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Energy-Band Structure of Lithium Atoms in the Diamond Lattice.

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Summary. — A hypothetical crystal of lithium atoms in the diamond lattice is considered. The value of the energies at the special points of the reduced zone with $\mathbf{k} = (0, 0, 0)$, $\mathbf{k} = 2\pi a^{-1}(1, 0, 0)$, $\mathbf{k} = 2\pi a^{-1}(\frac{1}{2}, 0, 0)$ and $\mathbf{k} = 2\pi a^{-1}(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ are calculated by the Orthogonalized Plane Wave method using the Wigner-Seitz crystal potential and the same electron density as in metallic lithium. The curves of energy versus \mathbf{k} are drawn in the $[1, 0, 0]$ and $[1, 1, 1]$ directions. The energy bands so obtained are compared with the energy bands of diamond evaluated by F. HERMAN. The relative positions of the energy bands appear to be the same in the two cases and this points to the possibility that the energy-band structure is mainly determined by the symmetry of the lattice. A comparison with metallic lithium gives a higher cohesive energy in the case of the pseudolattice, when one neglects electrostatic, exchange and correlation terms.

1. - Introduction.

The idea of studying the energy bands of pseudo-crystals, *i.e.* of lattices of atoms which are known to crystallize in some other lattice, was first suggested by F. SEITZ as a tool to study the influence of lattice symmetry and atomic potential on the energy-band structure.

CASELLA ⁽¹⁾ estimated the energy bands of carbon atoms in the face centered cubic lattice by the Orthogonalized Plane Wave method. The results he obtained are considerably different from the results HERMAN ⁽²⁾ obtained in diamond; in particular at the point Γ ($\mathbf{k} = 0$) the position of the energy-

⁽¹⁾ R. CASELLA: *Phys. Rev.*, **109**, 54 (1958).

⁽²⁾ F. HERMAN: *Phys. Rev.*, **88**, 1210 (1952); **93**, 1214 (1954).

states $\Gamma_{25'}$ and Γ_{15} are reversed. A calculation of the energy bands of sodium atoms in the diamond structure was performed by F. BASSANI⁽²⁾ by the O.P.W. method and the results displayed a strict similarity with the energy bands of silicon⁽⁴⁾.

A calculation of the energy-band structure of lithium atoms in a diamond lattice having the same atomic volume as metallic lithium is presented in this paper. The O.P.W. method is adopted because of the advantage of evaluating several energy bands and because of its successful application both to metals and to insulators.

In Section 2 an outline of the method is given in a form particularly suitable for the diamond symmetry. The energy states of the empty lattice are related to the irreducible representations of the group of the wave vector to which they belong. The crystal symmetry combinations of plane waves are also given at one of the points of interest.

The parameters which enter the actual calculations are discussed in Section 3 and numerical results for them are presented.

In Section 4 the results for the energy states of the lowest bands are given at four symmetry points of the reduced zone. A comparison is made with the energy bands in diamond and in metallic lithium in Section 5.

2. - General method and symmetry analysis.

The method of orthogonalized plane waves was introduced by HERRING⁽⁵⁾ and was recently discussed by many authors⁽⁶⁾. It is actually a variational procedure in which linear variation trial functions for valence and conduction states are formed with plane waves made orthogonal to the Bloch functions constructed from the atomic core states. For a certain value of the wave vector \mathbf{k} , inside the reduced zone, the plane waves to be considered are of the type $\exp[i(\mathbf{k} + \mathbf{h}_i) \cdot \mathbf{r}]$, where \mathbf{h}_i is any vector of the reciprocal lattice. These plane waves are the eigenfunctions of the «empty lattice», i.e. of a lattice with a constant potential, as classified in the reduced zone scheme.

From the set of plane waves belonging to a given value of $|\mathbf{k} + \mathbf{h}_i|^2$, linear combinations are constructed that transform according to a given column of a certain irreducible representation of the group of the \mathbf{k} vector. In this way the number of undetermined coefficients in the trial function is

(2) F. BASSANI: *Journ. of Chem. and Phys. of Solids* (to appear).

