. (London) **A263**, 378 (1961).

[27] W. H. Lien and N. E. Phillips, *Proceedings of the Seventh International Conference on Low-Temperature Physics* (University of Toronto Press, Toronto, 1960), p. 675. *Note added in proof.* A revision of their temperature scale has led Lien and Phillips to suggest (private communication) that 2.08, 2.39, and 3.28 mJ/g atom °K^2 should be more accurate values of γ for K, Rb, and Cs, respectively, than those given in their article. Corresponding values of m_T/m_0 are 1.25, 1.25, and 1.47.

[28] E. A. Stern, Phys. Rev. **121**, 397 (1961).

[29] Martin concluded that an earlier interpretation by Stern (reference 28) of available data was incorrect. This had held that m_t/m_0 for bcc Na was 1.7 and for hcp Na 1.1. Martin showed that there is an as yet unexplained slow time variation in the electronic specific heat of cast specimens which may have affected the earlier data.

[30] J. J. Quinn and R. A. Ferrell, J. Nuclear Energy **2**, 18 (1961).

[31] D. F. Dubois, Ann. Phys. (New York) **7**, 174 (1959); **8**, 24 (1959).

[32] J. G. Fletcher and D. C. Larson, Phys. Rev. **111**, 455 (1958).

[33] J. J. Quinn, in reference 16, p. 58.

[34] H. Fröhlich, Phys. Rev. **79**, 845 (1950).

his theory of the superconducting state, which is independent of the isotopic mass of the lattice ion. The conclusion that the electronic contribution to the specific heat at very low temperatures should be independent of the ion isotopic mass is in agreement with Martin's observations[26] that there is no significant difference between the electronic specific heats of normal lithium and a sample containing 99.3% of Li^6. Thus the absence of such a dependence does not mean that the electron-phonon effect on the density of states at the Fermi surface is necessarily small. Jones[35] has predicted the possibility that for a distorted Fermi surface there might be a contribution to the lattice specific heat which is linear in the temperature and which therefore might be mistakenly interpreted as part of the electronic specific heat. This effect arises from the dependence of the elastic shear constants on the electron occupation of states near the zone face, and if it is important it should be accompanied by an anomalously large temperature dependence of the shear constants. Since this contribution to the "apparent" electronic specific heat should vary inversely as the square root of the isotopic mass, Martin's results show that this effect is not important for lithium.

Although the thermal masses of the alkali metals are affected appreciably by correlation and electron-phonon effects, it is clear from Tables III and IV that these are not solely responsible for enhancing the thermal mass above the value calculated in the spherical approximation. The effect of the distortion in the Fermi surface is appreciable even for potassium and seems to be as large or larger than correlation and electron-phonon effects for lithium and cesium. There is of course also a considerable difference even in the spherical approximation between the effective mass at $k=0$ (m^* in Table VII of I) and the density-of-states mass $[(m_t/m_0)_s$ in Table IV$]$, at the Fermi surface. The latter differs from m^* because of significant fourth-order terms in the k dependence of the energy.

B. Optical Properties

Cohen[20] has obtained the values 0.98, 1.01, 1.08, 1.08, and 1.02 for the optical effective-mass ratios m_{op}/m_0 for Li, Na, K, Rb, and Cs, respectively, from an analysis of the measurements of Ives and Briggs[36] of the optical constants of Na, K, Rb, and Cs and from the ultraviolet transparency frequency for lithium determined by Wood and Lukens.[37] Unfortunately all these data are at wavelengths shorter than that which should correspond to the interband absorption edge, so that, as Cohen pointed out, the mass values m_{op} all should be less than that of the conduction band optical mass m_a.

