PHYSICAL REVIEW VOLUME 128, NUMBER 1 OCTOBER 1, 1962

Energy Bands of Alkali Metals. I. Calculated Bands

FRANK S. HAM
General Electric Research Laboratory, Schenectady, New York

(Received May 7, 1962)

The results of energy band calculations for all of the alkali metals Li, Na, K, Rb, and Cs, obtained using the quantum defect method and the Green's function method, are reported for points of low symmetry within the Brillouin zone as well as for the usual points of high symmetry. Definite trends in the band structure are revealed through the alkali metal series and as a function of lattice constant. The Fermi surfaces of Li and Cs are the most distorted by bulges in the [110] directions, while those of Na and K are nearly spherical; the corresponding gaps ($N_1-N_{1'}$) at equilibrium at 0°K are (in rydbergs): Li, +0.209; Na, +0.018; K, −0.037; Rb, −0.063; Cs, −0.088. Except for Na the gaps and distortion increase significantly in magnitude with decreasing lattice constant. However the Fermi surface of Li is found not to contact the zone face even under substantial pressure, while contact occurs for Cs at a slight compression. Excited bands are also given; there is a pronounced trend for *d* states to fall increasingly lower relative to *s*, *p*, and *f* states in the sequence Li to Cs, and for *p* states to rise in this sequence relative to *s* and *f* states. Detailed comparisons are given with calculations by Callaway, Brooks, Schlosser, Allen, and others. These comparisons support the view that the significant features of these band structures are not very sensitive to uncertainties in the crystal potential.

I. INTRODUCTION

THE energy band structures of the alkali metals have been the object of many theoretical investigations[1] since the pioneering studies of Wigner and Seitz,[2] because of the relative simplicity of these monovalent metals. Much of this work has been concerned primarily with cohesive properties and has been based upon an approximation introduced by Wigner and Seitz in which the polyhedral atomic cell is replaced in the calculations by a sphere of equal volume. The bands calculated in this way are accordingly spherical. In most other work full account has been taken of the correct shape of the cell, but calculations were attempted only for propagation vectors at points of high symmetry in the Brillouin zone.

The present investigation was undertaken in order to extend the calculations taking full account of the correct crystal structure to points of low symmetry within the Brillouin zone and thereby to determine directly the shape of the Fermi surface. Using more reliable interpolation schemes than those fitted only to calculated values at points of high symmetry, we wished to obtain values for the various effective masses and other parameters of the bands, which might be compared with experiment. We desired particularly to make our study for all of the alkali metals using the same approximations for each, so that trends in the band structure through the alkali metal series might be revealed clearly. While the existence of definite trends has been anticipated by Cohen and Heine,[3] these have not been made evident by the earlier calculations.

In this paper we present the direct results of these calculations for the energy bands of the five alkali metals in the body-centered cubic lattice structure. We discuss here the trends that are thereby revealed and compare our results with those of calculations by other workers. In a second paper[4] (hereafter referred to as II) we introduce an interpolation procedure suitable for a quantitative description of the nonspherical distortion of the bands near the Fermi surface, and we use this to calculate the Fermi energy, the various effective masses, and other parameters of the Fermi surface. A discussion of the comparison between our results and experiment is also reserved for II.

The calculations were done for three values of the lattice constant for each metal, in order to determine how the bands change as the lattice constant is varied. So extensive a series of calculations was made feasible by use of the Green's function method of Kohn and Rostoker[5] and by the prior preparation of tables of the necessary structure constants. This method, used in the manner described recently by Ham and Segall,[6] is a very convenient one for calculation and provides very rapid convergence for both energy values and wave functions.[7]

In order to achieve our goal of a systematic calculation for all of the alkali metals using the same approxi-

---

[1] An excellent review of all but very recent work has been given by J. Callaway, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7, p. 99.

[2] E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933); **46**, 509 (1934).

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

[4] F. S. Ham (to be published).

[5] W. Kohn and N. Rostoker, Phys. Rev. **94**, 1111 (1954).

[6] F. S. Ham and B. Segall, Phys. Rev. **124**, 1786 (1961).

[7] Most of the calculations were carried out on an IBM 704 digital computer, and tables of the structure constants were accordingly prepared in punched card form. However, convergence of the Green's function method is sufficiently rapid (see Appendix) that calculation with a desk computer is also quite feasible. An abbreviated tabulation suitable for such work has been prepared in printed form for the body- and face-centered cubic lattices and is available from the authors: B. Segall and F. S. Ham, General Electric Research Laboratory Report No. 61-RL-2876G (unpublished). A copy of this report has been deposited as Document No. 7236 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $6.25 for photoprints or $2.50 for 35 mm microfilms. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

mations for each, we have used the quantum defect method[8,9] to avoid having to construct explicit crystal potentials. This method, which was devised by Brooks,[10] starting from a less satisfactory procedure suggested by Van Vleck,[11] enables us to obtain from spectroscopic data the logarithmic derivatives of radial wave functions in the approximate crystal potential used by Wigner and Seitz,[2] at a point outside the ion core. This procedure is applicable to all of the alkali metals, and it takes accurate account of exchange, correlation, and relativistic effects in the interaction of a valence electron with electrons in the core, as Brooks and Ham have shown.[9] The quantum defect method was the basis of Brooks' systematic investigation using the Wigner-Seitz spherical approximation of the cohesive properties of the alkali metals.[10,12] Use of this method in the present work thus provides a direct extension of Brooks' work to a determination of the Fermi surface shape and of the energies of excited states. It avoids the uncertainties in the construction of a suitable potential which Callaway and his co-workers have faced in their extensive work[1] with the orthogonalized plane wave (OPW) method on the states of the alkali metals at symmetry points. While the quantum defect method has the disadvantage that it cannot be modified easily to correspond to a more nearly self-consistent potential, no calculation for an alkali metal using an explicit potential has yet improved significantly in this respect on the Wigner-Seitz potential. Improvements in self-consistency and a better treatment of many-electron aspects of the mutual interaction of the valence electrons will make changes in the parameters calculated for a given metal, but we believe that these will not change the significant features of the bands and the trends in the alkali series which the present calculations reveal.

While this work has been in progress, results have appeared from calculations by Schlosser[13] on lithium and sodium and Callaway[14] on lithium which also comprise low symmetry points within the zone. As these authors have noted from preliminary reports of our results,[15] the agreement between their results and ours is very close. Since their work was based on the Seitz potential[16] for lithium and the Prokofjew potential[17] for sodium, both of which reproduce the free atom spectrum quite closely, this agreement with the quantum defect method is to be expected if, as seems to be true, the energies of states in the conduction band are not unduly sensitive to the particular way in which the ion potential in one cell is made to join to that in neighboring cells.

This paper is arranged as follows. In Sec. II the choice of crystal potential is discussed, and a prescription is given for obtaining the precise form of extrapolation of the quantum defect parameters used in our calculations. In Sec. III results of the energy band calculations are given; however, instead of listing the vast number of calculated energy values at all the points in **k**-space we have considered for all the metals, we have summarized many of these results in graphical form. Together with the tables provided, these graphs give as accurate a summary of these results as is necessary for making significant comparison either with the results of other calculations or with experiment. The bands calculated for each metal at various lattice constants are shown, as are curves showing the variation as a function of lattice constant of the energy of the most important states at symmetry points. A table is given of excited states at symmetry points for each metal.

In Sec. IV we introduce a spherical interpolation procedure which provides an excellent fit for the low-energy region of the conduction band and usually a very good fit to the [100] and [111] axes up to somewhat above the Fermi energy. This procedure is comparable with the spherical approximation of Wigner and Seitz and, of course, fails to describe the bending down of the bands in the [110] direction as the zone face is approached. An interpolation procedure suitable to describe this distortion is reserved for II. A table is given of the parameters needed in this spherical interpolation for all of the calculated bands.

Section V presents a discussion of our results and compares them with those of other calculations, the comparison with experiment being given in II. We first discuss the trends revealed by our calculations and compare them with Cohen and Heine's proposals.[3] In comparing our results with other calculations we have included in our tables the results of other authors for which comparison is most significant. These include the energies at symmetry points computed by Callaway and others, and the parameters of the spherical approximation computed by Brooks[12] using the quantum defect method.

In an Appendix, a few examples are given from the calculations to illustrate the excellent convergence of the Green's function method in our use of it for these metals.

II. CRYSTAL POTENTIAL

The present calculations have been made strictly within the framework of the independent electron model. We have followed Wigner and Seitz[2] in using for the one-electron crystal potential of a monovalent metal a potential which in each cell is the same as that of the ion at the center of the cell.[8] In the cell corners, however,

---

[8] F. S. Ham, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1955), Vol. 1, p. 127.

[9] H. Brooks and F. S. Ham, Phys. Rev. **112**, 344 (1958).

[10] H. Brooks, Phys. Rev. **91**, 1027 (1953).

[11] T. S. Kuhn and J. H. Van Vleck, Phys. Rev. **79**, 382 (1950).

[12] H. Brooks, Suppl. Nuovo cimento, **7**, 165 (1958).

[13] H. Schlosser, Ph.D. thesis, Carnegie Institute of Technology, Pittsburgh, Pennsylvania, 1960 (unpublished).

[14] J. Callaway, Phys. Rev. **124**, 1824 (1961).

[15] 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.

[16] F. Seitz, Phys. Rev. **47**, 400 (1935). This potential was published incorrectly in Seitz's paper; the correct potential has been published by W. Kohn and N. Rostoker in reference 5.

[17] W. Prokofjew, Z. Physik **58**, 255 (1929).

outside the sphere inscribed in the cell, we replace the ion potential by a constant V_0 approximately equal to its average value in this region in order to achieve a "muffin-tin" form of potential suitable for the use of the Green's function method.[5,6] Use of the free ion potential within the inscribed sphere permits us to obtain the $s, p, d, f, \ldots$ radial functions and their derivatives at the inscribed sphere radius r_i for arbitrary energy, from the quantum defect method and spectroscopic data.[8,9] In this manner we avoid explicit construction of potentials for the ion cores, a particularly difficult and uncertain task for the heavier metals because of the importance of exchange.