(4) T. O. WOODRUFF: *Phys. Rev.*, **103**, 1159 (1956); F. BASSANI: *Phys. Rev.*, **108**, 263 (1957).

(5) C. HERRING: *Phys. Rev.*, **57**, 1169 (1940).

(6) J. CALLAWAY: *Phys. Rev.*, **97**, 933 (1955); T. O. WOODRUFF: *Solid State Physics*, edited by F. SEITZ and D. TURNBULL, vol. 4, 367 (1957).

greatly reduced and convergence is obtained to energy states that are automatically classified.

We shall estimate the energy levels at four points of the reduced zone: the point Γ with $\mathbf{k} = 0$, the point X with $\mathbf{k} = (2\pi/a)(1, 0, 0)$, the point $A(\frac{1}{2})$, with $\mathbf{k} = (2\pi/a)(\frac{1}{2}, 0, 0)$ and the point L with $\mathbf{k} = (2\pi/a)(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. For each of these points the lowest eigenvalues of the « empty lattice » are listed in Table I with the number of plane waves and the irreducible representations of the group of the wave vector belonging to each eigenstate. The symbols used are those introduced by BOUCKAERT, SMOLUCHOWSKY and WIGNER (7) and by HERRING (8).

TABLE I. - Classification of the « empty lattice » eigenvalues.

	Number of plane waves	Empty lattice eigenvalues in units $(\hbar^2/2m)(4\pi^2/a^2)$	Irreducible representations
Point Γ $\mathbf{k} = 0$	1	$(0, 0, 0)^2$	Γ_1
	8	$(1, 1, 1)^2$	$\Gamma_1 \Gamma_{25'} \Gamma_{15} \Gamma_2$
	6	$(2, 0, 0)^2$	$\Gamma_{25'} (\Gamma_{12'}) \Gamma_2$
	12	$(2, 2, 0)^2$	$\Gamma_1 \Gamma_{25'} \Gamma_{15} \Gamma_{12} \Gamma_{25}$
Point X $\mathbf{k} = 2\pi/a$ $(1, 0, 0)$	2	$(1, 0, 0)^2$	X_1
	4	$(0, 1, 1)^2$	$X_1 X_4$
	8	$(1, 2, 0)^2$	$X_1 X_2 X_3 X_4$
	8	$(2, 1, 1)^2$	$2X_1 X_3 X_4$
Point $A(\frac{1}{2})$ $\mathbf{k} = 2\pi/a$ $(\frac{1}{2}, 0, 0)$	1	$(\frac{1}{2}, 0, 0)^2$	A_1
	4	$(\frac{1}{2}, 1, 1)^2$	$A_1 A_2 A_5$
	1	$(\frac{3}{2}, 0, 0)^2$	A_2
	4	$(\frac{1}{2}, 2, 0)^2$	$A_2 A_3 A_4$
	4	$(\frac{3}{2}, 1, 1)^2$	$A_1 A_2 A_5$
	4	$(\frac{3}{2}, 2, 0)^2$	$A_1 A_2 A_5$
	1	$(\frac{5}{2}, 0, 0)^2$	A_2
Point L $\mathbf{k} = 2\pi/a$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	2	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})^2$	$L_1 L_2$
	6	$(\frac{3}{2}, \frac{1}{2}, \frac{1}{2})^2$	$L_1 L_2 L_3 L_3$
	6	$(\frac{1}{2}, \frac{3}{2}, \frac{3}{2})^2$	$L_1 L_2 L_3 L_3$
	6	$(\frac{5}{2}, \frac{1}{2}, \frac{1}{2})^2$	$L_1 L_2 L_3 L_3$
	2	$(\frac{3}{2}, \frac{3}{2}, \frac{3}{2})^2$	$L_1 L_2$

(7) L. P. BOUCKAERT, R. SMOLUCHOWSKI and E. WIGNER: *Phys. Rev.*, **50**, 58 (1936).