Our calculated values for m_a/m_0 are listed in Table V. For lithium and cesium they are appreciably larger than Cohen's values, while for potassium ours is slightly less, and for sodium and rubidium the values are in agreement. We would expect for these latter three metals that the experimental values from this frequency range should be smaller relative to our values than they are: Either the calculation underestimates these masses, or Cohen's analysis, which makes use of simplifying assumptions which are inaccurate in a range of frequency where important interband transitions occur, has led to values that are somewhat too large. Electron correlation effects may modify the optical mass of electrons in a real metal, as Wolff[38] has shown—for a free-electron gas no such effect occurs—but one would expect such an effect to be significant only for a substantially distorted Fermi surface. It would be most desirable in clarifying this comparison of the calculated and observed optical masses to have experimental data for the optical constants of all the alkali metals at wavelengths substantially longer than the interband edge.

We can estimate from our calculations the wavelength of the edge for interband absorption from the separation of the first and second bands in the [110] direction at the Fermi surface. Using Figs. 1–5 of I we obtain rough estimates of this edge for Li, Na, K, Rb, and Cs, respectively, as 3.6, 2.0, 1.2, 1.3, and 1.3, (in eV) or 3400, 6200, 10 000, 9500, and 9500 (in Å). The edge for sodium is of course essentially the same as predicted on a free-electron model and appears to be in good agreement with Ives and Briggs' data, as noted by Butcher.[39] The predicted edge for lithium occurs in the near ultraviolet, but no relevant data on the optical properties of lithium have been published.

An interesting point is that if the Fermi surface of lithium is actually sufficiently distorted by depression of the p state at N to account for the soft x-ray emission (see below), one would expect an optical interband edge substantially greater than the 3.6 eV we have calculated. Thus, an experimental determination of this edge would be of especial interest. Similarly, measurement of this edge for the other alkali metals would help determine the extent to which our calculations may place the p state at N too high relative to the s state, and thus overestimate the gap for the heavier metals, through an inexact treatment of the exchange-correlation hole, as Cohen and Heine suggest.[10]

The possibility, discussed by Cohen,[20] that one can deduce that the Fermi surface contacts the zone face if the ratio m_t/m_a is less than unity evidently requires optical data at longer wavelengths before it can be used fruitfully. At the present time the experimental values for the thermal mass all substantially exceed Cohen's values for m_{op}.

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[35] H. Jones, Proc. Roy. Soc. (London) **A240**, 321 (1957).

[36] H. E. Ives and H. Briggs, J. Opt. Soc. Am. **26**, 238 (1936); **27**, 181, 395 (1937).

[37] R. W. Wood and C. Lukens, Phys. Rev. **54**, 332 (1938).

[38] P. A. Wolff, Phys. Rev. **116**, 544 (1959).

[39] P. N. Butcher, Proc. Phys. Soc. (London), **A64**, 765 (1951).

C. Cyclotron Mass

Measurements of the cyclotron mass of the alkali metals by the Azbel'-Kaner procedure[21] have only recently been undertaken. Kip and Grimes[40] have obtained a value of m_c/m_0 for potassium of 1.21±0.02, finding no anisotropy within this accuracy. However, the full interpretation of their data is not yet clear, so that this value is tentative. Their value is only slightly less than Lien and Phillips' value of 1.28 for the thermal mass; agreement between these would be expected for a spherical Fermi surface if electron correlation and the electron-phonon interaction affect the cyclotron mass in an Azbel'-Kaner experiment in the same way as the thermal mass.[41] The absence of anisotropy appears to confirm the result of our calculations that the energy gap at N is quite small for potassium and the Fermi surface accordingly nearly spherical. Although our calculations predict a 6% anisotropy in the cyclotron mass for potassium, this arises from a very small distortion of the Fermi surface, the calculated anisotropy in the Fermi surface radius being only about 1%.

A smaller value of 0.95±0.09 has been obtained by Thorsen and Berlincourt[42] for m_c/m_0 in potassium from the temperature variation of the amplitude of the de Haas–van Alphen effect. This value ought to agree with the Azbel'-Kaner mass and with the thermal mass, since Luttinger[43] has shown that the amplitude of the de Haas–van Alphen oscillations should be calculated from the "single-particle" excitation spectrum of a real electron gas, which also determines the electronic heat capacity, in the same way as from the independent particle energies for a gas of noninteracting electrons. The discrepancy between the various experimental values of the effective masses has not yet been explained.

