desirable. Nevertheless, we may conjecture that this is a general result, namely: linear dielectric screening (choice 1) gives quantitatively correct results for the valence response to the longest and strongest wavelength component of the effective potential. An improvement of the theory of Sec. 3 would permit quantitatively accurate *a priori* estimate of the screened exchange potential as well.

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Energy Bands in Lithium

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A previous calculation of energy bands in lithium which employed the orthogonalized plane wave method, has been extended with the determination of the energies of states along the [100], [110], and [111] axes in the Brillouin zone. The Fermi energy has been determined. The Fermi surface predicted by these calculations is not in contact with the Brillouin zone, and is only slightly distorted from the sphere characteristic of free electrons.

INTRODUCTION

THE work reported here is an extension of a previous calculation of energy bands in lithium[1] based on the method of orthogonalized plane waves (OPW).[2] The earlier work considered only states at the four principal symmetry points in the Brillouin zone of the body-centered cubic lattice: Γ, H, P, and N (see Fig. 1). This calculation revealed the existence of a large energy gap (about 3.1 ev) between the two lowest states at the face center N. Since the Fermi surface of the electron distribution in a monovalent, body-centered cubic metal (considering the electrons to be free) approaches the boundary of the Brillouin zone most closely in the vicinity of the face center N, the question of possible contact between the Fermi surface and the zone became important. Cohen and Heine[3] concluded that existing experimental information suggested a large area of contact between the surface and the zone boundary. The experimental data which they considered are not, however, definitive in this regard since the crucial cyclotron resonance, de Haas-van Alphen effect, and ultrasonic attenuation measurements have not been reported. It seemed desirable to extend the energy band study to include enough points in the interior of the zone to make possible a determination of the Fermi energy and, hence, to make a definite prediction concerning contact.

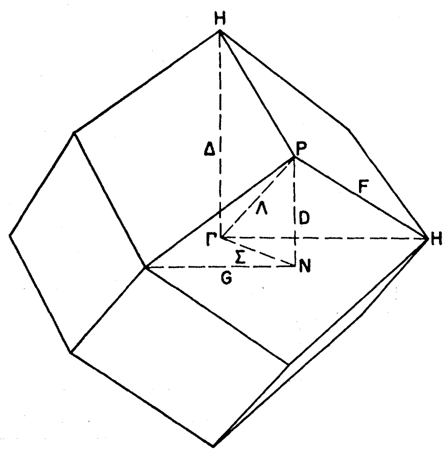

FIG. 1. The Brillouin zone for the body-centered cubic lattice. Points and lines of symmetry are shown.

The extension was made in the following way. The Fourier coefficients of the crystal potential (derived from the semi-empirical potential of Seitz[4] as quoted by Kohn and Rostoker[5]) were modified to take account of the fact that the normal component of the gradient of the crystal potential must vanish at many points on the surface of the atomic polyhedron. Energy levels were determined at twenty-one points on the surface and in the interior of the zone, including the four symmetry points previously mentioned and seventeen other points located along the [100], [110], and [111] axes (Δ, Σ, and Λ, respectively, in Fig. 1). These energy values were used to determine the seven lowest coefficients in the expansion of the energy in Kubic harmonics, and from these, the Fermi energy was determined according to a method proposed by de Launay[6] in a different problem.

While this work was in progress, other calculations of energy bands in lithium have been reported by Ham[7]

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[1] M. L. Glasser and J. Callaway, Phys. Rev. **109**, 1541 (1958). This paper contains references to previous work.

[2] C. Herring, Phys. Rev. **57**, 1169 (1940).

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

[4] F. Seitz, Phys. Rev. **47**, 400 (1935).

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

[6] J. de Launay, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 2, p. 219.

[7] 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 I. Fourier coefficients (in rydbergs) of the crystal potential as a function of $n^2=(a\mathbf{k}/2\pi)^2$.