The Wigner-Seitz potential is, of course, not fully self-consistent and takes only very rough account of effects of exchange and correlation among the conduction electrons. We have nevertheless felt it was of interest to make calculations for all of the alkali metals with this potential since use of the quantum defect method permits them all to be treated with the same approximations and should therefore best show up trends in the band structure through the alkali series. A serious attempt to improve the self-consistency of these potentials would, of course, be of great interest, but this would necessitate abandoning the quantum defect method and would make the calculations for the whole series of the metals a very much more difficult task. As for the many-particle aspects of the interaction among conduction electrons or electron-phonon interactions, there is still no agreement on their precise effect on the band structure at densities of actual metals. Since these affect the experimentally measured band structure parameters in different ways (as, for example, the effective mass measured in different types of experiments) it appears best at this stage of our understanding to make the band calculations for an independent electron model and subsequently to estimate corrections due to the many-particle effects. Exchange and correlation effects in the interaction between the valence and core electrons are, on the other hand, taken account of automatically by the quantum defect method.[9]

Brooks[12] has had considerable success accounting for the cohesive properties of the alkali metals on the basis of the quantum defect method, although the theoretical cohesive energies of the heavier metals were substantially low, and the lattice constants 10 to 15% too large. These quantities are rather more sensitive to changes in the potential than are the energies of individual states, so that his results lend support to our belief that an improved potential will not greatly alter the band structure we have found for each metal and in particular will not change the trends we have found in the alkali series.

One weakness of the Wigner-Seitz potential, which has been noted by Cohen and Heine,[3] is that the effective correlation-exchange hole is fixed on the cell instead of following the electron. As a consequence, the Wigner-Seitz potential should be too large in the outer part of the cell, and it should lead to too high an energy for states with wave functions concentrated in this region. Cohen and Heine have estimated that a better potential might lower a p state relative to an s state by roughly one electron volt. Such a correction would be of particular interest, as we shall see, in connection with the relative position of the p state $N_{1'}$ and the "s state" N_1 at the center of the zone face. However, there may be an offsetting effect in that N_1 has also a component of d symmetry which is especially important for the heavier alkali metals.

In using the quantum defect method in our actual calculations, we have taken the necessary expressions for the extrapolated parameter η from the tables given by Brooks and Ham[9] (Appendix C of their paper). The polarization correction for $L=0$ and 1 was evaluated from Eq. (C1) and Table III of their paper for a cutoff radius r_0 equal to the inscribed sphere radius r_i for the particular lattice constant being used. This expression was subtracted from that in their Table II, and the resulting expression was used to evaluate the radial functions at r_i and their derivatives, according to Eq. (B3) of their paper, from available tables for the calculation of the Coulomb functions.[18] For $L=2$, Table VI of Brooks and Ham lists expressions for the extrapolation of η, including a polarization correction, for a single value of the cutoff radius for each metal. This value of the cutoff radius is appropriate to that calculation, of the three or more we have done for each metal at different values of the lattice constant, for which the lattice constant used is closest to the experimental equilibrium value. Of the several expressions listed in Brooks and Ham's Table VI for each metal for the low-energy extrapolation ($1/n^2>0.14$ for K, for example), we have used that one they labeled "reasonable." For other choices of the lattice constant, we have obtained a similar extrapolation for $L=2$ by following the procedure outlined by Brooks and Ham in obtaining Table VI from Table V. For $L \geqslant 3$ we have used $\eta=0$.

As Brooks and Ham noted,[9] there is some uncertainty in the η extrapolation, particularly for $L=2$ of K, Rb, and Cs. For this reason they gave several possible extrapolations for the low-energy range of the latter as bounds on η's possible behavior. We have tested the sensitivity of our results to this uncertainty by making additional calculations for states in the low-energy range which have a large d component, using the curve Brooks and Ham labeled "upper bound." In no case did this change the energy of the state by more than 0.005 Ry, even for states such as H_{12} with only d character. This is an insignificant change when compared with the interesting features of the calculated curves.

There is considerable uncertainty in all extrapolations of η very far to positive energies.[8,9] We have done calculations for some excited bands, but because of the

---

[18] F. S. Ham, Technical Report No. 204, Cruft Laboratory, Harvard University, Cambridge, Massachusetts, 1955 (unpublished).

uncertainty we attach no great significance to calculations for energy greater than about +0.3 to +0.5 rydberg. Fortunately, for the heavier metals, for which the extrapolation is least certain, the large lattice constant causes quite a number of excited states of interest to lie in the range −0.2 to +0.2 Ry. There is, of course, least uncertainty in the quantum defect parameters in the range −0.2 to 0.0, where the spectroscopic levels lie.

As Brooks and Ham have noted,[9] our expressions for the quantum defect parameters ignore spin-orbit splitting and were obtained from a weighted average of the spectral doublets. Explicit inclusion of the spin-orbit effects would have a negligible effect on our results for the conduction band up to the Fermi energy. They would, however, lead to a splitting of excited states with orbital degeneracy such as H_{15} and P_4.

Once values were obtained from the quantum defect method of the radial functions and their derivatives at the inscribed sphere radius, evaluation of the energy eigenvalues for the states of different **k** was carried out with the Green's function method of Kohn and Rostoker,[5] used in the manner described by Ham and Segall.[6] Calculations were done for states along the [100], [110], and [111] axes within the Brillouin zone as well as at symmetry points at its center and on its surface. For the constant value V_0 of the "muffin-tin" form of potential in the cell corners, we used the average of the Coulomb potential $-2/r$ over the spherical shell between the inscribed sphere and the equivalent sphere.

The values which we have used for the lattice constant of the metals in making the calculations were chosen such that the inscribed sphere radius r_i equaled a value of $z^2/8$ (in atomic units; the unit of length is the first Bohr radius of hydrogen) for one of the values of z at which tables were available for the calculation of the Coulomb functions used in the quantum defect method.[18] Of the tabulated values, that one was chosen for each metal which gave the lattice constant a closest to the experimental value at equilibrium. At least two other values were then chosen in addition, one larger and one smaller. The values which we use for a_0, the equilibrium lattice constants at 0°K, are those given by Barrett[19] for 5°K.

III. RESULTS: CALCULATED ENERGY BANDS

Some of the results of the band energy calculations are shown graphically in Figs. 1 to 8. In these figures the calculated points are indicated by triangles, squares, and circles on the [100], [111], and [110] axes, respectively. The curves shown have been drawn to interpolate between calculated points on the same axis.

The states at the symmetry points and along the axes in these figures for the body-centered cubic structure have been labeled according to the representation of the group of the **k** vector to which they belong, the notation being that of Bouckaert, Smoluchowski, and Wigner.[20] To conserve space we have plotted all three axes against the same abscissa ($ka/2\pi$), the magnitude of **k** in the reduced Brillouin zone in nondimensional units. Thus, N denotes the points at the center of the 12 equivalent faces of the zone, at the end of the [110] axis, and P and H denote the zone corners in the [111] and [100] directions, respectively.

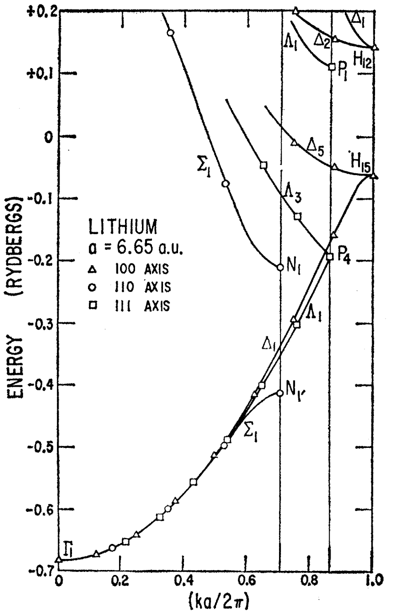

FIG. 1. Calculated energy bands of lithium for lattice constant of 6.65 a.u.

In excited bands above the conduction band we have calculated energies at symmetry points and at selected points along the axes, as indicated in the figures. In drawing the figures we have sometimes extended the curves beyond the calculated points to show schematically the way in which the states at N, H, and P are connected to those at Γ. When no points were calculated along the axis in a given band, the corresponding curve

TABLE I. Spherical harmonic classification of states.

State	Spherical harmonic type
Γ_1, H_1	$s, g, \ldots$
Γ_{12}, H_{12}, $\Gamma_{25'}$, $H_{25'}$	$d, g, \ldots$
Γ_{15}, H_{15}	$p, f, \ldots$
Γ_{25}, $H_{2'}$	$f, \ldots$
P_1	$s, f, g, \ldots$
P_4	$p, d, f, \ldots$
P_3	$d, g, \ldots$
P_5	$f, g, \ldots$
N_1	$s, d, g, \ldots$
$N_{1'}$, $N_{3'}$, $N_{4'}$	$p, f, \ldots$
N_2, N_3, N_4	$d, g, \ldots$
$N_{2'}$	$f, \ldots$
Δ_1, Λ_1, Σ_1	$s, p, d, f, \ldots$
Δ_2, $\Delta_{2'}$, Σ_2	$d, f, g, \ldots$
Δ_5, Σ_3, Σ_4, Λ_3	$p, d, f, g, \ldots$

---

[19] C. S. Barrett, Acta Cryst. 9, 671 (1956). For lithium we have used Barrett's value of the lattice constant for 78°K, since he gives no value at 5°K for this one metal.

[20] L. P. Bouckaert, R. Smoluchowski, and E. Wigner, Phys. Rev. 50, 58 (1936).

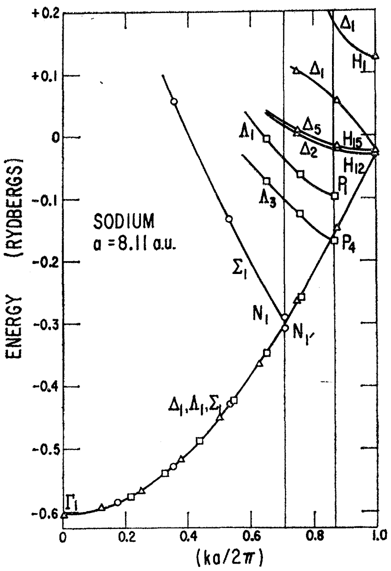

FIG. 2. Calculated energy bands for sodium for lattice constant of 8.11 a.u.

has usually been omitted entirely from the figure. The states at the symmetry points connected by these omitted bands can be found readily from the "compatibility relations" of Bouckaert, Smoluchowski, and Wigner.[20]

In Table I are listed, for reference, the types of spherical harmonics which are allowed by symmetry in the expansions of the wave functions of these states, when expanded about the ion at the center of the cell.