For sodium, Kip and Grimes[40] have observed cyclotron resonance in a polycrystalline sample. One sample gave a result $m_c/m_0 = 1.24$, in excellent agreement with Martin's value[26] of 1.27 for the thermal mass. For sodium the interpretation of the data is complicated by the martensitic transformation.

D. De Haas–van Alphen Effect

Thorsen and Berlincourt[42] have obtained a value of $1.74 \pm 0.02 \times 10^{16}$ cm^{-2} for the extremal cross-sectional area of the Fermi surface in a single crystal of potassium at 1–2°K from the measured de Haas–van Alphen period. This value agrees very well with the value 1.748×10^{16} cm^{-2} calculated on a free-electron model using Barrett's value[19] for the lattice constant at 5°K. This agreement appears to confirm the conclusion of Kohn[41] and Luttinger[43] that the period of the de Haas–van Alphen effect should be unaffected by electron correlation effects and the electron-phonon interaction for a spherical Fermi surface. Anisotropy was not looked for in Thorsen and Berlincourt's experiments; since it should be much less than anisotropy in the cyclotron mass, the result of Kip and Grimes leads us to expect no de Haas–van Alphen anisotropy for potassium. A search for such anisotropy is nevertheless very desirable in general as a means of establishing the degree of Fermi surface distortion.

Note added in proof. De Haas–van Alphen oscillations have now been observed in rubidium by K. Okumura and I. M. Templeton [Phil. Mag. **7**, 1239 (1962)] and by Thorsen (private communication), and in cesium by Templeton (private communication). The rubidium results which have so far been reported by Okumura and Templeton show a small anisotropy which seems to agree qualitatively with our calculations. The measured periods range from 6.26×10^{-9} G^{-1} to 6.32×10^{-9} G^{-1} in contrast to a free electron value of 6.24×10^{-9} G^{-1}.

E. "Diffusion" Component of Thermoelectric Power

From the observed thermoelectric power at temperatures larger than the Debye temperature, Dugdale[14] has given the values −6.7, +2.7, +3.8, +2.3, and +0.2 for the parameter ξ in Eq. (4.20) for Li, Na, K, Rb, and Cs, respectively. Comparing these values with those we have calculated in Table V for the term ξ_1 in (4.23) arising from the geometry of the energy surfaces, we see that an appreciable contribution to ξ must usually be made by the energy variation of the relaxation time τ. If τ increases moderately with increasing energy, (say $\tau \sim E^{(+1.0 \text{ to } +1.5)}$) as we might expect, the observed values of ξ for sodium and rubidium fit reasonably with our values for ξ_1. For cesium we estimated that $\xi_1 \cong -1.0$ for $a = 11.19$ au, where we found that the calculated Fermi surface barely touched the zone face. At room temperature, however, the lattice constant (11.67 a.u.) is greater than that of Table V so that $\xi_1 \cong -0.1$, which is already quite close to the observed value of ξ. The value of ξ for potassium is rather large, and the large negative value for lithium is very difficult to understand on the basis of a simple energy dependence of τ, since we found that even if the Fermi surface contacts the zone face ξ_1 can be at most about −1.0.

Thus we are led to the same conclusion for the alkali metals that Ziman[18,44] reached for the noble metals, that for certain metals τ may be appreciably anisotropic and not a simple function of energy. Although for the alkali metals we have been able to obtain small negative values for ξ_1, whereas for the noble metals Ziman found only positive values, we still cannot come even close to

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[40] A. F. Kip and C. C. Grimes (private communication).

[41] W. Kohn, Phys. Rev. **123**, 1242 (1961).

[42] A. C. Thorsen and T. G. Berlincourt, Phys. Rev. Letters **6**, 617 (1961). In this Letter the values given for the measured de Haas—van Alphen period and the effective mass are in error because of an error in the calibration of the magnet; the correct values are $P = 5.48 \times 10^{-9} \pm 1\%$ G^{-1} and $m^* = (0.95 \pm 10\%) m_0$ [A. C. Thorsen (private communication)].