(8) C. HERRING: *Journ. Franklin Inst.*, **233**, 525 (1942); see also, W. DÖRING and V. ZEHLER: *Ann. der Phys.*, **vi**, **13**, 214 (1953).

Linear combinations of plane waves (L.C.P.W.) belonging to a given row of any of the irreducible representations are derived from the sets of plane waves indicated in Table I by the standard method of projection operators⁽⁹⁾. Typical crystal symmetry L.C.P.W. at the points Γ and X are given in Table II of HERMAN's paper⁽²⁾. At the point L the C.S.L.C.P.W. are the same as in the face centered cubic lattice; a few of them are reported in Table V of CASELLA's paper⁽¹⁾. The C.S.L.C.P.W. we have used at the point $\Delta(\frac{1}{2})$ are given in Table II.

TABLE II. - Crystal symmetry linear combinations of plane waves at the point $\mathbf{k} = (2\pi/a)(\frac{1}{2}, 0, 0)$.

$(2\pi/a)^{-1}(\mathbf{k} + \mathbf{h})$	Δ_1	Δ_2	Δ_1	Δ_2	Δ_5^I	Δ_5^{II}
$(\frac{1}{2}, 0, 0)$	+1	-	-	-	-	-
$(\frac{1}{2}, 1, 1)$	+1	+1	-	-	+1	-1
$(\frac{1}{2}, \bar{1}, \bar{1})$	-1	-1	-	-	+1	-1
$(\frac{1}{2}, \bar{1}, 1)$	+1	-1	-	-	-1	-1
$(\frac{1}{2}, 1, \bar{1})$	+1	-1	-	-	+1	+1
$(\frac{3}{2}, 0, 0)$	-	+1	-	-	-	-
$(\frac{3}{2}, 1, 1)$	+1	+1	-	-	+1	-1
$(\frac{3}{2}, \bar{1}, \bar{1})$	-1	-1	-	-	+1	-1
$(\frac{3}{2}, \bar{1}, 1)$	-1	+1	-	-	+1	+1
$(\frac{3}{2}, 1, \bar{1})$	-1	+1	-	-	-1	-1
$(\frac{1}{2}, 2, 0)$	-	+1	+1	-	0	-1
$(\frac{1}{2}, \bar{2}, 0)$	-	-1	-1	-	0	-1
$(\frac{1}{2}, 0, 2)$	-	+1	-1	-	+1	0
$(\frac{1}{2}, 0, \bar{2})$	-	-1	+1	-	+1	0
$(\frac{5}{2}, 0, 0)$	-	+1	-	-	-	-
$(\frac{5}{2}, 2, 0)$	+1	-	-	+1	+1	0
$(\frac{5}{2}, \bar{2}, 0)$	-1	-	-	-1	+1	0
$(\frac{5}{2}, 0, 2)$	+1	-	-	-1	0	-1
$(\frac{5}{2}, 0, \bar{2})$	-1	-	-	+1	0	-1

In the first column the P.W.'s are indicated by the components of the vector $(2\pi/a)^{-1}(\mathbf{k} + \mathbf{h})$. The linear combination from a set of plane waves with given value of $|\mathbf{k} + \mathbf{h}|$ can be obtained from the table above multiplying each plane wave by the coefficient listed on the same row and in the column of the irreducible representation of interest. The two basis functions of the two-dimensional irreducible representation Δ_5 are indicated by Δ_5^I and Δ_5^{II} .

⁽⁹⁾ L. D. LANDAU and E. M. LIFSHITZ: *Quantum Mechanics* (translated) (London, 1958), p. 336; G. F. KOSTER: *Notes on Group Theory*, in *Technical Report No. 8-M.I.T.* (1956).

