

## Electronic Energy Bands in Lithium\*

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The orthogonalized plane wave method has been applied to a calculation of energy bands in metallic lithium. An empirical potential, constructed by Seitz, was used. Energies were obtained for states belonging to twenty-four symmetry types at four points of the Brillouin zone. The energy of the lowest state of a valence electron determined in this work is in good agreement with a previous cellular method calculation. The states which bound the lowest band were found to be of predominantly  $P$  type.

### I. INTRODUCTION

THE band structures of the lighter alkali metals, particularly lithium<sup>1-11</sup> and sodium, have been studied extensively for many years.

Because the atom is so simple, lithium has been used as a test case for nearly every method of band calculation. Much of the work has been concerned with states below the Fermi surface and the determination of the cohesive energy, whereas this calculation involves principally the normally unoccupied states. It is not our intention to review the previous work in detail; we cite in particular only two calculations which bear most closely on ours: that of Parmenter<sup>6</sup> who also used the OPW (orthogonalized plane wave) method, and that of Schiff<sup>9</sup> who calculated some of the same states but with a different potential and the cellular method.

Parmenter used as a crystal potential a lattice sum of atomic potentials,  $V = -2Z_p(r)/r$ , where  $Z_p$  is an effective charge determined on the basis of an electronic configuration  $(1s)^2(2s)^{5/8}(2p)^{3/8}$ , constructed by using self-consistent field wave functions, and approximated by a sum of Gaussians. Exchange effects were included by using Slater's free-electron exchange potential. This potential is probably not as satisfactory as the Seitz empirical potential.<sup>2</sup> The core state was obtained by a variation procedure using a single exponential. At most five orthogonalized plane waves were used in the expansions and states were examined in the (100), (111), and (110) directions in  $\mathbf{k}$  space. It is not clear that this procedure was adequate to insure convergence. Although some features of the results—the width of the conduction band and the effective mass values—are qualitatively reasonable, the energies obtained do not have quantitative significance.

Schiff used a potential which was obtained similarly to that of Prokofjew<sup>12</sup> for sodium but which is somewhat weaker than the Seitz potential near the nucleus. This would tend to make a difference in the relative position of  $s$  and  $p$  states. Schiff was interested in the shape of the soft  $K$  x-ray emission spectrum and particularly in the nature of the states on the zone faces. His results are listed in Table IV, where they are compared with ours.

In the present calculation the OPW method is used with Seitz's empirical potential.<sup>13</sup> This potential reproduces the observed spectrographic energy values of the free atom with considerable accuracy. Of particular interest are the convergence of the method and agreement with the cellular method for the state  $\Gamma_1$ . The chief advantage of using the OPW method is that it eliminates the need for explicitly satisfying boundary conditions. For this reason it is possible to determine the energies of a large number of states.

Our principal objective in determining the energies of states high above the Fermi level is to test the hypothesis that the order of levels of a particular type with respect to each other is reasonably independent of the crystal potential.<sup>14</sup> Also of interest is the proposal of Mott,<sup>15</sup> advanced to explain the observed x-ray emission spectrum of lithium,<sup>16</sup> that states on the boundary of the first Brillouin zone are of  $s$  character.

### METHOD

Only the body-centered cubic form of lithium is considered here. The lattice constant is taken as 6.5183 in atomic units. The crystal potential is devised on the basis of the Wigner-Seitz approximation that an electron sees only the spherically symmetric potential in each cell of the lattice, the other cells appearing electrically neutral. Thus, the crystal potential is taken to be a lattice sum of ionic potentials, in this case the Seitz potential  $V_s$ .

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<sup>1</sup> J. Millman, Phys. Rev. **47**, 286 (1935).

<sup>2</sup> F. Seitz, Phys. Rev. **47**, 400 (1935).

<sup>3</sup> J. Bardeen, J. Chem. Phys. **6**, 367 (1938).

<sup>4</sup> C. Herring, Phys. Rev. **59**, 598 (1939), and **82**, 282 (1951).

<sup>5</sup> R. A. Silverman and W. Kohn, Phys. Rev. **80**, 912 (1950), and **82**, 283 (1951).

<sup>6</sup> R. H. Parmenter, Phys. Rev. **86**, 552 (1952).

<sup>7</sup> T. Wainwright and G. Parzen, Phys. Rev. **92**, 1129 (1953).

<sup>8</sup> W. Kohn and N. Rostoker, Phys. Rev. **94**, 1111 (1954).

<sup>9</sup> B. Schiff, Proc. Phys. Soc. (London) **A67**, 2 (1954).

<sup>10</sup> H. Brooks, Phys. Rev. **91**, 1027 (1953).

<sup>11</sup> E. Brown and J. A. Krumhansl, Phys. Rev. **109**, 30 (1958).

<sup>12</sup> W. Prokofjew, Z. Physik **58**, 255 (1929).

<sup>13</sup> An error exists in the potential published by Seitz in reference 2. The potential is given correctly by Kohn and Rostoker in reference 8.

<sup>14</sup> J. Callaway, Phys. Rev. **103**, 1219 (1956).