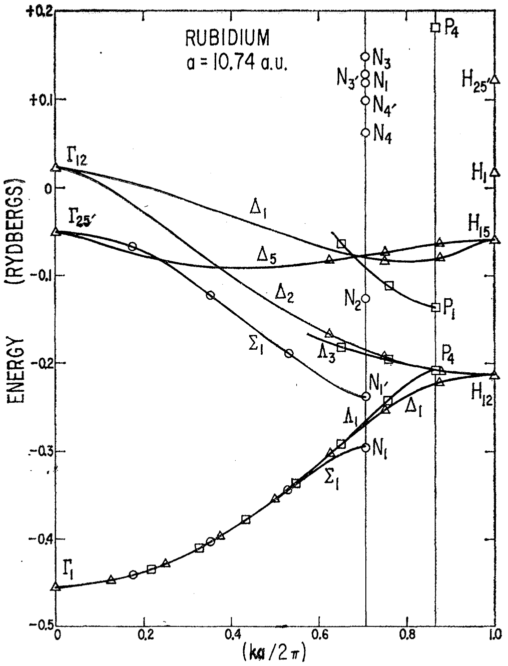

FIG. 4. Calculated energy bands for rubidium for lattice constant of 10.74 a.u.

Figures 1 to 5 give the calculated bands at the near-equilibrium value of the lattice constant for each metal. Thus, these curves show very nearly quantitatively what our calculations lead us to expect for the bands at equilibrium. Values for the energies and band gaps at

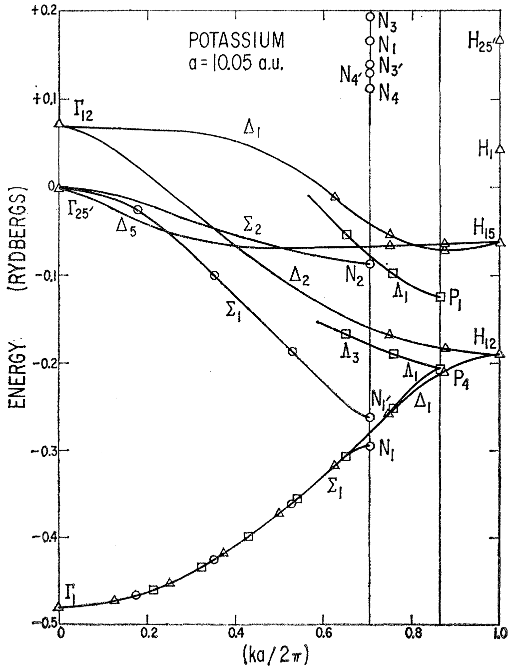

FIG. 3. Calculated energy bands for potassium for lattice constant of 10.05 a.u.

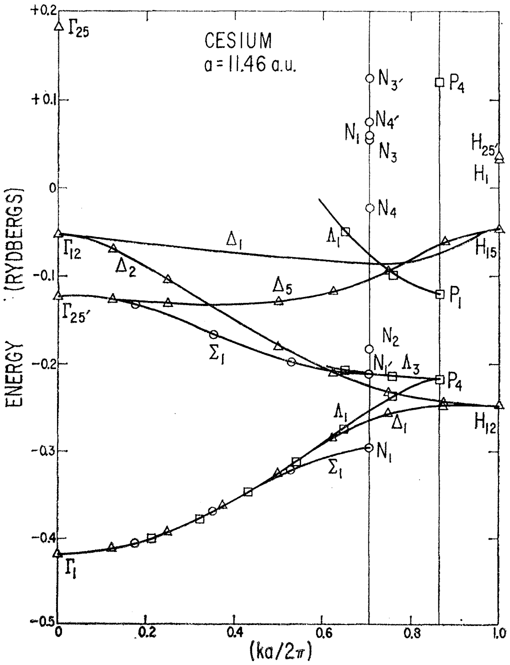

FIG. 5. Calculated energy bands for cesium for lattice constant of 11.46 a.u.

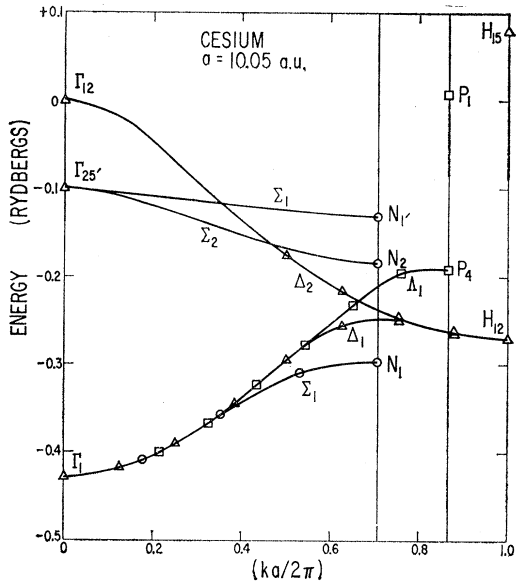

FIG. 6. Calculated energy bands for cesium for lattice constant of 10.05 a.u.

equilibrium have been obtained by plotting our results versus lattice constant and interpolating.

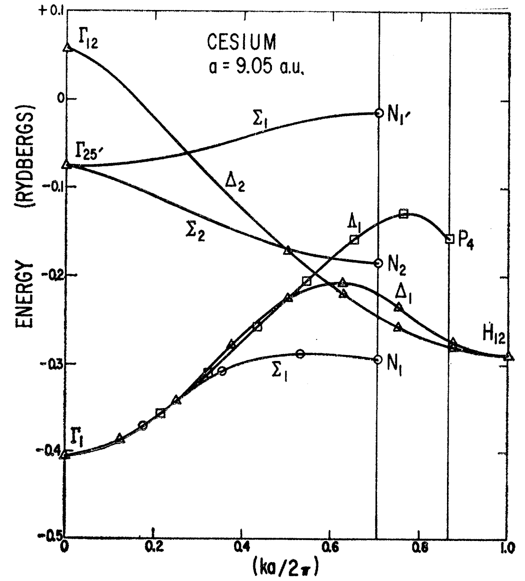

FIG. 7. Calculated energy bands for cesium for lattice constant of 9.05 a.u.

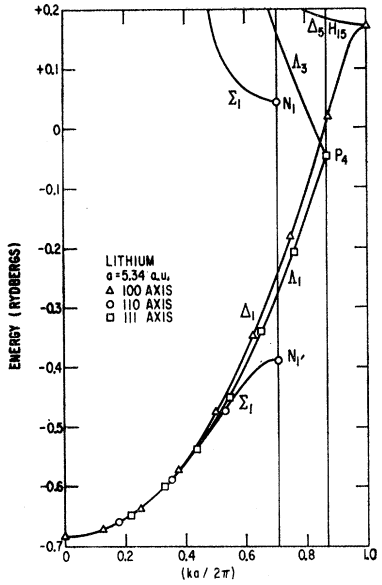

FIG. 8. Calculated energy bands for lithium for lattice constant of 5.34 a.u.

An interesting feature of the conduction bands at equilibrium, as judged from Figs. 1 to 5, is that the surfaces of constant energy remain very nearly spherical with increasing energy until they almost touch the zone faces at N. They then bulge out along the [110] directions. But even for lithium (Fig. 1), with an energy gap at N that is 3/4 of the width of the band from Γ_1 to $N_{1'}$, this distortion is small at the Fermi surface, the radius of the Fermi surface in the [110] direction being increased by only some 5% over the radius in the [100] and [111] directions. That this distortion can, however, be much greater is illustrated by Figs. 6 and 7 for cesium at values of the lattice constant less than at equilibrium. Here the gap at N is large relative to the conduction band width, and in addition the twofold degenerate state H_{12} is greatly depressed. Indeed in the situation represented by Fig. 7 there are occupied pockets in the [100] corners of the zone in addition to the greatly warped central portion of the Fermi surface.

In Fig. 8 results for lithium are shown at a lattice constant nearly 20% smaller than the equilibrium value.

The variation of the energies of the lower states at the symmetry points as the lattice constant varies is summarized in Figs. 9 to 12. The abscissa in these figures is the ratio of the lattice constant a to its equilibrium value a_0 at 0°K. The circles denote the computed values, and

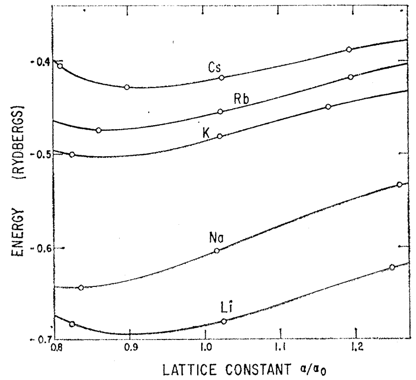

FIG. 9. Energy of ground state (Γ_1) for all the alkali metals as a function of the ratio of the lattice constant a to its 0°K equilibrium value a_0. [The following values for a_0 for Li and Cs were used in plotting Figs. 9 to 12: Li 3.429 A; Cs 5.921 A. These are ~2% smaller than Barrett's values.]

TABLE II. Energy values (in rydbergs) of lower states at symmetry points (as interpolated to lattice constant a_0 for 0°K).

Metal	Li	Na	K	Rb	Cs
a_0 (A)	3.491	4.225	5.225	5.585	6.045
a_0 (a.u.)	6.597	7.984	9.874	10.555	11.424
Γ_1	−0.683	−0.610	−0.485	−0.458	−0.419
N_1	−0.203	−0.284	−0.293	−0.295	−0.296
$N_{1'}$	−0.412	−0.302	−0.256	−0.232	−0.208
$N_1 - N_{1'}$	+0.209	+0.018	−0.037	−0.063	−0.088
P_1	+0.129	−0.073	−0.109	−0.124	−0.117
P_4	−0.188	−0.160	−0.202	−0.205	−0.216
H_1	∼+0.47	+0.145	+0.062	+0.034	+0.035
H_{15}	−0.055	−0.014	−0.053	−0.048	−0.045
H_{12}	+0.153	−0.023	−0.192	−0.216	−0.250

the curves have been drawn to interpolate smoothly. In interpolating the values for the ground state Γ_1 in Fig. 9, we have located the minimum point approximately by using the result of the Wigner-Seitz spherical approximation that the minimum occurs when the potential at the equivalent sphere radius r_s equals the ground-state energy. We have used for $V(r_s)$ the constant part V_0 of the muffin-tin potential.

The variation of the band gap at N with lattice constant, and its sign, is seen directly from the difference between the curves for N_1 and $N_{1'}$ in Fig. 10.

From Figs. 9 to 12 we obtain by interpolation the energies of the various states at the lattice constant for equilibrium at 0°K. These values are tabulated in Table II.