The problem of finding the energy eigenvalues E corresponding to every irreducible representation thus reduces to that of diagonalizing a secular determinant whose elements are sums of matrix elements of the operator $(H - E)$ between the plane waves of two C.S.L.C.P.W. orthogonalized to the core states. The order of the secular determinant is fixed by the number of C.S.L.C.P.W. used. If the crystal one-electron potential is chosen to be a sum of suitable atomic potentials V_a centered at the atomic sites, the matrix element of $(H - E)$ between the O.P.W.'s having wave vectors $\mathbf{k} + \mathbf{h}_i$ and $\mathbf{k} + \mathbf{h}_j$ for a crystal having diamond symmetry and only $(1s)$ core states has the form:

$$(1) \quad \langle \mathbf{k} + \mathbf{h}_i | H - E | \mathbf{k} + \mathbf{h}_j \rangle = [(\mathbf{k} + \mathbf{h}_i)^2 - E] \delta_{ij} + \\ + \cos[(\mathbf{h}_i - \mathbf{h}_j) \cdot \mathbf{d}] [V(|\mathbf{h}_i - \mathbf{h}_j|) - (E_{1s} - E) A_{1s}^*(|\mathbf{k} + \mathbf{h}_i|) A_{1s}(|\mathbf{k} + \mathbf{h}_j|)].$$

The vector \mathbf{d} has components $a/4$ (1, 1, 1), a being the lattice constant; $V(|\mathbf{h}_i - \mathbf{h}_j|)$ is the Fourier coefficient of the potential defined by:

$$(2) \quad V(|\mathbf{h}_i - \mathbf{h}_j|) = \Omega_0^{-1} \int V_a(\mathbf{r}) \exp[-i(\mathbf{h}_i - \mathbf{h}_j) \cdot \mathbf{r}] d^3 \mathbf{r},$$

where Ω_0 is the volume per atom; E_{1s} is the energy of the core state $(1s)$; finally the A_{1s} are the orthogonality coefficients defined by:

$$(3) \quad A_{1s}(|\mathbf{k} + \mathbf{h}_i|) = \Omega_0^{-\frac{1}{2}} \int \varphi_{1s}^*(\mathbf{r}) \exp[i(\mathbf{k} + \mathbf{h}_i) \cdot \mathbf{r}] d^3 \mathbf{r},$$

where φ_{1s} is the atomic wave function. It is assumed that the Bloch sums for the core states are eigenfunctions of the same hamiltonian H as the valence and conduction states.

3. - Calculation of the parameters.

From Section 2 it can be seen that the parameters needed for the application of the O.P.W. method are: the lattice constant a , the core state energy E_{1s} , the orthogonality coefficients given by (3) and the Fourier coefficients of the potential given by (2). For the present calculation it is assumed that the atomic volume Ω_0 of the hypothetical lithium in the diamond structure is the same as the atomic volume of actual body-centered cubic lithium. This seemed a reasonable choice also because of the experimental evidence that allotropic transformations cause only slight density variations. The lattice constant of metallic lithium extrapolated at 0 °K is taken as 6.5183 in atomic

units; hence the atomic volume is $\Omega_0 = 138.47$ a.u. and the lattice constant in the diamond lattice turns out to be $a = 10.347$ a.u. For the choice of the potential we have followed a recent calculation of energy levels in metallic lithium performed by GLASSER and CALLAWAY⁽¹⁰⁾. They have used the semi-empirical free atom potential constructed by SEITZ⁽¹¹⁾ and have found by numerical integration a core energy $E_{1s} = -3.765$ Ry and its appropriate wave function. We have taken the same value for E_{1s} and have approximated the wave function by the sum of two exponentials $\varphi_{1s}(\mathbf{r}) = A \exp[-\alpha r] + B \exp[-\beta r]$; the parameters A , B , α , β were adjusted so as to obtain all the orthogonality coefficients given by GLASSER and CALLAWAY to within 1%. The error so introduced is probably less than the error involved in using atomic functions in the Bloch sum, neglecting overlap. The satisfactory values of the parameters were found to be $A = 6.422$; $B = 2.171$; $\alpha = 3.019$; $\beta = 1.907$; it was verified that with these values the approximated function φ_{1s} was automatically normalized to unity within 1%. The orthogonality coefficients obtained from formula (3) by using this analytical approximation for $\varphi_{1s}(\mathbf{r})$ are listed in Table III.