n^2	$-V_n^2$	n^2	$-V_n^2$
0	1.0021	30	0.0186
2	0.1486	32	0.0176
4	0.0901	34	0.0167
6	0.0675	36	0.0158
8	0.0549	38	0.0151
10	0.0465	40	0.0144
12	0.0403	42	0.0137
14	0.0356	44	0.0131
16	0.0319	46	0.0126
18	0.0289	48	0.0120
20	0.0264	50	0.0116
22	0.0243	52	0.0111
24	0.0225	54	0.0107
26	0.0210	56	0.0104

and Schlosser.[8] These authors employed the Kohn-Rostoker method[5] and the augmented plane wave method, respectively. Ham's calculation is related to the quantum defect method[9] in that spectroscopic data were used to determine the values of the logarithmic derivatives on the inscribed sphere required in the Kohn-Rostoker procedure, so that use of an explicit potential could be avoided. Both the augmented plane wave method and the Kohn-Rostoker procedure require, however, that the crystal potential be constant in the region between the inscribed sphere and the cell boundary, a characteristic not necessarily possessed by actual crystal potentials.[10] The orthogonalized plane wave method, while restricted to the use of an explicit potential, does not require any specific assumption of this sort, and it is particularly interesting to see the comparison between the various methods of band calculations in this case.

BAND CALCULATION

Only the body-centered cubic form of lithium is considered here. The lattice constant was taken as 6.5183 in atomic units. It was mentioned in the introduction that it was necessary to modify the Fourier coefficient of the Seitz potential from the values given in reference 1. The modification is accomplished by writing the Seitz potential $V_s(r)$ as a sum of a point-charge potential, and that of a core, V_c (atomic units throughout):

$$V_s(r)=V_c(r)-2/r \tag{1}$$

[where $V_c(r_s)$ is zero to a very good approximation]. In the Fourier analysis, we replace the Fourier coefficients of the point-charge potential $(-2/r)$ (for $k\neq 0$) by those pertaining to a body-centered cubic lattice of positive point charges screened by a uniform distribution of negative charge. The resulting potential has the properties required by crystal symmetry, and in addition, is neither spherically symmetric nor constant in the part of a cell external to an inscribed sphere. The Fourier coefficients, which are determined from the expression

$$V(K_n)=\Omega_0^{-1}\int_{\Omega} e^{i\mathbf{K}_n\cdot\mathbf{r}}V(\mathbf{r})d^3r, \tag{2}$$

where $\mathbf{K}_n$ is a reciprocal lattice vector and Ω_0 is the volume of an atomic cell, are presented in Table I.

The orthogonality coefficients μ_{jk}, which are defined by

$$\mu_{jk}=\Omega_0^{-\frac{1}{2}}\int \phi_j^*(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}d^3r, \tag{3}$$

in which ϕ_j is the wave function of the (core) state j, are given in reference 1.

If $\mathbf{k}$ is the position vector of a point in the Brillouin zone, the wave vectors of the plane waves in which $\psi_{\mathbf{k}}$ may be expanded are of the form $\mathbf{k}+\mathbf{K}_n$. In this calculation, the forty-three orthogonalized plane waves formed by letting $\mathbf{K}_n$ include all the reciprocal lattice vectors with $(a/2\pi)^2K^2\leqslant 6$ were employed in the expansion of each ψ_k. For points on the [100] axis, this gave an 11×11 determinantal equation; for points on the [111] axis, the determinant is 12×12; for the [110] axis, 16×16. The convergence of the expansion with this number of plane waves may be checked at symmetry points, where a larger number of plane waves may be included without increasing the size of the determinantal equation beyond a reasonable limit. The results of this check are shown in Table II. It is seen that the error caused by truncation does not exceed 0.005 rydberg. The energies of all the states considered are presented in Table III. The bands are shown graphically in Fig. 2.

In order to facilitate the determination of the Fermi energy, the coefficients in an expansion of the energy in Kubic harmonics,

$$E(k)=E_0+E_2k^2+k^4(E_4^{(1)}+E_4^{(2)}K_{4,1})+k^6(E_6^{(1)}+E_6^{(2)}K_{4,1}+E_6^{(3)}K_{6,1})+\cdots \tag{4}$$

were determined by a least-square procedure, including all the states in Table III with $k^2\leqslant 2\pi^2/a^2$. In this equation $K_{4,1}$ and $K_{6,1}$ are the normalized (to 4π) Kubic harmonics, representation Γ_1, of fourth and sixth order, respectively, and are given explicitly by von der Lage

TABLE II. Comparison of energies (in rydbergs) obtained with OPW expansion with differing numbers of terms.

State	Number of waves	Energy	Number of waves	Energy
Γ_1	43	−0.6821	135	−0.6853
N_1'	43	−0.4083	72	−0.4128
P_4	43	−0.1765	80	−0.1788
N_1			88	−0.1801

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

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

[10] This assumption may not be a bad one since the normal component of the gradient must vanish at many points on the cell.