Energies of higher states at the symmetry points are listed in Table III. These are given for the same lattice constant for each metal as in Figs. 1 to 5 (near the 0°K value), since we did not calculate many of these states for other values of a. We have included in Table III all those states at Γ, H, N, and P which occur in these metals at energies below roughly +0.3 Ry, and a number

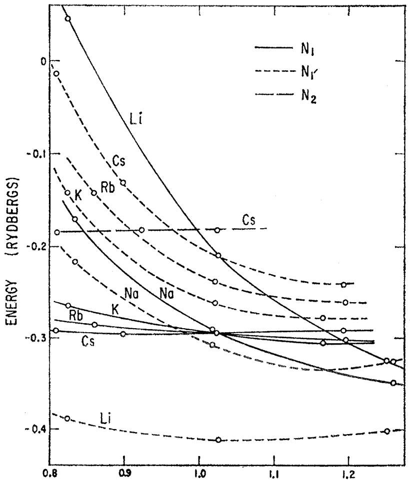

FIG. 10. Energy of the states N_1, $N_{1'}$ for all the alkali metals, and of the state N_2 for cesium, as a function of the ratio of the lattice constant a to its 0°K equilibrium value a_0.

TABLE III. Energy values (in rydbergs) of states at symmetry points (as computed). Previous values obtained by other authors are listed in parentheses (see also Table V).

	Li	Na	K	Rb	Cs
a (a.u.)	6.65	8.11	10.05	10.74	11.46
Γ_1 (1st)	−0.681	−0.604	−0.481	−0.455	−0.419
Γ_1 (2nd)	(+1.879)[a]	+1.004 (+1.101)[b]	+0.660 (+0.835)[c] (+0.781)[e]	+0.569	+0.536 (+0.602)[d]
Γ_{15}	+0.506 (+0.617)[a]	+0.513 (+0.632)[f] (+0.529)[b]	+0.356 (+0.699)[c] (+0.465)[e]	+0.336	+0.326 (+0.269)[d]
Γ_{12}	∼+1.1 (+1.146)[a]	+0.510 (+0.52)[b]	+0.069 (+0.264)[c] (+0.118)[e]	+0.022	−0.054 (+0.042)[d]
$\Gamma_{25'}$	+0.93 (+0.854)[a]	+0.424	−0.004 (+0.220)[c] (+0.046)[e]	−0.051	−0.124 (−0.116)[d]
Γ_{25}	∼+1.1 (+1.156)[a]	+0.607	+0.301 (+0.289)[c] (+0.309)[e]	+0.234	+0.181 (+0.114)[d]
H_1	+0.455	+0.124	+0.042	+0.016	+0.031
H_{12}	+0.144	−0.031	−0.190	−0.214	−0.249
H_{15}	−0.061	−0.025	−0.064	−0.060	−0.048
$H_{25'}$	(+1.84)[a]	+0.867	+0.168 (+0.537)[c] (+0.222)[e]	+0.121	+0.032 (+0.130)[d]
$H_{2'}$	+1.88 (+1.73)[a]	+1.14	+0.635 (+0.705)[c]	+0.522	+0.429 (+0.204)[d]
P_1	+0.114	−0.096	−0.125	−0.137	−0.120
P_3	(+1.603)[a]	+0.743	+0.119 (+0.486)[c] (+0.175)[e]	+0.070	−0.019 (+0.098)[d]
P_4 (1st)	−0.192	−0.167	−0.206	−0.207	−0.217
P_4 (2nd)	(+1.338)[a]	+0.785	+0.220 (+0.934)[c] (+0.208)[e]	+0.182	+0.119 (0.485)[d]
P_5	+1.77 (+1.86)[a]	+1.08	+0.610 (+0.597)[c]	+0.505	+0.418 (+0.354)[d]
N_1 (1st)	−0.210	−0.291	−0.294	−0.296	−0.296
N_1 (2nd)	+0.753 (+0.871)[a]	+0.338	+0.166 (+0.268)[c] (+0.105)[e]	+0.121	+0.059 (+0.345)[d]
N_1 (3rd)		+0.759	+0.528 (+0.627)[c] (+0.254)[e]	+0.481	
$N_{1'}$ (1st)	−0.412	−0.308	−0.262	−0.239	−0.211
$N_{1'}$ (2nd)	(+1.433)[a]	+0.865	+0.494 (+0.556)[c] (+0.526)[e]	+0.409	+0.338 (+0.276)[d]
N_2	+0.543 (+0.524)[a]	+0.210	−0.086 (+0.055)[c] (−0.046)[e]	−0.126	−0.183 (−0.167)[d]
N_3	(+2.21)[a]	+0.979	+0.195 (+0.694)[c] (+0.251)[e]	+0.149	+0.056 (+0.242)[d]
$N_{3'}$	+0.250 (+0.274)[a]	+0.250 (+0.301)[f]	+0.138 (+0.176)[c]	+0.126	+0.124 (−0.009)[d]
N_4	(+1.477)[a]	+0.697	+0.111 (+0.436)[c] (+0.167)[e]	+0.062	−0.024 (+0.099)[d]
$N_{4'}$ (1st)	+0.363 (+0.475)[a]	+0.284 (+0.310)[f]	+0.130 (+0.356)[c]	+0.099	+0.075 (+0.069)[d]
$N_{4'}$ (2nd)	(+1.37)[a]	+0.812	+0.538 (+1.072)[c]	+0.484	+0.440 (+0.420)[d]

[a] Glasser and Callaway, reference 22. These energies are for $a = 6.5183$ a.u.
[b] Schlosser, reference 13. $a = 8.043$ a.u.
[c] Callaway, reference 24. $a = 9.83$ a.u.
[d] Callaway and Haase, reference 25. $a = 11.45$ a.u.
[e] Allen, reference 29. $a = 9.83$ a.u.
[f] Callaway, reference 23. $a = 8.002$ a.u.

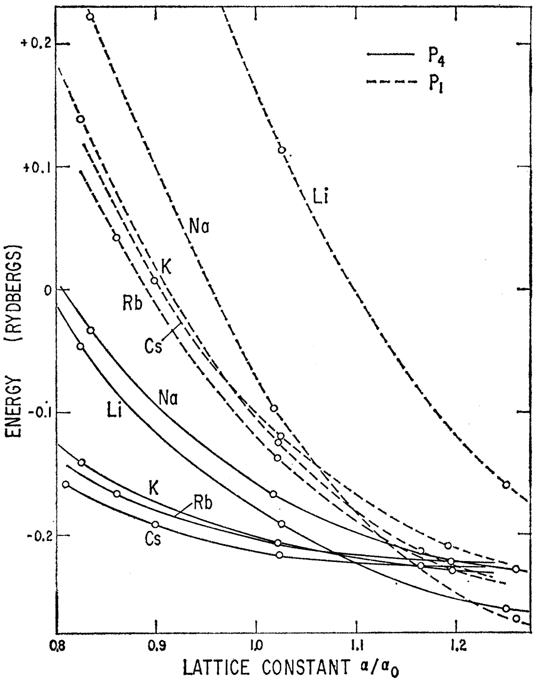

FIG. 11. Energy of the states P_1 and P_4 for all the alkali metals as a function of the ratio of the lattice constant a to its 0°K equilibrium value a_0.

of states of higher energy. The locations of these and other low-lying states in the empty lattice are given in Table IV, where ϵ is the reduced energy such that the empty lattice energy E is

$$E=[(2\pi/a)^2\epsilon+V_0]. \quad (1)$$

Comparing Tables III and IV, we see not only that many states are displaced substantially in the metals from their empty lattice energy, but also that states degenerate in the empty lattice but of different symmetry are often found to be widely separated in the metals.

For comparison of our results with those calculated by other people, we have included in Table III the energies of these states obtained by others, wherever available. These are listed in parentheses following our values, with the source indicated in the footnotes to the table. For the more important states of lower energy included in Table II, we have collected the results of other calculations in Table V. These various results are compared and discussed in Sec. V.

TABLE IV. Empty lattice states at symmetry points for bcc lattice, classified by reduced energy ϵ.

ϵ	Degenerate states
0.0	Γ_1
0.5	$N_1+N_{1'}$
0.75	P_1+P_4
1.00	$H_1+H_{12}+H_{15}$
1.50	$N_1+N_2+N_{3'}+N_{4'}$
2.00	$\Gamma_1+\Gamma_{15}+\Gamma_{25'}+\Gamma_{12}+\Gamma_{25}$
2.50	$N_1+N_4+N_{1'}+N_{4'}$
2.75	$P_1+P_3+2P_4+P_5$
3.00	$H_1+H_{2'}+H_{15}+H_{25'}$
3.50	$N_1+N_2+N_3+N_4+N_{1'}+N_{2'}+N_{3'}+N_{4'}$

IV. INTERPOLATION OF ENERGY BANDS: SPHERICAL APPROXIMATION

In order to obtain a more useful description of the energy bands than is afforded by energy values at a few points, we seek analytical expressions which serve to interpolate as smoothly as possible between these calculated values. A particularly convenient description of the nearly spherical low-energy part of the conduction band is obtained by expressing $E(\mathbf{k})$ as the sum of a power series in k^2:

$$E_s(\mathbf{k})=E_0+E_2k^2+E_4k^4+\cdots, \quad (2)$$

and an expression representing in powers of k_x, k_y, k_z the cubic distortions of the energy surfaces from spherical symmetry:

$$E_a(\mathbf{k})=E_4^{(2)}K_4(\mathbf{k})+E_6^{(2)}K_6(\mathbf{k})+\cdots. \quad (3)$$

Here $K_4(\mathbf{k})$ and $K_6(\mathbf{k})$ are Kubic harmonics,[21] and explicitly

$$K_4(\mathbf{k})=(k_x^4+k_y^4+k_z^4-\tfrac{3}{5}k^4).$$

If we examine Figs. 1 to 7, we see that the conduction band in each alkali metal is distorted from spherical

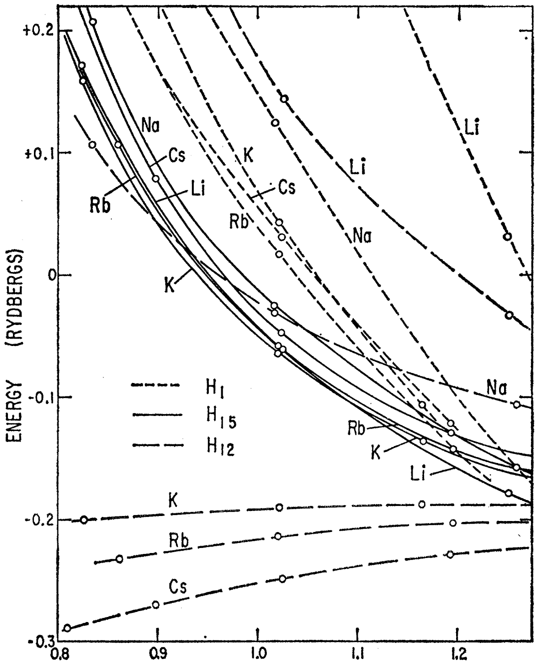

FIG. 12. Energy of the states H_1, H_{15}, H_{12} for all the alkali metals as a function of the ratio of the lattice constant a to its 0°K equilibrium value a_0.