TABLE III. - Orthogonality coefficients between the 1s core wave function and the plane waves.

$(a^2/4\pi^2)(\mathbf{k}+\mathbf{h})^2$	$A_{1s}(\mathbf{k}+\mathbf{h})$	$(a^2/4\pi^2)(\mathbf{k}+\mathbf{h})^2$	$A_{1s}(\mathbf{k}+\mathbf{h})$
0	0.329 01	4	0.199 55
$\frac{1}{4}$	0.317 01	$\frac{17}{4}$	0.194 41
$\frac{3}{4}$	0.295 17	$\frac{19}{4}$	0.184 78
1	0.285 21	5	0.180 26
2	0.250 59	6	0.163 90
$\frac{9}{4}$	0.243 05	$\frac{25}{4}$	0.160 19
$\frac{11}{4}$	0.229 09	$\frac{27}{4}$	0.153 18
3	0.222 61	8	0.137 71

The crystal potential was constructed following the Wigner-Seitz method as in metallic lithium. In the diamond structure the atomic polyhedra are truncated tetrahedra rather different from spheres. In order to obtain the Fourier coefficients of the potential, however, the integral (2) has been extended over the atomic sphere of radius $r_s = (3\Omega_0/4\pi)^{1/3} = 3.2094$ a.u. Overlapping of nearest spheres corrects in the right way the atomic spherically symmetric

⁽¹⁰⁾ M. L. GLASSER and J. CALLAWAY: *Phys. Rev.*, **109**, 1541 (1958).

⁽¹¹⁾ F. SEITZ: *Phys. Rev.*, **47**, 400 (1935). The potential for Lithium is correctly tabulated by W. KOHN and N. ROSTOKER: *Phys. Rev.*, **94**, 1111 (1954).

potential about each nucleus. The Fourier coefficients calculated from eq. (2) by numerical integration of the Seitz potential are listed in Table IV.

TABLE IV. - Fourier coefficients of the crystal potential (in Rydbergs).

$(a^2/4\pi^2) \mathbf{h} ^2$	$V(\mathbf{h})$	$(a^2/4\pi^2) \mathbf{h} ^2$	$V(\mathbf{h})$
0	-1.0022	19	-0.07277
3	-0.38012	24	-0.06856
8	-0.06216	27	-0.05799
11	-0.04070	32	-0.03813
16	-0.06307		

4. - Results.

The values given in Section 3 for the various parameters can be substituted in the matrix elements of the secular determinant described in Section 2. The various roots of each of the resulting secular equations converge to the successive eigenvalues of the Hamiltonian as has been proven by MACDONALD (12). The determinantal equations of third, fourth and fifth order have been solved with the electronic computer of the Engineering School in Milan. The results obtained for the lowest energy levels at different stages of approximation are given in Table V.

It can be seen from Table V that the convergence is not very good with the number of plane waves we have included. This applies particularly to the eigenstates which are automatically orthogonal to the s states by reasons of symmetry, as it was found by F. HERMAN in the case of diamond. Nevertheless we feel confident that the present approximation is sufficiently accurate to determine the energy-band structure in the reduced zone. Adding plane waves of higher energy would lower all levels with-

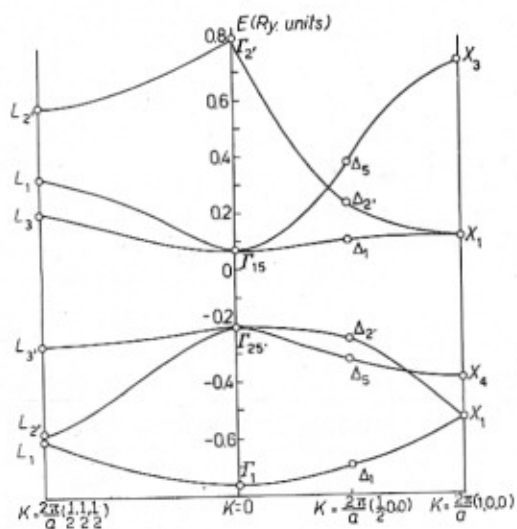


Fig. 1. - Profile of some energy bands of lithium atoms in the diamond structure in the $[1, 0, 0]$ and $[1, 1, 1]$ directions.