TABLE III. Energies (in rydbergs) of states in the lowest band along the [110], [111], and [110] axes. All values were obtained from an OPW expansion with 43 waves.

$5a\mathbf{k}/\pi$	E	$5a\mathbf{k}/\pi$	E
0 0 0	−0.682	1 1 1	−0.661
1 0 0	−0.675	2 2 2	−0.598
2 0 0	−0.654	3 3 3	−0.493
3 0 0	−0.619	4 4 4	−0.352
4 0 0	−0.568	5 5 5	−0.177
5 0 0	−0.506		
6 0 0	−0.427	1 1 0	−0.668
7 0 0	−0.331	2 2 0	−0.627
8 0 0	−0.222	3 3 0	−0.558
9 0 0	−0.098	4 4 0	−0.473
10 0 0	−0.009	5 5 0	−0.408

and Bethe.[11] The coefficients which were determined are given in Table IV.

The utility of an expansion of this sort has been questioned, since it does not provide the proper periodicity properties for the energy, and presumably does not converge for k larger than the radius of the inscribed sphere (in the Brillouin zone). However, with the coefficients given, the differences between the energies of the states, as given in Table III for k less than the radius of the inscribed sphere, and as computed from the expansion (4) is not greater than ± 0.0022 rydberg, including the lowest state at N. Consequently, we can accept Eq. (4) as a useful empirical representation.

In examining the values of the coefficients given in Table IV, one notes immediately the large size of the sixth order terms relative to those of fourth order. This is, however, to be expected. The distortion of a free electron band structure which lowers the energy of states on the 110 axis, as is shown in Fig. 2, requires significant sixth order terms, and occurs in Eq. (4) through an interference between $K_{4,1}$ and $K_{6,1}$. A single $K_{4,1}$ term cannot produce the required depression of states on the [110] axis. Thus, it is not surprising that previous calculations, such as that of Kohn and Rostoker,[5] which have considered only states along the [100] and [111] axes have indicated only small departures from a spherical band structure.[12] The value of E_2 obtained here, 0.748 is in fair agreement with the value obtained in a cellular method calculation,[13] 0.727. I do not know whether the difference is significant.

TABLE IV. Coefficients in the expansion of the energy [Eq. (4)].

E_0	−0.6821
E_2	0.748
$E_4^{(1)}$	0.105
$E_4^{(2)}$	−0.020
$E_6^{(1)}$	−0.545
$E_6^{(2)}$	0.537
$E_6^{(3)}$	0.175

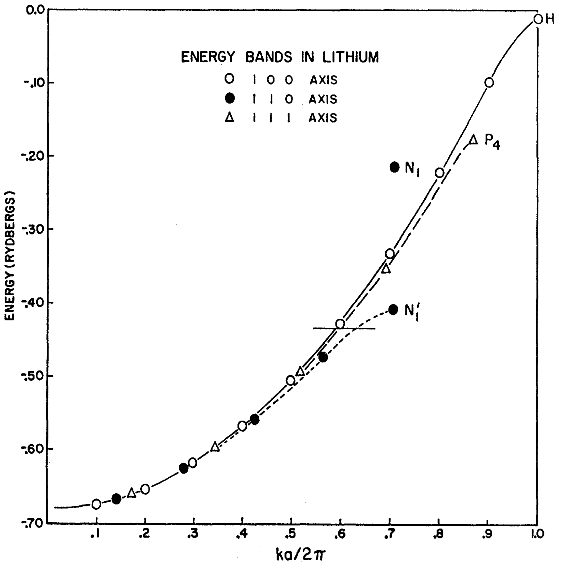

FIG. 2. Energy bands along the [100], [111], and [110] axes. The horizontal line at −0.433 rydberg represents the Fermi energy. Only a relatively small distortion of the Fermi surface is to be expected.

The agreement of these results with those of Schlosser is quite good. Except in the vicinity of H, the differences are in the third decimal place, and would not show in Fig. 2. This gives confidence that both methods of solving the band problem are reliable. The augmented plane wave method appears, however, to converge somewhat more readily in this case. It is more difficult to compare these results with those of Ham, since he has not published in detail the energy values he has found, and has used a slightly different lattice constant. Comparison of Fig. 2 of this paper with figure 1 of Ham's report[7] indicates, however, that the band structures predicted in both calculations are at least in semiquantitative agreement. In particular, Ham obtained an energy gap at N of 0.225 ry, whereas the present result is 0.232 rydberg (using the most accurate value for N_1'). Finally we note reasonably good agreement with the results of Brown and Krumhansl,[14] who did not, however, consider points on the [110] axis.