---

[21] F. von der Lage and H. Bethe, Phys. Rev. **71**, 612 (1947).

symmetry in having energies along the [110] direction depressed relative to those for the same $|\mathbf{k}|$ along the [111] and [100] directions. This is expected from the proximity of the zone face to points on the [110] axis. But the Kubic harmonic $K_4(\mathbf{k})$ represents a distortion in which the [110] direction is intermediate between the [100] and [111] directions. Accordingly $K_4(\mathbf{k})$ alone can not represent even qualitatively the type of distortion found for the alkali metals.

Thus, a representation of the form of the sum of (2) and (3) must include terms through at least the sixth order if it is to describe at all correctly the nonspherical distortion. This already requires an inconveniently large number of independent terms for a least-squares fitting procedure. Moreover, if sixth-order terms are important, one hesitates to exclude terms of eighth and higher order for $\mathbf{k}$ near the zone face.

TABLE V. Energies (in rydbergs) of lower states at symmetry points as calculated by various authors.

State	Li	Na	K	Cs
Γ_1	-0.6863^{a} -0.615^{e} -0.6834^{h} -0.6853^{j} -0.685^{k}	-0.597^{b} -0.608^{f} -0.6076^{i}	-0.430^{c} -0.451^{g}	-0.427^{d}
N_1	-0.176^{a} -0.114^{e} -0.19^{h} -0.1801^{j} -0.192^{k}	-0.263^{b} -0.315^{f} -0.2938^{i} -0.287^{l}	-0.224^{c} -0.251^{g}	-0.285^{d}
$N_{1'}$	-0.404^{a} -0.304^{e} -0.4105^{h} -0.4128^{j} -0.411^{k}	-0.316^{b} -0.268^{f} -0.2944^{i} -0.292^{l}	-0.190^{c} -0.234^{g}	-0.342^{d}
$N_1-N_{1'}$	$+0.228^{a}$ $+0.190^{e}$ $+0.22^{h}$ $+0.233^{j}$ $+0.219^{k}$	$+0.053^{b}$ -0.047^{f} $+0.0005^{i}$ $+0.005^{l}$	-0.034^{c} -0.017^{g}	$+0.057^{d}$
P_1	$+0.330^{a}$ $+0.150^{k}$	-0.041^{b} -0.110^{f} -0.1048^{i}	$+0.054^{c}$	-0.118^{d}
P_4	-0.189^{a} -0.184^{h} -0.1788^{j} -0.182^{k}	-0.162^{b} $+0.020^{f}$ -0.1546^{i}	-0.126^{c} -0.177^{g}	-0.259^{d}
H_1	$+0.571^{a}$ $+0.55^{e}$ $+0.50^{k}$	$+0.193^{b}$ $+0.100^{f}$ $+0.0882^{i}$ $+0.136^{l}$	$+0.265^{c}$	$+0.144^{d}$
H_{15}	-0.092^{a} -0.120^{e} -0.046^{h} -0.009^{j} -0.047^{k}	-0.015^{b} -0.014^{f} -0.0198^{i} -0.018^{l}	$+0.062^{c}$	-0.173^{d}
H_{12}	$+0.227^{a}$ $+0.202^{e}$ $+0.168^{k}$	$+0.017^{f}$ $+0.006^{l}$	-0.132^{c} -0.165^{g}	-0.208^{d}

[a] Glasser and Callaway, reference 22, $a=6.5183$ a.u.
[b] Callaway, reference 23, $a=8.002$ a.u.
[c] Callaway, reference 24, $a=9.83$ a.u.
[d] Callaway and Haase, reference 25, $a=11.45$ a.u.
[e] Schiff, reference 28, $a=6.531$ a.u.
[f] Howarth and Jones, reference 26, $a=8.138$ a.u.
[g] Allen, reference 29, $a=9.83$ a.u.
[h] Schlosser, reference 13, $a=6.5183$ a.u.
[i] Schlosser, reference 13, $a=8.043$ a.u.
[j] Callaway, reference 14, $a=6.5183$ a.u.
[k] Present work on lithium interpolated to $a=6.5183$ a.u.
[l] Ham, reference 8, $a=8.048$ a.u.

TABLE VI. Parameters of spherical approximation for energy bands of the alkali metals as obtained by a least squares fitting to calculated points (energy in rydbergs, lattice constant a and propagation vector $\mathbf{k}$ in atomic units).

	a	E_0	$(2\pi/a)^2E_2$	$(2\pi/a)^4E_4$
Lithium	5.338	-0.6844	$+0.7620$	$+0.1759$
	6.651	-0.6821	$+0.6757$	$+0.0012$
	8.109	-0.6226	$+0.5094$	-0.0137
Sodium	6.651	-0.6440	$+0.9490$	-0.1152
	8.109	-0.6040	$+0.6207$	-0.0232
	10.049	-0.5342	$+0.3957$	-0.0059
Potassium	8.109	-0.4997	$+0.8183$	-0.4488
	10.049	-0.4815	$+0.4509$	-0.0822
	11.458	-0.4500	$+0.3309$	-0.0309
Rubidium	9.053	-0.4739	$+0.7353$	-0.4324
	10.742	-0.4549	$+0.4320$	-0.1103
	12.575	-0.4181	$+0.2870$	-0.0349
Cesium	10.049	-0.4286	$+0.6503$	-0.4718
	11.458	-0.4190	$+0.4121$	-0.1650
	13.348	-0.3886	$+0.2680$	-0.0557

Accordingly, we choose to employ an entirely different representation of distortions from spherical symmetry near the zone faces. This is based on the nearly free electron model and will be described in II. For the nearly spherical central part of the band we shall simply neglect nonspherical distortions and seek as accurate a description of this part of the band as is possible within the spherical approximation. Retaining as parameters only E_0, E_2, and E_4 in (2), we have then determined these by a least-squares procedure using calculated energy values for the following points:

$$\begin{aligned}
&[100]\text{ axis: } (ak_x/2\pi)=0,\ 1/8,\ 1/4,\ 3/8,\ 1/2,\ 5/8,\\
&[110]\text{ axis: } (ak_x/2\pi)=1/8,\ 1/4, \qquad\qquad (4)\\
&[111]\text{ axis: } (ak_x/2\pi)=1/8,\ 3/16,\ 1/4,\ 5/16,\ 3/8.
\end{aligned}$$

The resulting representation should thus be a good description of the spherical part of the conduction band at low energies. At higher energies up to roughly the Fermi level it represents an average of the [100] and [111] directions. But it does not take appreciable account of the depression of the band near the Fermi level in the [110] direction, since the states at large $|\mathbf{k}|$ along the [110] axis were excluded from the fitting process. This spherical representation may be compared directly with the results of calculations using the spherical approximation of Wigner and Seitz.

The parameters resulting from this fitting are listed in Table VI. These are given for three values of the lattice constant for each metal at which energy values were calculated. In Table VII we list values of E_4 and

TABLE VII. Effective mass m^* (at $\mathbf{k}=0$) and E_4 for alkali metals, interpolated to equilibrium lattice constant for 0°K.

	Li	Na	K	Rb	Cs
a_0 (a.u.)	6.597	7.984	9.874	10.555	11.424
m^*/m_0	$+1.330$	$+0.965$	$+0.861$	$+0.779$	$+0.727$
E_4	$+0.004$	-0.069	-0.58	-1.01	-1.85

the effective mass (at $k=0$) $m^*=(E_2)^{-1}$, interpolated from Table VI to the 0°K equilibrium lattice constant.

We have found that this spherical representation gives an exceedingly good fit in some cases to the points used in the fitting. Thus for sodium, potassium, and rubidium at the lattice constants used in Figs. 2 to 4, the difference between the energy as originally calculated by the Green's function method and that given by Eq. (2) with the best choice of E_0, E_2, and E_4 was for none of these points greater than 0.0005 Ry. This result incidentally provides excellent support for our belief that the Green's function method as used here usually gives energy values accurate to at least 0.001 Ry. In other cases when the band gap is large and the band appreciably distorted, this difference at points of larger $|\mathbf{k}|$ is typically about half the energy difference between the [100] and [111] axes for that $|\mathbf{k}|$. Elsewhere in the band the difference is typically less than 0.001 Ry.

In Table VIII we compare our results for these parameters, suitably interpolated, with those obtained by Brooks[12] using the method of Wigner and Seitz.

V. DISCUSSION: BAND STRUCTURE TRENDS AND COMPARISON WITH OTHER CALCULATIONS

Quite a number of people have made energy band calculations for individual alkali metals using various procedures, and Brooks[10,12] has made a systematic study of the cohesion of all the alkali metals using the spherical approximation and the quantum defect method. In the most extensive previous study that has taken account of the actual lattice structure, Callaway and his collaborators have calculated energy values for many states at symmetry points for lithium,[22] sodium,[23] potassium,[24] and cesium[25] using the OPW method. The present work has been the first systematic attempt to seek trends in the band structures and Fermi surface shapes of all five alkali metals from direct calculations at low symmetry points within the Brillouin zone as well as the usual points of high symmetry, while treating all the metals on the same basis by means of the quantum defect method and taking full account of the polyhedral form of the unit cell.

Our results have indeed shown a definite trend in the band structure at equilibrium which agrees qualitatively with that proposed by Cohen and Heine[3] on the basis of some simple theoretical considerations and their interpretation of experimental data. The Fermi surface is distorted from a sphere by depression of the bands in the [110] directions as a result of an energy gap between the s- and p-like states N_1 and $N_{1'}$ at the center of the zone face. For lithium $N_{1'}$ is about 3 eV below N_1, and the Fermi surface is distorted appreciably, although not so much as to touch the zone face in contrast to Cohen and Heine's proposal. Sodium has a very small gap and a spherical Fermi surface, while for potassium, rubidium, and cesium $N_{1'}$ is above N_1 by an amount that increases in that sequence. The Fermi surface of potassium is only slightly distorted; the distortion is greater for rubidium and sufficient for cesium to cause contact for a lattice constant 2% less than the equilibrium value at 0°K (see II). The results of Callaway and his colleagues for the symmetry point N fit this trend for lithium, sodium, and potassium, but not for cesium, while Howarth and Jones' result[26] for sodium does not fit the trend if compared with any of the calculated values of the gap for potassium.