(12) J. K. L. MACDONALD: *Phys. Rev.*, **43**, 830 (1933).

out probably changing their relative positions. This was shown to be the case for the Γ point in diamond ⁽²⁾, silicon ⁽⁴⁾ and germanium ⁽¹³⁾.

The energy values given in Table V, the compatibility relations and the non-crossing rule allow to draw the profile of the lowest energy bands along the symmetry directions $[1, 0, 0]$ and $[1, 1, 1]$, which is presented in Fig. 1. Naturally this procedure leaves uncertain some of the detailed features of the energy bands such as the curvatures, but we have preferred not to use an interpolation scheme, since we are mainly interested in the sequence of the energy bands and in their qualitative features.

TABLE V. - Energies at the points $\mathbf{k}=0$ $\mathbf{k}=2\pi a^{-1}(1, 0, 0)$, $\mathbf{k}=2\pi a^{-1}(\frac{1}{2}, 0, 0)$, $\mathbf{k}=2\pi a^{-1}(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (in Rydbergs).

	Γ_1	$\Gamma_{25'}$	Γ_{15}	Γ_2	—	—
E_1	-0.667	0.166	0.166	0.828	—	—
E_2	-0.757	-0.163	0.068	0.825	—	—
E_3	-0.771	-0.206	—	—	—	—
	$X_1(1)$	X_4	$X_1(2)$	X_3	—	—
E_1	-0.356	-0.203	—	0.904	—	—
E_2	-0.439	-0.382	0.208	0.732	—	—
E_3	-0.455	-0.392	0.186	—	—	—
E_4	-0.503	—	0.121	—	—	—
E_5	-0.534	—	0.111	—	—	—
	$\Delta_1(1)$	$\Delta_5(1)$	$\Delta_1(1)$	$\Delta_1(2)$	$\Delta_2(2)$	$\Delta_5(2)$
E_1	-0.591	-0.110	0.053	—	—	—
E_2	-0.647	-0.243	-0.127	0.253	0.375	0.627
E_3	-0.688	-0.262	-0.142	0.138	0.316	0.385
E_4	-0.701	-0.320	-0.237	0.099	0.233	0.376
E_5	—	—	-0.250	—	—	—
	$L_1(1)$	$L_2(1)$	L_2	L_3	$L_1(2)$	$L_2(2)$
E_1	-0.370	-0.510	-0.166	0.314	—	—
E_2	-0.427	-0.551	-0.223	0.220	0.477	0.668
E_3	-0.565	-0.553	-0.268	0.204	0.476	0.666
E_4	-0.574	-0.569	—	—	0.385	0.662
E_5	-0.598	-0.589	—	—	0.327	0.577

The subscripts attached to E indicate the order of the secular determinant used in obtaining the energies.

⁽¹³⁾ F. HERMAN: *Physica*, **20**, 801 (1954).

5. - Conclusions.

First it seems of interest to compare Fig. 1 with Fig. 1 of HERMAN's paper on the diamond energy-band calculation with the O.P.W. method. There the crystal potential is taken as a sum of carbon atomic potentials extending to infinity, furthermore the carbon atoms are more closely packed than the lithium atoms in the pseudo-crystal, the lattice constant in diamond being 6.73 a.u. to be compared with our 10.347 a.u. In spite of these differences the sequence of the energy bands at each point is the same in both cases and their relative positions at different points of the reduced zone are also preserved. The maximum of the valence bands and the minimum of the conduction bands occur at the center of the zone, the energy gap being larger in the case of diamond (0.45 Ry to 0.27 Ry). This last result is due to the smaller electron density in the pseudo-crystal than in diamond, which results in a smaller width of the energy bands consistently with the fact that in the « empty lattice » the eigenvalues are closer when the lattice constant is larger. A comparison with Herman's data also shows that in our case the states I_1 and I_2 are shifted to higher energies with respect to I_{15} and I_{25} . This can be attributed to the larger effect of the (1s) core state, whose wave function is more spread out in lithium than in carbon.

