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A Method for Obtaining Electronic Eigenfunctions and Eigenvalues in Solids with An Application to Sodium*

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As in the Wigner-Seitz and Slater cellular approximation it is assumed that the valence electron potential is spherically symmetrical within a lattice cell. Then the Schrödinger equation becomes separable in spherical coordinates so that the eigenfunction can be expanded in terms which are products of spherical harmonics and solutions to the radial equation. The method differs from the previous ones in that: (1) eigenfunctions belonging to special wave vectors are first constructed by suitable linear combinations of spherical harmonics so as to satisfy symmetry requirements and thus, essentially, including more terms in the expansion without increase in labor and (2) surface boundary conditions are satisfied exactly, in effect, at points which are more representative of the cell surface. The method was tested by applying it to the Shockley empty lattice (body centered cubic) for which the eigenvalues are known exactly. The lowest four eigenvalues belonging to the reduced wave vector (0,0,0) and the lowest three belonging to $(0,0,\pi/a)$ showed errors of one percent or less in energy using from two to four terms in the eigenfunction expansion. When applied to sodium results showed that electrons in the first few Brillouin zones are indeed very nearly free, having free electron energies within a few percent even at points near the center and corners of reduced wave vector space. Furthermore on the boundary of reduced wave vector space in the (0,0,1) direction there is no energy gap between the first and second Brillouin zone eigenvalues since they "stick together" at that and equivalent points.

INTRODUCTION

IN the W–S[1,2] cellular method because of the periodicity of the electron-potential it suffices to focus attention upon a single cell of the crystal lattice. Schrödinger one-electron solutions for the valence electrons are sought satisfying the *BC* (cell boundary conditions) imposed by symmetry and periodicity. The interactions of valence electrons with nuclei and core electrons of the cell are represented in this approximation by an ordinary, appropriately chosen, potential V. Because of high symmetry and the essentially neutral electrical nature of surrounding cells, their contribution to this potential is assumed to be zero.

In the interest of mathematical simplicity and justified[1,2] on grounds of high symmetry the potential, V, is assumed to have spherical symmetry within a cell. The Schrödinger equation then becomes separable in polar coordinates and the one-electron eigenfunction, ψ, can be expressed as

$$\psi=\Sigma_l A_l[\Sigma_m C_{lm} Y_l{}^m(\phi,\theta)]R_l(E,\rho) \qquad (1)$$

where the $Y_l{}^m$ are *SH* (surface spherical harmonics), and the $R_l(E,\rho)$ are the solutions to the radial equation with an energy parameter, E. The constant coefficients A_l, C_{lm} and the energy parameter E can all be chosen in principle so as to fit the appropriate *BC* at the surface of the cell. (The split between A_l and C_{lm} is of course largely arbitrary but convenient for some of the following.)

The labor without limit implied in (1) was reduced by Slater[3] to practical limits by the approximation of assuming all C_{lm}'s to be zero for l greater than a certain fixed value. Then, of course, the *BC* cannot be fitted over the entire surface of the *LC*. Slater therefore selects certain points on the surface of the *LC* at which he satisfies the *BC* by appropriate choice of the C_{lm}'s which are not assumed zero. The fitting is done in this way for any arbitrary wave vector[4] **k**. However, Shockley[5] has shown that Slater's procedure leads to large errors for an empty

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* The method and results were presented in condensed form at the New York Meeting of the American Physical Society, January 14–15, 1944.

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[1] A. Sommerfeld and H. Bethe, "Electronentheorie der Metalle," *Handbuch der Physik* (Verlagsbuchhandlung, Julius Springer, Berlin, 1933), Vol. 24/2; F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940); N. F. Mott and H. Jones, *Theory of Properties of Metals and Alloys* (Oxford Press, New York, 1936).

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

[3] J. C. Slater, Phys. Rev. **45**, 794 (1934).

[4] It is assumed that these eigenfunctions, ψ, have been brought into the Bloch form *viz.* $\psi=u_{\mathbf{k}}(\boldsymbol{\rho})\exp i\mathbf{k}\cdot\boldsymbol{\rho}$ where **k** is a reduced wave vector and $u_{\mathbf{k}}(\boldsymbol{\rho})$ is periodic with the period of the crystal lattice.

[5] W. Shockley, Phys. Rev. **52**, 866 (1937).

lattice for which the value of the energy E as a function of $\mathbf{k}$ is known. He concluded that a much larger number of C_{lm}'s will have to be used than was done in Slater's calculations.

It is the aim of this paper to include C_{lm}'s up to much larger l's without increasing the labor. This can be done for eigenfunctions belonging to certain points in $\mathbf{k}$ space (reduced wave vector space) of especially high symmetry, i.e., points having the complete symmetry of the cubic lattice, or lying on symmetry lines or planes. The symmetry of the wave functions at such special points in $\mathbf{k}$ space was discussed by BSW.[6] Our method consists now of constructing, once and for all, combinations $\Sigma_m C_{lm} Y_l^m$ which have the correct symmetry required according to BSW; these we call Kubic Harmonics (*KH*). Then choice of the A_l in (1) serves to fit the *BC*; note that the *BC* need to be fitted only on a few of the surfaces of the *LC*, symmetry then makes them automatically satisfied on a number of other surfaces. By using only 3 or 4 different A_l's we can generally include values of l up to 6 which would require 49 coefficients C_{lm} in Slater's method.