[43] J. M. Luttinger, Phys. Rev. **121**, 1251 (1961).

[44] J. M. Ziman, Phys. Rev. **121**, 1320 (1961).

the observed value of ξ for lithium if τ does not have a complicated behavior. Deutsch, Paul, and Brooks[45] have, in fact, shown recently that it is necessary to assume an anisotropy in τ of a factor of about 3 over the Fermi surface in order to account for the absolute magnitude of the Hall coefficients of the alkali metals and their variation with pressure.

At sufficiently low temperatures, below about $\frac{1}{2}°$ to 2°K, MacDonald and his co-workers[46,47] have shown that the thermoelectric powers of the alkali metals are again linear in T and may be interpreted as being due primarily to the "diffusion" component alone. The phonon drag component is small at these temperatures because of the small value of the lattice specific heat and the quenching effect of impurity scattering. The sign of ξ remains negative at these temperatures for lithium and for various alloys of lithium with magnesium, indium, and aluminum (however, it is positive at higher concentrations of magnesium and indium). The sign of ξ is also negative for cesium, for some specimens of rubidium, and for alloys of potassium with rubidium and cesium. The magnitude of ξ for all the alkali metals is quite sensitive to impurities. Thus, in the residual resistivity range it appears necessary again to appeal to a complicated behavior of τ, rather than simply to the properties of the band structure to explain the thermoelectric power.

Despite the difficulty of giving a detailed theory of the thermoelectric power, it is suggestive that the two alkali metals which we believe to have the most distorted Fermi surfaces, lithium and cesium, have the algebraically smallest values for ξ. As Dugdale[14] has pointed out, this correlation extends as well to copper, silver, and gold, for which we have good evidence[48] that the Fermi surface contacts the zone face and for which the high-temperature values for ξ are -1.6, -1.1, and -1.5, respectively.[14] Moreover, our calculations predict that the anisotropy of the Fermi surface of cesium increases rapidly with decreasing lattice constant, and Dugdale and Mundy[49] have found that the thermoelectric power of cesium at 0°C changes sign at a pressure of 400 atm. While these correlations suggest that a negative value of ξ implies contact, an adequate theory of the relaxation time may show that a substantial negative value of ξ can occur without contact.

F. Pressure Variation of the Electrical Resistivity

Dugdale[14] has pointed out that there is an experimental correlation between the parameter ξ in the high-temperature thermoelectric power and the pressure variation of the interaction constant characterizing the ideal electrical resistivity ρ_i of the alkali and noble metals. If ρ_i has the form

$$\rho_i = \frac{K}{T} f(T/\theta_R), \tag{5.1}$$

where θ_R is a temperature characteristic of the electrical resistivity due to phonon scattering, then $d\ln K/d\ln V$ can be obtained either from the value of $d\ln\rho_i/d\ln V$ at high temperatures on the assumption that $-d\ln\theta_R/d\ln V$ is given approximately by the Grüneisen parameter, or from a plot of $d\ln\rho_i/d\ln V$ against $d\ln\rho_i/d\ln T$ over an intermediate temperature range in which the latter quantity varies.[14] Dugdale shows that $d\ln K/d\ln V$ at atmospheric pressure is negative for the noble metals (Cu: -1.0; Ag: -0.9; Au: -0.7) and for lithium (-2.3 to -3), the same metals for which ξ is negative, and positive for sodium ($+2.0$), potassium ($+3.1$), and rubidium ($+0.7$), though small for rubidium (data for cesium are uncertain). This behavior accords, as Dugdale notes, with what one might plausibly expect from a simple model in which K is changed by two opposing influences: K decreases as the kinetic energy of the electrons increases, for a spherical Fermi surface; K increases with increasing distortion of the Fermi surface, more rapidly the closer the distorted surface is to the zone face. For sodium and potassium, with nearly spherical surfaces, the former influence evidently prevails; the large negative value of $d\ln K/d\ln V$ for lithium suggests considerable distortion for lithium with contact probable; rubidium apparently has an intermediate distortion. Dugdale notes also that further empirical correlations appear between the magnitudes of the reduced high-temperature resistivities of these metals, and also between their ratios of the temperature θ_R in (5.1) to the actual Debye temperature, all of which accords with the presumed differences in degree of distortion of the Fermi surfaces of these metals.