From our calculations at different lattice constants, we find that for all the alkali metals except sodium the magnitude of the gap at N increases substantially as the lattice constant is decreased and that the Fermi surface distortion increases correspondingly. For lithium this reflects the rapid increase of the s state N_1 relative to the p state $N_{1'}$, as proposed by Cohen and Heine,[3] although we find that the resulting distortion is not sufficient for contact even with a 20% reduction in lattice constant (Fig. 8). For potassium, rubidium, and cesium, however, $N_{1'}$ rises relative to N_1 with compression, the reverse of Cohen and Heine's proposal. For sodium N_1 and $N_{1'}$ move very nearly together, so that the gap remains small. Sodium evidently not only is the metal in the alkali series that has the most nearly free-electron-like energy bands at equilibrium, but it preserves this behavior as the lattice constant varies. Its effective mass even remains close to unity (see Table III of II)!

The accuracy of the calculated band structure of a given metal obviously depends on that of the assumed potential. We have not attempted to improve the self-consistency of the potential beyond that of the Wigner-Seitz assumption and the quantum defect method, for to do so would largely remove the advantages of the latter method in dealing with all of the metals on the same basis. Accordingly we have no accurate estimate

TABLE VIII. Comparison of parameters of spherical approximation with values calculated by Brooks using Wigner-Seitz method.

		Present work[a]			Brooks[b]		
	a (au)	E_0	E_2	E_4	E_0	E_2	E_4
Li	6.499	-0.685	$+0.741$	$+0.009$	-0.6865	$+0.7305$	-0.0303
Na	8.124	-0.603	$+1.034$	-0.064	-0.6011	$+1.022$	-0.0096
K	9.871	-0.486	$+1.161$	-0.58	-0.4876	$+1.149$	-0.3

[a] Interpolated from values of Table VI to lattice constant used by Brooks.
[b] H. Brooks, reference 12.

---

[22] M. L. Glasser and J. Callaway, Phys. Rev. **109**, 1541 (1958).
[23] J. Callaway, Phys. Rev. **112**, 322 (1958).
[24] J. Callaway, Phys. Rev. **103**, 1219 (1956).
[25] J. Callaway and E. L. Haase, Phys. Rev. **108**, 217 (1957).

[26] D. J. Howarth and H. Jones, Proc. Phys. Soc. (London) **A65**, 355 (1952).

of the error in a given calculation arising from this source. We shall point out below, however, in a short discussion of each metal, that there is close agreement between the important features of the conduction band and Fermi surface predicted by our work and the results of some other recent calculations on lithium, sodium, and potassium, despite significant differences in the potentials used. Numerical differences of course appear, but even these are fairly small. In summary, this comparison supports the view that the structure of the conduction band of each metal is not very sensitive to uncertainties in the potential (excited bands are more sensitive but less interesting) and that the present calculations give the important features of the alkali band structures correctly.

The reliability of the calculated band structure also requires, obviously, that the method of calculation for a given potential be accurate. The Green's function method provides, in principle, a very accurate method, giving very rapid convergence (Appendix). We have carried out the calculations on an IBM-704 digital computer in order to minimize the possibility of computational errors and to make sure that the same procedure was followed in all the calculations. Permanent tables of the necessary data such as radial functions and structure constants were prepared on punched cards for repeated re-use in the calculations. A check on the results was provided by the mutual consistency of the calculated determinants for a given state and adjacent energies, and by that of the energy eigenvalues for neighboring states for a given metal, and for the same state for adjacent metals in the alkali series or for different values of the lattice constant for the same metal. Use of this standardized procedure, together with the good agreement between our results and those of some other recent calculations for lithium, sodium, and potassium which should be reliable, give us confidence in the reliability of our results. In particular, substantial unexplained differences between our results for the heavier metals and the results of some earlier calculations by others lead us to doubt the reliability of these earlier results.

Our use of the same approximations in dealing with all of the alkali metals should insure that the calculated trends in the band structure are correct, both as to variation in the alkali series and variation with lattice constant. In comparing with experiment in II it is the trends which we emphasize. However, this comparison again suggests that the actual numerical results may not, in fact, be too seriously off, once corrections for electron-electron correlation and electron-phonon interaction are allowed for, of course. Brooks' partial success in accounting for the cohesive properties of these metals[12] on much the same basis supports the same conclusion, since these properties are sensitive to smaller changes in the band structure than would be needed to change the relative position of individual states by significant amounts. Of particular interest is that all the evidence seems to support the conclusion that sodium is, in fact, very nearly free-electron-like as predicted. It may well be, however, that we underestimate the degree of Fermi surface distortion for lithium and overestimate it for the heavier metals, perhaps as suggested by Cohen and Heine[3] because we have treated the correlation-exchange hole rather inaccurately.

Trends among the excited states of the metals are also evident (Table III). There is first of all an over-all reduction in the energy of a given state and in the energy difference between states as we go from lithium to cesium, corresponding to the increase in lattice constant. This trend is illustrated by Γ_{25}, P_5 and $H_{2'}$, which as f states (Table I) are in these calculations independent of the core potential characterizing the individual metal. There also appears a lowering of d states relative to s, p, and f states in the sequence lithium to cesium. This behavior is clearly evident in the relative position (Figs. 1 to 5) of the states $H_{12}(d)$, $H_{15}(p)$, and $H_1(s)$ and also in the relative depression of the d states Γ_{12} and $\Gamma_{25'}$ for the heavier metals relative to the states $\Gamma_1(s)$, $\Gamma_{15}(p)$ and $\Gamma_{25}(f)$ which are degenerate with these at $\mathbf{k}=0$ in the empty lattice (Table IV). This effect is also in part responsible for N_1 falling increasingly below $N_{1'}$ for the heavier metals, since N_1 mixes s and d functions, and the latter were found to contribute a greater energy shift for the heavier metals. Finally, there is a rise in p states relative to s and f states in the same sequence, as seen from $H_{15}(p)$ and $H_1(s)$, from $\Gamma_{15}(p)$, $\Gamma_1(s)$, and $\Gamma_{25}(f)$, and from $N_{1'}(p)$ and $N_1(s,d)$. The precise numerical values of the energy of states appreciably above the conduction band are of little importance: Our extrapolation of the quantum defect parameters becomes increasingly uncertain beyond a few tenths of a rydberg into the positive energy range, and the excited states appear to be increasingly sensitive to changes in the potential with increasing energy. (Note the differences in Table III between the results of different calculations; these differences may however also reflect poorer convergence of the OPW method for excited states, and for potassium and cesium there appears to be some unexplained additional source of error in the OPW results.) It is interesting that there appear to be substantial departures among these excited states from a free-electron behavior even for sodium.

The order of states at symmetry points agrees with but two exceptions with the "normal order" proposed by Callaway.[1] Assigning states at Γ, N, P, and H to s, p, d, or f "bands" according to the term of lowest l in the spherical harmonic expansion of the wave function (Table I), we obtain the "normal order" of states in, say, the "s band" from the order of the energies of these states in the empty lattice (Table IV). Examination of Table III reveals the same order of states within each such "band" for each metal, with two minor exceptions: (1) in the "s band" the third state N_1 falls below the second Γ_1; (2) in the "p band" the first P_4 is slightly below $N_{1'}$ for cesium; the second P_4 is below the second $N_{1'}$ and $N_{4'}$ for all the metals and below Γ_{15} for potassium, rubidium, and cesium. These exceptions appear to reflect in part the effect of *d* states, which also contribute to N_1 and P_4, in depressing these states.

The order of states which are degenerate in the empty lattice but which belong to different "bands" can be interpreted qualitatively from the point of view of the OPW method, as Bassani and Celli have shown.[27] As these authors note, the sharp rise in *p* states relative to *s* or *d* states in going from lithium to sodium corresponds to the fact that in sodium there is a filled *p* state in the core, which has the effect of raising the energies of valence *p* states because of the orthogonality requirement. The more gradual rise in *p* states in the sequence sodium to cesium indicates that as successive shells are filled in the core the effect of the *p* states is somewhat greater than that of *s* states in repelling corresponding valence states. The lowering of *d* states for potassium, rubidium, and cesium, on the other hand, results from the changing potential of the ion and corresponds in particular to these ions' position in the periodic table just preceding the transition metals. The fact that the *d* states of rubidium are not raised in comparison with potassium despite a filled *3d* shell in the core evidently indicates that the *3d* states, which are some 10 ry deep, are relatively ineffective in repelling the valence states.

Lithium

Agreement between our results for the low-lying states at symmetry points, interpolated to $a=6.5183$ a.u., and those of Glasser and Callaway,[22] Schlosser,[13] and Callaway[14] for this value of *a* is good (Table V). Glasser and Callaway used the empirical Seitz potential,[16] Schlosser a "muffin-tin" form of potential based on the Seitz potential, and Callaway a smoothed Seitz potential that avoids causing any discontinuity in the crystal potential or its first derivatives. The Seitz potential reproduces the atomic term values of lithium within a fraction of a percent so that close agreement would be expected for a muffin-tin potential based on this and one based on the quantum defect method. Our values indeed agree with all of those given by Schlosser within 0.002 Ry. Agreement with Glasser and Callaway and with Callaway is excellent for the ground-state energy (0.001 Ry), and very good for N_1, $N_{1'}$, and P_4 (0.02 Ry). It becomes worse with increasing energy, as seen for the states at *H* ($\sim$0.06 Ry), P_1, and the high excited states in Table III, presumably because of increasing sensitivity to differences in the potential.

Some results due to Schiff[28] are also listed in Table III which do not agree with any of the other recent work. Schiff's potential, however, was considerably less satisfactory than the Seitz potential, as Kohn and Rostoker have noted,[5] so that we shall not consider his results further.

Schlosser[13] and Callaway[14] have also made calculations for points within the zone on the [100], [111], and [110] axes. The graphs for their results appear indistinguishable from our curves for the conduction band in Fig. 1, apart from Callaway's somewhat different numerical values near H_{15}. Callaway finds that the bulges in the Fermi surface protrude by about 5%, in agreement with our conclusion (see II). The various estimates for the gap at *N* all agree within 7%.