FERMI ENERGY

To determine whether the Fermi surface is in contact with the Brillouin zone, it is necessary to compute the Fermi energy, and compare it with the energy of N_1'. If $g(E)$ is the density of states [$g(E)$ gives the number of states between E and $E+dE$] the Fermi energy, E_F,

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[11] F. C. von der Lage and H. A. Bethe, Phys. Rev. 71, 612 (1947).

[12] If we consider states along the [100] and [111] axes, and with $k^2 \leqslant 2\pi^2/a^2$, a very good fit to the energy can be obtained with an expression of the form of (4) with the sixth order terms omitted. The coefficients of the fourth-order terms are quite small, in agreement with reference 5.

[13] R. A. Silverman and W. Kohn, Phys. Rev. **80**, 912 (1950); **82**, 283 (1951).

[14] E. Brown and J. A. Krumhansl, Phys. Rev. **109**, 30 (1958).

is determined by the requirement that

$$\int_0^{E_F} g(E)dE = N/V, \tag{5}$$

in which N/V is the number of electrons per unit volume of the crystal. The density of states can be found through the relation

$$\int_0^{E} g(E')dE' = \frac{2}{8\pi^3}\int d^3k = \frac{1}{12\pi^3}\int k^3(E,\theta,\phi)d\Omega. \tag{6}$$

The volume integral in k space in (6) includes the volume bounded by a surface of constant energy, E. The final integral on the right of (6) includes all solid angle. A practical method of handling (5) and (6) in a case in which the occupied portion of the band does not include a critical point (in the terminology of van Hove[15]) is to invert Eq. (4) to obtain a series for k^3 as a function of energy and angle, which can be integrated readily on account of the orthogonality of the Kubic harmonics. This has been done, and a Fermi energy of −0.433 ry obtained. A rather generous estimate of the possible error in this value should be ±0.010 ry. Evidently, the predicted Fermi surface does not touch the zone face.

In his thesis, Schlosser agrees with the conclusion of no contact between the Fermi surface and the zone face (as Ham does also), but obtains a Fermi energy of −0.421 ry. The disagreement between these two values is apparently outside the limits set by the difference between the energy levels at corresponding points of the bands in the two calculations.

Recently, Cornwell[16] has reported the application of an interpolation scheme to the determination of the Fermi energy in lithium, basing his work on the energy levels previously obtained by Glasser and Callaway[1] at symmetry points of the Brillouin zone. His result, −0.425 ry, also supports the conclusion of no contact.

When the Fermi energy is known, the Fermi surface can be mapped with the use of Eq. (4). It is largely spherical. A cross section of the Fermi surface in the k_xk_y plane is shown in Fig. 3. There are small bulges, of the order of 5% of the radius along the [110] axis, which may be significant in the understanding of electron transport properties. An experimental determination of the Fermi surface in lithium is urgently required for further progress.

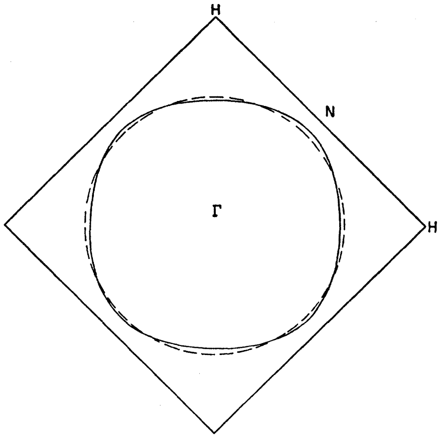

FIG. 3. Cross section of the Fermi surface in the k_xk_y plane of the Brillouin zone (solid line) for $E_F = -0.433$ ry. The dashed circle is a cross section of the spherical Fermi surface for free electrons.

The width of the occupied portion of the band is 3.39 ev in fair agreement with the experimental "reduced width" of 3.22 ev found in the x-ray emission measurements of Bedo and Tomboulian.[17] The author has, however, no explanation for the shape of the emission spectrum.

ACKNOWLEDGMENTS

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[15] L. Van Hove, Phys. Rev. **89**, 1189 (1953).

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

[17] D. E. Bedo and D. H. Tomboulian, Phys. Rev. **109**, 35 (1958).