<sup>15</sup> N. F. Mott, Phil. Mag. **44**, 187 (1953).

<sup>16</sup> D. Tomboulian, in *Handbuch der Physik* (Springer Verlag, Berlin, 1956), Vol. 30, p. 246. See also D. E. Bedo and D. H. Tomboulian, Phys. Rev. **109**, 35 (1958).

TABLE I. Fourier coefficients of the potential given as a function of  $n^2 = (ak/2\pi)^2$ .

$n^2$	$V_{n^2}$	$n^2$	$V_{n^2}$	$n^2$	$V_{n^2}$
0	-1.00221	22	-0.02724	42	-0.01217
2	-0.18090	24	-0.02917	44	-0.01381
4	-0.04155	26	-0.02830	46	-0.01466
6	-0.05866	28	-0.02518	48	-0.01523
8	-0.07491	30	-0.02133	50	-0.01518
10	-0.06461	32	-0.01750	52	-0.01440
12	-0.04705	34	-0.01316	54	-0.01317
14	-0.02812	36	-0.01113	56	-0.01208
16	-0.01998	38	-0.01051		
18	-0.02038	40	-0.01101		
20	-0.02337				

The orthogonalized plane wave method, used in this calculation, has been thoroughly discussed in a number of papers,<sup>17-19</sup> and it is not necessary to repeat this material here.<sup>20</sup> The notation used below is that of reference 18. The Fourier coefficients of the crystal potential, defined by

$$V(\mathbf{k}) = \Omega_0^{-1} \int_{\Omega} e^{i\mathbf{k}\cdot\mathbf{r}} V(\mathbf{r}) d^3r,$$

where  $\mathbf{k}$  is proportional to a reciprocal lattice vector,  $\Omega_0$  is the volume of the atomic cell, and  $V(\mathbf{r})$  is the potential within one cell, are tabulated in Table I. The wave function of the core 1s state required in the application of the OPW method, was determined by numerical integration. The energy of the core state was found to be  $-3.765$  Rydbergs. This result differs considerably from that of Wainwright and Parzen,<sup>7</sup> and is presumably more accurate. The orthogonality coefficients  $\mu_{jk}$  which were used are defined by

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

where  $\phi_j$  is the wave function of an electron in state  $j$ ; these coefficients are given in Table II.

### RESULTS AND DISCUSSION

The energies of twenty-four states at the points  $\Gamma$ ,  $H$ ,  $N$ , and  $P$  of the Brillouin zone (Fig. 1) were

TABLE II. The orthogonality coefficients as a function of  $n^2$ .

$n^2$	$\mu_{(1s)k}$	$n^2$	$\mu_{(1s)k}$
0	0.32905	10	0.050408
2	0.17958	12	0.039928
4	0.11676	14	0.033101
6	0.083317		
8	0.062964		

<sup>17</sup> C. Herring, Phys. Rev. **57**, 1169 (1940).

<sup>18</sup> J. Callaway, Phys. Rev. **97**, 933 (1955).

<sup>19</sup> T. O. Woodruff, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 4, p. 367.

<sup>20</sup> Further details of the calculation may be found in M. L. Glasser, Master's thesis, University of Miami, 1957 (unpublished).

TABLE III. Lowest energy states in lithium (in Rydbergs). The quantity  $n^2 = (ak/2\pi)^2$ , where  $\mathbf{k}$  is the wave vector of the lowest plane wave in each representation, is also given. The two lowest values for each state are given and compared with Schiff's values.

Representation	Degen-eracy	Order of determinant	$n^2$	No. of waves	Energies (in Rydbergs)		Lowest value (Schiff <sup>a</sup> )
					Two lowest values (this work)		
<i>s</i> -like states							
$\Gamma_1$	1	8	0	135	-0.6863	1.8786	-0.6148
$N_1$	1	4	0.5	18	-0.176	0.871	-0.114
$P_1$	1	4	0.75	40	0.330	2.75	
$H_1$	1	4	1.0	62	0.571	2.60	0.550
<i>p</i> -like states							
$N_1'$	1	13	0.5	72	-0.404	1.433	-0.304
$P_4$	3	13	0.75	80	-0.189	1.338	
$H_{15}$	3	9	1.0	92	-0.092	1.739	-0.120
$N_3'$	1	4	1.5	20	0.274	2.11	
$N_4'$	1	4	1.5	20	0.475	1.37	
$\Gamma_{15}$	3	4	2.0	42	0.617	2.71	
<i>D</i> -like states							
$H_{12}$	2	4	1.0	54	0.227	3.52	0.202
$N_2$	1	4	1.5	28	0.524	2.44	
$\Gamma_{25'}$	3	4	2.0	48	0.854	4.35	
$\Gamma_{12}$	2	4	2.0	54	1.146	2.84	
$N_4$	1	4	2.5	28	1.477	2.49	
$P_3$	2	3	2.75	36	1.603	3.57	
$H_{25}$	3	4	3.0	56	1.84	3.61	
$N_2$	1	4	3.5	28	2.21	3.35	
<i>F</i> -like states							
$\Gamma_{25'}$	3	3	1.0	48	1.156	4.85	
$H_2$	1	3	3.0	56	1.73	7.18	
$P_5$	3	3	2.75	36	1.86	3.65	
$N_2$	1	2	3.5	24	2.40		
$H_{25}$	3	3	5.0	48	3.70	4.00	
$\Gamma_{2'}$	1	3	6.0	32	4.49	10.18	