Sodium

Other calculations (Table V) for low-lying symmetry points of sodium show poorer agreement with our results (Table II) than in the case of lithium, but the agreement is still quite good. The Prokofjew potential,[17] used by Howarth and Jones[26] and in "muffin-tin" form by Schlosser,[13] reproduces the atomic term values less accurately than does the Seitz potential for lithium; hence we expect greater differences from a quantum defect calculation. Callaway[23] used a pseudopotential with two parameters chosen to fit spectral data, and Ham[8] used the quantum defect method (without polarization correction) but did not flatten the potential in the outer parts of the cell as in the present work.

These differences in potential and small differences in lattice constant probably account for most of the differences among these various results and between them and our present work. Our results agree for Γ_1, N_1, $N_{1'}$, H_{15}, and P_4 within about 0.01 Ry with those of Schlosser[13] (when interpolated to his value of the lattice constant) and with Ham's old values[8] for N_1 and $N_{1'}$. There is a greater discrepancy with Schlosser for P_1 and H_1 (0.02 and 0.06 Ry), but both of these states seem to be particularly sensitive to changes in the potential as well as to changes in lattice constant (Figs. 11 and 12).

Differences between our results and those of Howarth and Jones[26] and between these latter and Schlosser's are greater than we would have expected. In particular Howarth and Jones found a value of -0.047 Ry for the gap ($N_1-N_{1'}$) in contrast to our value of $+0.019$ Ry and Schlosser's essentially zero value; also their value for P_4 is $+0.18$ Ry above ours, and therefore their order of P_1 and P_4 is the reverse of that other people have found. We were able to account[8] for the discrepancy in the gap ($N_1-N_{1'}$) on the basis of inaccuracies in the particular boundary conditions used by Howarth and Jones in finding their eigenvalues. Discrepancies in P_1 and H_1 are in part the result of their use of a lattice constant 2% larger than ours in Table II. But the large discrepancy in P_4 would appear to reflect a computational error in their work.

The various values for the energy gap ($N_1-N_{1'}$) (even discounting Howarth and Jones') differ by larger amounts than in the case of lithium, but there is general agreement that the gap is small, so that the Fermi surface should be very nearly spherical. All agree too that the effective mass of sodium is very close to unity. The

---

[27] F. Bassani and V. Celli, J. Phys. Chem. Solids **20**, 64 (1961); *Studia Ghisleriana* (Pavia) Ser. IV, 2 (1959).

[28] B. Schiff, Proc. Phys. Soc. (London) **A67**, 2 (1954).

only calculations besides ours for interior points in the zone, those of Schlosser, find no significant difference between the bands on the [100], [110], and [111] axes within the Fermi surface, in agreement with Fig. 2.

Potassium

Construction of an explicit atomic potential for potassium is more difficult than for lithium and sodium and the uncertainties greater, because of the importance of exchange interaction with the core electrons.[24] We should, therefore, expect poorer agreement between results of our quantum defect calculation and those based on an explicit potential, as is found. Callaway,[24] using the OPW method, employed different potentials for states of different (s,p,d) symmetry according to the predominant character of the state, in order to take approximate account of the l dependence of the effective potential due to exchange. Allen[29] used the same potentials as Callaway (except that Allen flattened the potential into muffin-tin form), but he made his calculations with the augmented plane wave (APW) method.

In comparing the various results at symmetry points, we note in Tables III and V that Allen's values differ from Callaway's despite their use of similar potentials. The discrepancy increases from 0.02 Ry for Γ_1 to as much as 0.4 to 0.7 Ry for some of the positive energy states. These latter discrepancies are very much greater than the change produced in these eigenvalues if the exchange potential is changed from that appropriate for, say, a d state to that for an s or p state. Allen found such changes for excited states to be typically 0.01 to 0.1 Ry, and those for the lowest states Γ_1, N_1, $N_{1'}$, P_4 and H_{12} to be quite small, less than 0.005 Ry. These differences between Callaway's results and Allen's have not been accounted for with certainty, although Callaway has suggested that they may arise from incomplete convergence of his OPW calculations for potassium. Since our results show similar large differences from Callaway's, and since the APW method in general provides much better convergence than does the OPW method, we shall compare our results only with Allen's.

Allen's values for the low-lying states (Table V) lie between 0.02 and 0.04 Ry above ours. The potential used by Allen, however, took no account of the contribution of core polarization to the interaction with a valence electron, and Brooks[12] has shown that for potassium this lowers the energy of Γ_1 by about 0.035 Ry. With a somewhat smaller correction for p and d states, this accounts quite well for the differences, the remainders being within what is expected from the remaining differences in the potentials. For the higher states of Table III our values agree in general fairly well with Allen's, most of our values being below his by about 0.05 Ry. The only major difference is in the location of the second and third states N_1; Allen's values are surprisingly low with respect to both our values and the position of these states in the empty lattice.

Although there are no other calculations along the symmetry axes for potassium, it appears certain from Allen's small value for the gap at N that his calculations if extended would agree with ours in finding a nearly spherical Fermi surface.

Cesium

Callaway and Haase[25] used a potential for cesium which Sternheimer[30] had constructed taking account of exchange interactions appropriate to a $6s$ state. Their values for the states Γ_1, N_1, and P_1 are in quite good agreement with ours. However, they find a value for $N_{1'}$ which is 0.13 ry below ours and which reverses the sign of the gap at N. Their values for the other p states P_4 and H_{15} are also very low compared to ours. These discrepancies are undoubtedly due in part to Callaway and Haase's use of an exchange potential that is not really appropriate for p states, although they are surprisingly large if this is their only cause. Such large discrepancies for cesium and the somewhat similar unexplained differences between Callaway's results for potassium and those of Allen suggest that for some reason the results of the OPW calculations for potassium and cesium are not as reliable as those for lithium. In view of these uncertainties, a detailed comparison of our results for cesium with those of Callaway and Haase does not seem worth while.

Our result that the d states like H_{12}, Γ_{12}, $\Gamma_{25'}$, and N_2 are lower relative to s and p states for cesium than for the other alkali metals gives some support to a suggestion of Fermi's, which Sternheimer[30] investigated, that a high-pressure phase transformation observed in cesium by Bridgman[31] arises from the presence of a d band slightly above the Fermi energy which crosses the Fermi energy with increasing compression. Sternheimer's calculation of the position of the lowest d band at Γ was, however, marred by his use of very inaccurate boundary conditions which even in the empty lattice lead to a 40% error in the energy of the d state relative to Γ_1.[8] Sternheimer found a value of about -0.235 Ry for this state at equilibrium; we see from Table III that this is 0.11 Ry below our $\Gamma_{25'}$ but very close to H_{12}. As shown in Figs. 5 to 7, H_{12} decreases relative to the rest of the conduction band with decreasing lattice constant, in such a way as ultimately to form occupied pockets of electrons in the corners H of the cell. These results are, of course, for the body-centered lattice; Bridgman[31] has found that cesium becomes face-centered at a lower pressure than that at which the "electronic phase transition" occurs. Thus, the present calculations are not really relevant to the high-pressure transition, and similar calculations on the d bands should be done for

---

[29] L. C. Allen, Quarterly Progress Report, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, Cambridge, Massachusetts, October 1958 (unpublished), p. 45.

[30] R. M. Sternheimer, Phys. Rev. **78**, 235 (1950).

[31] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **76**, 55 (1948).

fcc cesium. The low position of the d bands for bcc cesium and the related rapid increase in Fermi surface distortion with pressure, however, show that the compressibility of cesium can not be calculated satisfactorily in the spherical approximation. This importance of the d bands is no doubt in large measure responsible for Brooks' result that the theoretical compressibility calculated in the spherical approximation is substantially less than that found experimentally.[10,12]

Spherical Approximation of Wigner and Seitz

Brooks[12] has recently given a thorough discussion of the method of Wigner and Seitz, in which the parameters in the spherical approximation to the band structure are evaluated from simplified boundary conditions on the sphere of volume equal to that of the actual polyhedral atomic cell. We wish here to compare Brooks' values for these parameters for the alkali metals to those we have obtained by a least-squares fitting of the expression (2) to the spherical low-energy portion of our calculated conduction bands.

Brooks' results are directly comparable with ours because in his work on lithium, sodium, and potassium he used the quantum defect method with the same form of polarization correction we have used. Thus, the only difference in the potential is that we used the muffin-tin potential beyond the inscribed sphere, while Brooks used the ion potential out to the radius of the equivalent sphere. The only further difference is that our calculation takes direct account of the polyhedral shape of the cell.

The comparison in Table VIII, with our results interpolated to the lattice constant used by Brooks, shows that the ground-state energies E_0 differ by no more than 0.002 Ry, and the inverse effective masses E_2 by about 0.01. There is little agreement, however, for E_4, apart from general order of magnitude.

Brooks[12] has estimated that use of polyhedral boundary conditions instead of those on the sphere should make only very small changes in E_0 and E_2 but that changes in E_4 can be comparable with E_4 itself and can not be estimated reliably. These conclusions are borne out by the comparison. The small differences in E_0 and E_2 appear reasonable on the basis of the differences in the potential and uncertainties in interpolation. Our values for E_4 increase rapidly from lithium to cesium (Tables VI and VII) and are typically roughly twice as large as Brooks' values.

The value of E_4 one obtains from a least squares fitting depends very sensitively on which points are selected for fitting. We have chosen in (4) only those up to slightly above the Fermi energy which seem little affected by the non-spherical distortion caused by the bending down of the [110] axis. Thus, our parameters are appropriate near the Fermi level only to the parts of the band away from the [110] directions; at lower energies they suffice for all directions. The fourth-order term in our procedure thus does *not* represent an average departure of states near the Fermi energy from a parabolic dependence on k.

While these results support Brooks' conclusion[12] that the effective mass at $k=0$, $m^*=(E_2)^{-1}$, is given accurately by the Wigner-Seitz spherical approximation, this approximation is not accurate for calculating the thermal, optical, and cyclotron effective masses *at the Fermi surface*. These depend on E_4 as well as E_2 even in the spherical approximation and are affected significantly by Fermi surface distortion. These effective masses will be considered in II.

Callaway and his colleagues have also given values for these parameters for all the alkali metals, obtained mostly from the Wigner-Seitz method with various explicit potentials. The agreement of their values for E_0 and E_2 with ours and with Brooks' is reasonable, in view of the differences in potential: the largest difference is between their value[32] $E_2=1.181$ for rubidium ($a=10.58$ a.u.) and our value (for this a) of 1.28. Their values of E_4 are however even greater than ours: They find -0.153, -0.85, -1.28, and -3.64 for sodium,[33] potassium,[34] rubidium,[32] and cesium,[35] respectively. For lithium Callaway[14] has fitted a polynomial of sixth order to his calculated points along the three axes, including in the polynomial the anisotropic cubic terms of fourth and sixth order. He finds $E_4=+0.105$, in contrast to our value of $+0.01$ and Brooks' -0.03, but he also finds a large symmetric sixth-order term with $E_6=-0.545$ as well as large anisotropic terms of fourth and (most important) sixth order that describe the nonspherical distortion. The contrast between Callaway's results and ours for bands which appear almost identical illustrates how sensitive these high-order terms are to the number of terms used in the expansion and the points used in the fitting.