These results seem to point to the possibility discussed by T.O. WOODRUFF⁽⁶⁾ and by J. CALLAWAY⁽¹⁴⁾ that the sequence of the energy bands is independent of the specific atomic potential and can be predicted by the lattice symmetry and the atomic structure.

A calculation analogous to the one reported here was recently performed by F. BASSANI⁽⁵⁾ on sodium atoms in the diamond lattice. The energy bands which result in that case display a strict similarity with the energy bands of silicon. They both differ from the bands in diamond and in our pseudo-crystal because the energy at I_{15} lies higher than at $X_1(2)$. This may be attributed to the presence of the (2p) core states in sodium and silicon, since they raise the energies at I_{15} and I_{25} more than at $X_1(2)$. In fact the leading crystal symmetry combination of plane waves which corresponds to the eigenstate $X_1(2)$ is orthogonal to the p states and consequently, in the perturbation approach described in Appendix A, the eigenvalue is insensitive to the effect of the p core states, up to the second order.

It might be of interest to compare our results with the energy bands in metallic lithium^(10,15). In that case there is no possibility for an energy gap due to the order of appearance of the energies at the points $k=0$ and

(14) J. CALLAWAY: *Phys. Rev.*, **103**, 1219 (1956).

$\mathbf{k} = 2\pi a^{-1} (1, 0, 0)$ in the b.c.c. lattice. The value of the energy at Γ_1 lies lower in our case than in lithium. The value of the effective mass obtained averaging the values calculated by fitting parabolas to the points given in Fig. 1 for the lower band is about the same as in metallic lithium⁽¹⁵⁾.

For these reasons, if one neglects the contribution to the cohesive energy due to electrostatic interactions, exchange and correlation effects, the cohesive energy should be greater in our case than in metallic lithium by about 0.1 Ry. Very likely this means that in the diamond structure electrostatic interaction, exchange and correlation effects do not compensate as in the body centered cubic structure⁽¹⁶⁾.

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APPENDIX

The determination of the crystal eigenstates by the O.P.W. method may be regarded approximately as a perturbation procedure on the « empty lattice » eigenstates.

A crystal eigenfunction $\psi_i^\alpha(\mathbf{k}, \mathbf{r})$ belonging to the α irreducible representation of the group of \mathbf{k} can be expanded as follows:

$$(A.1) \quad \psi_i^\alpha(\mathbf{k}, \mathbf{r}) = S_i(\mathbf{k}, \mathbf{r}) - \sum_l \langle \Phi_l | S_i \rangle \Phi_l(\mathbf{k}, \mathbf{r}) + \\ + \sum_j a_j S_j(\mathbf{k}, \mathbf{r}) - \sum_l \sum_j a_j \langle \Phi_l | S_j \rangle \Phi_l(\mathbf{k}, \mathbf{r}) + \dots$$

Here $S_j(\mathbf{k}, \mathbf{r})$ are the linear combinations of plane waves belonging to the α irreducible representation; the unperturbed wave function $S_i(\mathbf{k}, \mathbf{r})$ belongs to an eigenstate of the « empty lattice », whose degeneracy has been fully removed by the symmetry analysis. The Bloch wave function of the l core state has been indicated by $\Phi_l(\mathbf{k}, \mathbf{r})$. The expansion coefficients a_j and the square moduli of the « orthogonality coefficients » $\langle \Phi_l | S_i \rangle$ will be considered small quantities, higher order terms having been omitted in expansion (A.1).