The relative degree of Fermi surface distortion among the alkali metals to which Dugdale is led by these considerations agrees broadly with our calculations, as do the changes of distortion with pressure. However, the calculations predict greater distortion for cesium than for lithium, the reverse of the empirical conclusion, and, no contact for lithium even for a substantial decrease in lattice constant. From Table VI of I and Table III we see that the calculated kinetic energy at the Fermi surface (the difference between the Fermi energy E_F and the ground-state energy E_0) increases with decreasing lattice constant. For sodium the Fermi surface remains very nearly spherical with decreasing volume, corresponding to the fact, evident from Fig. 10 of I, that the gap at N remains small for sodium over a considerable range of volume. The distortion of the calculated Fermi surfaces of the other alkali metals increases substantially

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[45] T. Deutsch, W. Paul, and H. Brooks, Phys. Rev. **124**, 753 (1961).

[46] D. K. C. MacDonald, W. B. Pearson, and I. M. Templeton, Proc. Roy. Soc. (London) **A256**, 334 (1960); Phil. Mag. **6**, 1431 (1961).

[47] D. K. C. MacDonald and A. M. Guenault, Proc. Roy. Soc. (London) **A264**, 41 (1961).

[48] D. Shoenberg, Phil. Mag. **5**, 105 (1960).

[49] J. S. Dugdale and J. N. Mundy, Phil. Mag. **6**, 1463 (1961).

with decreasing volume, as seen from Table III by comparing the Fermi energy E_F with the energy $E(N)$ of the lowest state at N and from the change in the gap at N in Fig. 10 of I. This increase of distortion is most rapid for cesium and somewhat less rapid for rubidium and lithium. For potassium the distortion is small at lattice constants equal to or larger than the equilibrium value but increases rapidly for smaller values.

Dugdale[14] has noted further that when the interaction constant K is plotted from Bridgman's high-pressure measurements as a function of reduced volume V/V_0, minima occur for cesium, rubidium, and potassium at values of V/V_0 of 0.92, 0.8, and 0.75, respectively. Dugdale[14] and Cohen[50] noted that the relative order of these minima corresponds to the relative increase in distortion which is presumably necessary for each of these metals for contact to occur. From Table III we see that our calculations do predict that contact occurs in this order of relative compression. For cesium we found that contact occurs at $a=11.19$ a.u., while the equilibrium lattice constant at 20°C is 11.67 a.u. Thus, $V/V_0 \cong 0.88$ is predicted for contact to occur at room temperature, in good agreement with the position of the minimum in K for cesium. For rubidium and potassium, however, our calculations would indicate that contact requires greater compression than is obtained if the minimum in K is assumed to occur at contact. It is an open question what relation this minimum in fact bears to the occurrence of contact, and the two might well be correlated in some way without coinciding. Dugdale showed that sodium also has a broad minimum, at $V/V_0 \cong 0.8$, whereas our calculations show no significant Fermi surface distortion for sodium for much greater compression. Thus changes in other parameters of the Fermi surface, the phonon spectrum, or the scattering probabilities may be as important as distortion of the surface in fixing the minimum, as Bailyn's work[13] suggests.

The situation with lithium is of considerable interest, since the empirical correlations suggest that the Fermi surface contacts the zone face, yet the calculated surface does not make contact even for a 20% decrease in the lattice constant (Fig. 8 of I). Despite the large gap at N at equilibrium and its rapid increase with decreasing lattice constant, the energies of states on the [110] axis in the conduction band are not enough depressed relative to [111] and [100] to cause sufficient distortion for contact. Cohen and Heine's suggestion[10] that a more accurate treatment of the exchange-correlation hole might lower the energy of p states relative to s states by about one electron volt *might* suffice to cause contact; however, states on [100] and [111] at the Fermi surface also have a preponderant p character, and it is not clear that [110] states would be lowered by a sufficiently large amount relative to other states at the Fermi surface for contact to occur. It does appear very hard to understand on this basis how the state $N_{1'}$ could lie 0.65 eV below the Fermi surface, as the straightforward interpretation of the soft x-ray emission spectrum would seem to require (see below).