Simplified Calculations of Cohen and Heine

Cohen and Heine[3] have proposed some simple criteria for estimating the energies of the states N_1 and $N_{1'}$ relative to Γ_1, the gap $(N_1-N_{1'})$, the effective mass, and the Fermi surface distortion. By comparing their proposals with our calculated bands we find[15] that while they predict the same trend in the band structure at equilibrium through the alkali series, these proposals are not, in general, reliable. Their formula for the "s state" N_1 is fairly accurate as long as d functions make no large contribution to this state, as for lithium and sodium, but it may be quite inaccurate when the d contribution is important, as is the case for the heavier alkali metals and also for the noble metals. Their formula for $N_{1'}$, for which they, in fact, claimed no great accuracy, except for lithium predicts entirely the wrong variation of this state with changing lattice constant, even as to sign.

---

[32] J. Callaway and D. F. Morgan, Phys. Rev. **112**, 334 (1958).
[33] J. Callaway, Phys. Rev. **123**, 1255 (1961).
[34] J. Callaway, Phys. Rev. **119**, 1012 (1960).
[35] J. Callaway, Phys. Rev. **112**, 1061 (1958).

This led Cohen and Heine to predict that the gap in potassium, rubidium, and cesium should decrease with compression if $N_{1'} > N_1$, whereas our calculations show an increase. While their formula gives roughly the correct value for $N_{1'}$ at equilibrium, this agreement seems fortuitous since Cohen and Heine gave no justification for the factor 1/2 by which they related the depression of $N_{1'}$ below the free atom p state ϵ_p to the corresponding difference $(\epsilon_s - \Gamma_1)$.

VI. CONCLUSION

Our calculations have revealed clear trends in the band structures of the alkali metals, in both the degree of the distortion of the conduction band and the location of excited bands. Of special interest, the gap $(N_1 - N_{1'})$ at the zone face is large and positive for lithium (~3 eV at equilibrium), almost zero for sodium, and negative and increasingly large in the sequence potassium, rubidium, cesium. Accordingly, the Fermi surface is practically spherical for sodium and potassium and distorted the most for lithium and cesium. Although our calculations may underestimate the distortion for lithium and overestimate it for cesium, they indicate that the Fermi surface of lithium does not contact the zone face, while that of cesium nearly touches at equilibrium at 0°K. Except for sodium, the distortion for all the alkali metals increases significantly with a decrease in lattice constant.

While our results differ in important respects from those of some earlier calculations, they agree closely with several recent calculations for individual metals despite differences in the potentials used. Our comparison of these various results indicates that the significant features of the calculated bands are not very sensitive to uncertainties in the potential, provided that an accurate method of calculation is used. While improvements in the self-consistency of the potential will certainly give values for the band parameters somewhat different from those we have obtained with the quantum defect method, we believe accordingly that the present calculations should give the significant features of the bands correctly.

Comparison with Brooks' results with the Wigner-Seitz spherical approximation supports his conclusion that the ground-state energy and the effective mass at $\mathbf{k}=0$ are given accurately in that approximation but that the fourth-order energy parameter E_4 is not. Since effective masses at the Fermi surface depend on E_4, as well as on the nonspherical distortion, they cannot be calculated accurately in the spherical approximation. The present work has confirmed the usefulness of the rapidly convergent Green's function method of Kohn and Rostoker in making possible extensive calculations at points of low symmetry within the zone.

ACKNOWLEDGMENTS

The author is particularly indebted to Mrs. Josephine Morecroft for her expert assistance in carrying out these calculations and especially in programming and operating the IBM-704 computer. He gratefully acknowledges many helpful discussions with B. Segall and other colleagues.

APPENDIX: CONVERGENCE OF GREEN'S FUNCTION METHOD

In Table IX are listed representative examples illustrating the convergence of the Green's function method[5,6] in our calculations. Approximate energy eigenvalues have been found from the zeroes of the $n \times n$ determinant obtained when n independent terms (different spherical harmonics) are included in the trial function.[6] [Energy eigenvalues are given in Table IX in terms of

TABLE IX. Examples of the convergence of the Green's function method for energy eigenvalues and wave function coefficients of the alkali metals. The following results are for the state of symmetry Δ_1 at the point $\mathbf{k} = (2\pi/a)(5/8,0,0)$ in the conduction band, for the lattice constants of Figs. 1–5. The approximate eigenvalue (in terms of the reduced energy ϵ) obtained with a trial wave function containing n independent spherical harmonics is denoted by ϵ_n. The coefficients C_s, C_p, and C_d in the spherical harmonic expansion of the wave function inside the inscribed sphere are listed together with the terms of the series used to obtain C_p and C_d. These terms are labeled as follows: $(C_p)_n$ denotes the term obtained in the series for C_p when the nth spherical harmonic is added to the trial function. Spherical harmonics were added in this work in order of increasing l: s, p, d, f, ...

	Li	Na	K	Rb	Cs
Energy eigenvalue					
ϵ_2	+0.2715	+0.2920	+0.3130	+0.3345	>+0.35
ϵ_3	+0.2635	+0.2810	+0.2875	+0.2905	+0.3070
ϵ_4	+0.2635	+0.2805	+0.2870	+0.2905	+0.3055
ϵ_7	+0.2640	+0.2805	+0.2870	+0.2900	+0.3065
Wave function coefficient					
C_s	1.00	1.00	1.00	1.00	1.00
$(C_p)_2$	−3.44±0.03	−2.43 ±0.05	−1.75 ±0.04	−2.75 ±0.04	+2.03 ±0.05
$(C_p)_3$	+0.23±0.01	+0.41 ±0.01	+0.85 ±0.03	+2.10 ±0.08	−2.49 ±0.10
$(C_p)_4$	+0.01±0.01	+0.006±0.001	+0.003±0.001	+0.002±0.002	+0.001±0.001
C_p	−3.20±0.05	−2.01 ±0.06	−0.90 ±0.07	−0.65 ±0.12	−0.46 ±0.15
$(C_d)_3$	−3.4 ±0.1	−1.40 ±0.02	−0.437±0.010	−0.316±0.006	−0.153±0.005
$(C_d)_4$	+0.2 ±0.2	+0.08 ±0.02	+0.010±0.003	+0.004±0.004	+0.001±0.001
C_d	−3.2 ±0.3	−1.32 ±0.04	−0.427±0.013	−0.312±0.010	−0.152±0.006

the reduced energy ϵ of Eq. (1).] For the states in Table IX there is no significant change in the eigenvalues as spherical harmonics with $l \geqslant 3$ are added, the accuracy of interpolation in locating the zero of the determinant being estimated as $\Delta\epsilon = \pm 0.001$. We have found that for states in the conduction band a trial function including all allowed terms with $l \leqslant 2$ suffices to give the eigenvalue to an accuracy of at least $\Delta\epsilon = \pm 0.002$. For states in excited bands above the conduction band, terms with $l=3$ and 4 contribute shifts in ϵ of a few thousandths.

Coefficients in the spherical harmonic expansion of the wave function within the inscribed sphere have also been calculated for some states, using the procedure given previously.[6] The examples of Table IX illustrate the accuracy that is achieved for the coefficients C_s, C_p, and C_d of the s, p, and d terms. (The coefficients as given in the table are not normalized, so that their values are of no direct use without information on the normalization of the radial functions.) The coefficients were calculated by setting C_s equal to unity and expressing C_p and C_d as a series of terms such that the change in each coefficient caused by addition of one more independent term in the trial wave function is expressed simply as an additional term in the series. These additional terms equal zero when addition of terms to the total function causes no further change in the eigenvalue. Each term in the coefficient series was evaluated by interpolating the appropriate expressions to the energy of the final eigenvalue, and an estimate was made of the uncertainty resulting from this procedure. The various terms in the coefficient series and their uncertainties are listed in Table IX as well as the final sum. The series are terminated with the term arising from adding the $l=3$ term to the trial function. This term is small, and its uncertainty is often as large as the term itself; higher terms appear to make negligible contributions. For the state of lithium given in the table, the estimated accuracy of C_p appears to be very good, about 2%, while that of C_d is about 10%. For the heavier metals, however, there is appreciable cancellation between the first and second terms in the series for C_p, so that although the individual terms should be accurate to a few percent, the final value of C_p for cesium is uncertain by some 30%. For the heavier metals the accuracy of C_d appears, however, to be good. To eliminate the cancellation in the series for C_p, and thereby presumably increase its accuracy, we should change the sequence in which terms are added to the trial function from s, p, d, f, at present, to s, d, p, f. The uncertainty can, of course, also be reduced by directly calculating the various necessary quantities at energies very close to the eigenvalue so that interpolation is more accurate.

Outside the inscribed sphere the wave function can be expressed as a sum of plane waves of propagation vector $(\mathbf{k}+\mathbf{K}_i)$, where the $\mathbf{K}_i$'s are reciprocal lattice vectors. Although this expansion is not unique, an optimum representation in terms of a given selection of a few plane waves can be made.[6] We have not made such calculations for most of the metals; however, for the state of lithium listed in Table IX with $\mathbf{k}=(2\pi/a)(5/8,0,0)$ we have found, using the plane waves obtained from $\mathbf{k}$ with the reciprocal lattice vectors (1) $\mathbf{K}=0$, (2) $\mathbf{K}=(4\pi/a)(-1/2, \pm 1/2, 0)$ and $\mathbf{K}=(4\pi/a)(-1/2, 0, \pm 1/2)$, (3) $\mathbf{K}=(4\pi/a)(-1, 0, 0)$, and (4) $\mathbf{K}=(4\pi/a)(0, \pm 1/2, \pm 1/2)$, values for the coefficients of these waves (the wave function again unnormalized) $C_1=-0.651$, $C_2=+0.033$, $C_6=+0.025$, $C_4=-0.005$. These results support the view that in this region of the cell the wave function is predominantly a single plane wave. However, it is not clear that one can always safely ignore the other terms in the expansion, particularly since there are four waves of set (2), and the various plane waves are not mutually orthogonal over the region of the cell outside the inscribed sphere.