<sup>a</sup> See reference 9.

calculated; the results and sizes of the determinants used are listed in Table III. The relative positions of the states are shown in Fig. 2. Fourth-order determinants were solved to determine the energy in most (thirteen) cases. The four states bounding the lowest band were studied in much higher order as indicated in Table III. Some of the states of higher energy were carried only to third, and in one case, second order. The relative position of the latter states should not change if larger determinants be used and since these states are far above the occupied parts of the bands, a more careful calculation is not necessary. The convergence of the lowest eigenvalue for  $\Gamma_1$  is shown in Table IV. It is to be noted that the convergence of  $\Gamma_1$  is very good and gives

TABLE IV. Lowest eigenvalues according to determinantal order for  $\Gamma_1$ .

Order	Lowest $E$
1	-0.6667
2	-0.6667
3	-0.6796
4	-0.6859
8	-0.6863

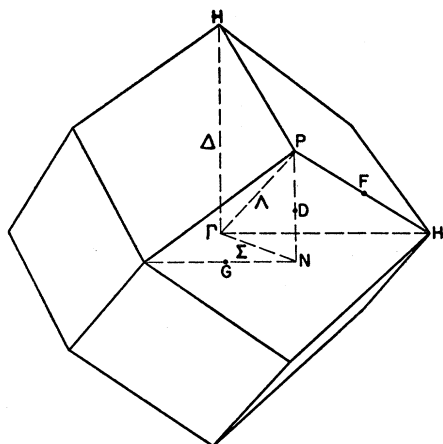


FIG. 1. Brillouin zone for body-centered cubic lattice.

excellent agreement with the value  $-0.6832$  Rydbergs obtained by the cellular method.<sup>5</sup> The states at  $N$  and  $P$  cannot be expected to converge as well as those at  $\Gamma$  and  $H$  because of the lesser symmetry and hence the smaller number of OPW's used in the expansions at these points. Also  $p$ -like states will not converge as fast as the  $s$ -like states.

Our results agree fairly well with those of Schiff; some difference is expected because of the difference in potentials. The main feature of both sets of results is that the states at the zone faces are predominantly  $p$ -like, the lowest state at  $N$  being the  $p$  state  $N_1'$  rather than the  $s$  state  $N_1$ . The difference ( $N_1' - N_1$ ) obtained is  $0.228$  ry as compared with Schiff's value,  $0.190$  ry. The calculation does not support Mott's conjecture,<sup>15</sup> and leaves the problem of explaining the x-ray emission still unresolved.

It can be observed from Table IV that the relative order of levels of a particular type at symmetry points corresponds to the kinetic energy of the lowest plane wave appearing in the expansion of the wave function. That is to say, the order of levels in a particular band is the same as for the corresponding free-electron band of the same symmetry. This result was also obtained

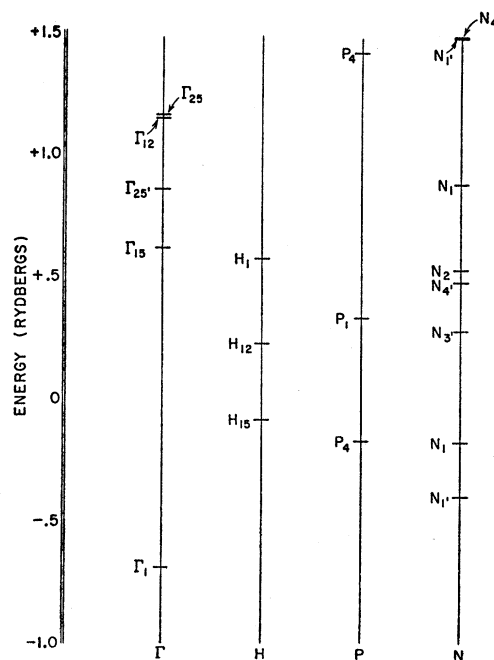


FIG. 2. Order of the energy levels at the four symmetry points. Levels up to 1.5 Rydbergs are shown.

for potassium,<sup>14</sup> cesium,<sup>21</sup> and iron.<sup>22</sup> Of course, the relation of bands of different symmetries is dependent on the potential. For example, we find in lithium that the  $p$  levels are relatively much closer to the Fermi surface than they are in potassium. In the latter element,  $d$  levels play a much greater role. It is also worth noting that the bands in lithium tend to be considerably wider than in potassium and cesium. This is consistent with the smaller lattice constant.

#### ACKNOWLEDGMENT

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<sup>21</sup> J. Callaway and E. L. Hasse, Phys. Rev. **108**, 217 (1957).

<sup>22</sup> J. Callaway, Phys. Rev. **99**, 500 (1955).