It is possible that the strong empirical correlation noted by Dugdale and others between the properties of lithium and those of the noble metals occurs not because contact occurs for lithium as it is believed to occur for copper, silver, and gold, but because lithium, alone of the alkali metals, has both a large gap at the zone face and the p state below the s state, as is also believed to be true for all the noble metals,[44,51] with a consequent enhancement of the p character of states at the Fermi surface and particularly of those near the zone face. Collins and Ziman[11,12] have shown that both umklapp and impurity scattering can be rather different in form for predominantly p or s states, and both Collins[11] and Bailyn[13] have shown that umklapp processes dominate phonon scattering in the electrical resistivity except at very low temperatures. The relative importance of this dependence of umklapp scattering on the character of the states at the Fermi surface, on the degree of distortion of the Fermi surface itself, and on the shape of the phonon spectrum will obviously be difficult to sort out with certainty until definitive experiments on these properties have been completed.

G. Soft X-Ray Emission

The soft x-ray emission spectra[52] of metallic sodium and potassium conform quite well in shape to what one expects from a free electron model for a monovalent metal. The K spectrum of lithium, however, has long been puzzling, for instead of showing a sharp drop in intensity from a maximum at the short-wavelength edge, the spectrum has been found to have a peak nearly one-electron volt below the edge and to fall gradually to zero above this peak. Recently, Crisp and Williams,[53] using a photomultiplier technique for accurate and rapid detection, have found that the lithium spectrum in fact does have a high-energy edge of more or less the expected width extending to 75% of the peak intensity and that below this edge the spectrum rises more gradually to the peak. The peak occurs about 0.65 eV below the midpoint of the edge.

This result of Crisp and Williams accords with Cohen and Heine's interpretation[10] that the strange shape of the spectrum occurs because the Fermi surface of lithium touches the zone face and that the peak occurs at the energy of the lower state at N. This interpretation requires then that the Fermi energy exceed $E(N_{1'})$ by 0.65 eV (0.048 Ry)!

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[50] M. H. Cohen (private communication).

[51] B. Segall, Phys. Rev. **125**, 109 (1962).

[52] D. H. Tomboulian, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. XXX, p. 246.

[53] R. S. Crisp and S. E. Williams, Phil. Mag. **5**, 525 (1960).

We find surprising so large a value for the difference between E_F and $E(N_{1'})$ for, as we have discussed above, the calculated Fermi surface for lithium resists making contact with the zone face even for a substantial compression and the accompanying large increase in the gap at N. Even for the highly distorted Fermi surface of cesium with $a=10.05$ a.u. (Table III), we find $E_F-E(N)$ only 0.012 Ry. Values of ~ 0.05 Ry do occur for the corresponding difference $E_F-E(L_{2'})$ in the noble metals; however, for these the situation is different because the d bands midway in the energy range spanned by the s-p band tend to "repel" levels in the latter band quite strongly in selective direction of $\mathbf{k}$ and thereby enhance the distortion.[51] We consider it unlikely that a better treatment of the exchange-correlation hole would cause so large a depression of the p state $N_{1'}$, for the reasons mentioned in the previous subsection, although it seems possible that this *might* cause sufficient distortion for contact to barely occur. Thus, if further experiments substantiate Cohen and Heine's interpretation of the lithium spectrum, there will arise a theoretical problem in accounting for so great a distortion.