The crystal Hamiltonian H , in atomic units, is:

$$(A.2) \quad H = -\nabla^2 + V(0) + V_1 = H_0 + V_1.$$

In this formula $V(0)$ is the Fourier coefficient of the crystal potential V for $\mathbf{k} = 0$, i.e. the space average of V , and $V_1 = V - V(0)$ shall be considered as

⁽¹⁵⁾ R. H. PARMENTER: *Phys. Rev.*, **86**, 552 (1952).

⁽¹⁶⁾ F. SEITZ: *Modern Theory of Solids* (New York, 1940), p. 364.

a perturbing potential. Let the eigenvalue of H_0 belonging to the eigenfunction S_j be W_j ; let the first and second order corrections to the unperturbed energy W_i be W'_i and W''_i . By substituting expansion (A.1) into the equation:

$$(A.3) \quad H\psi_i^e(\mathbf{k}, \mathbf{r}) = (W_i + W'_i + W''_i + \dots)\psi_i^e(\mathbf{k}, \mathbf{r}),$$

and using the techniques of perturbation theory one obtains to first order:

$$(A.4) \quad \langle S_j | V_1 | S_i \rangle - \sum_j \langle \Phi_i | S_i \rangle \langle S_j | H | \Phi_i \rangle + a_j W_j = \\ = W'_i \delta_{ij} - W_i \sum_j \langle \Phi_i | S_i \rangle \langle S_j | \Phi_i \rangle + a_j W_j.$$

As usual, one can assume for the core states:

$$(A.5) \quad H\Phi_i(\mathbf{k}, \mathbf{r}) = E_i \Phi_i(\mathbf{k}, \mathbf{r}),$$

where E_i is the atomic value. Then from (A.4):

$$(A.6) \quad W'_i = \langle S_i | V_1 | S_i \rangle + \sum_j (W_j - E_i) |\langle \Phi_i | S_i \rangle|^2.$$

The values of the coefficients a_j can be obtained from formula (A.4) for $i \neq j$. The value of the coefficient a_i is found to be $\frac{1}{2} \sum_j |\langle \Phi_i | S_i \rangle|$ by requiring normalization of $\psi_i^e(\mathbf{k}, \mathbf{r})$ to first order.

Proceeding to second order one finds:

$$(A.7) \quad W''_i = \sum_j (W_j - W_i)^{-1} \langle S_j | V_1 | S_i \rangle - \sum_j (E_i - W_j) \langle \Phi_i | S_i \rangle \langle S_j | \Phi_i \rangle^2 + \\ + \sum_j |\langle \Phi_i | S_i \rangle|^2 W'_j.$$

It can be seen from formulae (A.6) and (A.7) that the core wave function $\Phi_i(\mathbf{k}, \mathbf{r})$ has no effect on the energy when $\langle \Phi_i | S_i \rangle = 0$.

RIASSUNTO

Si considera un ipotetico cristallo costituito di atomi di litio nella struttura del diamante e avente la stessa densità di elettroni del litio metallico. Usando un potenziale del tipo di Wigner e Seitz, si calcolano col metodo delle onde piane ortogonalizzate i valori delle energie nei punti speciali della zona ridotta con $\mathbf{k} = (0, 0, 0)$, $\mathbf{k} = 2\pi a^{-1}(1, 0, 0)$, $\mathbf{k} = 2\pi a^{-1}(\frac{1}{2}, 0, 0)$ e $\mathbf{k} = 2\pi a^{-1}(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ e si tracciano le curve dell'energia in funzione di \mathbf{k} nelle direzioni $[1, 0, 0]$ e $[1, 1, 1]$. Le bande di energia così ottenute sono paragonate con le bande di energia del diamante valutate da F. HERMAN. Il fatto che le posizioni relative delle bande risultino le stesse nei due casi indica la possibilità che la struttura delle bande di energia sia principalmente determinata dalla simmetria del reticolo. Dal confronto con il litio metallico, si trova che l'energia coesiva è maggiore nel caso dello pseudoreticolo, quando si trascurino i termini elettrostatici, di scambio e di correlazione.