The x-ray bandwidths agree in their trends from metal to metal with the calculated difference (E_F-E_0). The experimental values are, however, made uncertain by the presence of a low-energy tail due to lifetime broadening, and our calculated values do not include the effect of electron-electron or electron-phonon interactions. Crisp and Williams' bandwidth for lithium is 4.2 eV including the tail, and the "reduced width" without the tail is 3.0 ± 0.1 eV. Tomboulian[52] gives 3.05 ± 0.15 eV for the "reduced width" for sodium, and Crisp[54] finds 1.62 ± 0.04 eV for potassium.[55] From Table II of I and Table III we obtain the corresponding calculated values 3.5, 3.3, and 2.3 eV.

H. Magnetoresistance

The magnetoresistance has appeared to offer a promising source of information about the Fermi surface of the alkali metals.[56,57] In particular, if the transverse magnetoresistance should fail to saturate as a function of magnetic field at high fields and low temperatures $(\omega\tau>1)$ for certain directions in a single-crystal specimen, we would be able to conclude that the Fermi surface touched the zone faces and that open orbits existed. Garcia-Moliner[56] has interpreted the low-field data on polycrystalline specimens as indicating that the Fermi surface of lithium is quite anisotropic, that of sodium nearly spherical, and that of potassium of an intermediate anisotropy.

Recent measurements by Bowers[58] at helium temperatures $(\omega\tau\cong0.4)$ on a specimen of lithium that was a single crystal at room temperature showed no anisotropy. However the interpretation of this result is complicated by the martensitic transformation, the effects of which on a single crystal are not known. High-field measurements by Lüthi[59] on polycrystalline lithium present difficulties of interpretation,[57,59] in part also apparently related to this transformation. Bowers has observed anisotropy in a single crystal of sodium but the situation here is obscured by other anisotropies having nothing to do with the Fermi surface.[58]

It is now clear from the discussion of the thermoelectric power and from Deutsch's work[45] on the Hall effect that a quantitative analysis of the low-field magnetoresistance must take account of an appreciable anisotropy in the relaxation time even for sodium. Moreover an analysis like that of Garcia-Moliner[56] must be extended to include anisotropic terms proportional to the Kubic harmonic K_6, since K_4 alone does not describe an anisotropy in which [110] directions are an extreme.[16,45] Thus, interpretation of the low-field magnetoresistance of the alkali metals in terms of the distortion of the Fermi surface will be no more simple or straightforward than that of the other transport properties, but good single-crystal measurements are, nevertheless, desirable.

VI. CONCLUSION

Our calculated trends in the shape of the Fermi surface and its parameters for the alkali metal series agree qualitatively except in their pressure variation with those which Cohen and Heine inferred from their interpretation of experimental data. Lithium and cesium have the most distorted Fermi surfaces but represent opposite extremes in the sequence of distortion, since their band gaps at N are large but of opposite sign. Sodium has a spherical Fermi surface and very small gap. The gap and distortion are small for potassium and larger for rubidium. However, differences with Cohen and Heine arise in the extent of the distortion for individual metals, the most significant being that the calculated Fermi surface of lithium does not contact the zone face even under a substantial compression. Indeed, our Fermi surface for lithium is less distorted than that for cesium, which very nearly touches the face at the 0°K equilibrium lattice constant. While there is reason to expect that a more nearly self-consistent crystal potential might decrease the calculated distortion for the heavier metals and increase it for lithium, it is very difficult to see how the Fermi surface could be so distorted that the Fermi energy exceeds the lowest energy at N by 0.65 eV, as is required if Cohen and Heine's interpretation of the soft x-ray spectrum of lithium is correct.

The calculated trends agree very well with one of the alternative sets of inferences of band structures made

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[54] R. S. Crisp, Phil. Mag. **5**, 1161 (1960).

[55] A. Value of 1.9 ± 0.2 eV for the "reduced width" for potassium was obtained by R. H. Kingston [Phys. Rev. **84**, 944 (1951)] using a different extrapolation in the tail.

[56] F. Garcia-Moliner, Proc. Phys. Soc. (London), **72**, 996 (1958).

[57] R. G. Chambers, in reference 16, p. 100.

[58] R. Bowers, Bull. Am. Phys. Soc. **6**, 145 (1961), and (private communication).

[59] B. Lüthi, Helv. Phys. Acta, **33**, 161 (1960).

from experimental data by Collins and Ziman on the assumption that differences in the transport properties of the alkali metals arise primarily from differences in electronic structure. The trends agree also for the most part with inferences made by Dugdale from various empirical correlations; however, these correlations suggest that contact occurs for lithium.

Kip and Grimes' tentative results on the cyclotron resonance of potassium appear to provide the first conclusive experimental evidence on the Fermi surface shape of an alkali metal. The observed isotropy shows that the Fermi surface of potassium is at most only slightly distorted from a sphere, in agreement with our calculations. The calculations, however, slightly overestimate this distortion in predicting a 5% anisotropy in the cyclotron mass, corresponding to a 1% anisotropy in the Fermi surface radius.

Apart from Kip and Grimes' work on potassium, definitive experiments on the Fermi surface shapes of, the alkali metals are still lacking. Moreover, Bailyn's studies have shown that differences in the transport properties may be due to differences in the phonon spectra or in transition matrix elements rather than to differences in Fermi surface shape. The over-all consistency with which the interpretation that the latter differences are the important ones accounts for different experimental properties, however, lends support to this interpretation. The general agreement of our calculated results with the band structures required by this interpretation gives it further support, and conversely this agreement supports the view that changes in the band structures for more nearly self-consistent crystal potentials will not be large. Nevertheless, we still very badly need conclusive experiments on the Fermi surface shapes for each of the alkali metals. In particular, the question of Fermi surface contact in lithium and cesium at equilibrium remains unsettled, as does that of what pressure causes contact for each metal.

Our calculated values for the various parameters of the Fermi surface show that these are changed substantially for a distorted surface from the values calculated in the spherical approximation. For example, the thermal effective masses (m_t/m_0) for lithium through cesium, respectively, at equilibrium (0°K) were found to be 1.66, 1.00, 1.09, 1.21, and 1.76 in contrast to the values 1.32, 1.00, 1.02, 0.99, and 1.06 which we obtained in the spherical approximation. The distortion also leads to anisotropy in the cyclotron effective mass and in the extremal area of cross section of the Fermi surface measured by the de Haas–van Alphen effect, as well as in the linear dimensions of the Fermi surface. We find $m_{c[110]}<m_{c[100]}<m_{c[111]}$ and $A_{[110]}<A_{[100]}<A_{[111]}$ if contact does not occur. Our calculations predict roughly 20% anisotropy in the cyclotron mass for lithium, an even larger anisotropy for cesium, 5% for potassium, and 15% for rubidium. For the anisotropy in the area of cross section we find 3.5, 0, 1.2, 3.4, and 10% for lithium through cesium, respectively.

Comparison of our values of the thermal effective masses with the experimental values indicates that electron-electron correlations and electron-phonon interactions enhance the mass by some 20 to 40% for lithium and sodium but that the correction decreases for the heavier metals and may become negative (~10%) for cesium. Alternatively, the calculations may overestimate the distortion for the heavier metals.

The calculations show that the geometrical contribution to the "diffusion" component of the thermoelectric power of an alkali metal can be positive for a sufficiently distorted Fermi surface. However, agreement with experiment requires that the relaxation time be appreciably anisotropic and not a simple function of energy.

The results of the calculations show clearly that experiments on the anisotropy of cyclotron resonance and the de Haas–van Alphen effect for the alkali metals should provide very useful information concerning the extent of Fermi surface distortion. Our results also make clear the inadequacy of present data on the optical properties of the alkali metals. Optical studies are needed particularly at wavelengths longer than the interband absorption edge and also are needed to determine this edge, which we calculate to be at 3.6, 2.0, 1.2, 1.3, and 1.3 (eV) for lithium through cesium, respectively. Measurement of this edge for lithium would be of especial value in checking the accuracy of the band calculation, in helping to answer the question of Fermi surface contact, and in seeking the explanation of lithium's puzzling soft x-ray spectrum.

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