Actual calculations in the present work were confined to the specially symmetrical points $\mathbf{k}=(0,0,0)$ and $\mathbf{k}=(0,0,\pi/a)$ of $\mathbf{k}$-space belonging to the body centered cubic lattice. The method was tested by applying it to the limiting concept of Shockley's[5] empty lattice for which the value of the energy E is known. For the eigenfunctions tested, the results of the *ELT* (empty lattice test) were encouraging beyond expectation; the corresponding eigenfunctions and energies were therefore obtained for sodium.

METHOD OF CONSTRUCTING EIGENFUNCTIONS: KUBIC HARMONICS

For any distinct wave vector[7] $\mathbf{k}$, there is a certain group of symmetry operations on the coordinates which do not change $\mathbf{k}$. This "group of $\mathbf{k}$" is the full cubic symmetry group for the two values of $\mathbf{k}$ here considered, $(0,0,0)$ and $(0,0,\pi/a)$. The eigenfunctions can then be classified according to the irreducible representation of the group of $\mathbf{k}$ which describes their transformation under the symmetry operations of the group; each irreducible representation represents a "type." For the cubic group, for instance, there are 10 different types (see below). For each type, we can find various "sets" of *KH* which transform according to the representation characteristic of the type. By a set we mean functions which transform into each other by the symmetry operations of the group of $\mathbf{k}$. A set will contain only functions of the same order l, and of course of the same type. Not all types occur for a given l, nor all l's for a given type.

It is the aim now to show how each correct linear combination of spherical harmonics $\Sigma_m C_{lm} Y_l^m$ belonging to a type, for each order l in which the type occurs, may be constructed. This construction proceeds in three steps: (1) constructing a "group table" showing the behavior of each type under transformation of each element of the group of $\mathbf{k}$, i.e., whether the element of the type is unchanged, designated by $+$, or changed in sign only, $-$, or whether it is transformed into a linear combination of other members of its type, 0. (2) constructing "characteristic polynomials," *CP*, in x, y, z for each type and order l which have the transformation properties of the group table constructed above, and (3) deriving the correct linear combinations of the *SH* by dividing the *CP* by $\rho^l=(x^2+y^2+z^2)^{l/2}$ and orthonormalizing. This process is carried out below for the types belonging to wave vectors $(0,0,0)$ and $(0,0,\pi/a)$ of the body-centered cubic lattice. These correct linear combinations for these wave vectors are the *KH* sought.

The group of these wave vectors is the full cubic symmetry group.[6] It consists of 48 elements, 24 rotations forming a normal divisor, N, and these 24 rotations followed by inversion about the center forming a coset, JN. N and JN each contain five classes and, therefore, there are 10 irreducible representations and ten types of *KH* α, β, γ, δ, ϵ, and α', β', γ', δ', ϵ' corresponding to the five "positive" irreducible representations Γ_1, Γ_2, Γ_3, Γ_4, Γ_5, and the five "negative" irreducible representations Γ_1', Γ_2', Γ_3', Γ_4', Γ_5', with dimensions 1, 1, 2, 3, 3, respectively.

It is useful to know the type of *KH* and the number of sets of a type that can be constructed

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[6] L. Bouchaert, R. Smoluchowski and E. Wigner, Phys. Rev. **50**, 58 (1936).

[7] For the meanings of "distinct $\mathbf{k}$" and "group of $\mathbf{k}$" the reader is referred to BSW, reference 6.

TABLE I. Group Table. Behavior of Kubic Harmonic types under operations of the Cubic Symmetry Group. Plus indicates invariance under the element; minus means change of sign only; zero indicates change to one of the other functions with which the given function is degenerate. If the type is degenerate the behavior of that function is listed which has the z axis as a unique axis.

1 Class	2 Operation	3 Rotation	4 α	5 α'	6 β	7 β'	8 γ	9 γ'	10 δ	11 δ'	12 ϵ	13 ϵ'
E	$x\ \ y\ \ z$	none	+	+	+	+	+	+	+	+	+	+
C_2	$-x\ \ -y\ \ z$	z through π	+	+	+	+	+	+	+	+	+	+
	$x\ \ -y\ \ -z$	x through π	+	+	+	+	+	+	−	−	−	−
	$-x\ \ y\ \ -z$	y through π	+	+	+	+	+	+	−	−	−	−
C_3	$-y\ \ x\ \ z$	z through $+\pi/2$	+	+	−	−	+	+	+	+	−	−
	$y\ \ -x\ \ z$	z through $-\pi/2$	+	+	−	−	+	+	+	+	−	−
	$x\ \ -z\ \ y$	x through $\pi/2$	+	+	−	−	0	0	0	0	0	0
	$x\ \ z\ \ -y$	x through $-\pi/2$	+	+	−	−	0	0	0	0	0	0
	$z\ \ y\ \ -x$	y through $\pi/2$	+	+	−	−	0	0	0	0	0	0
	$-z\ \ y\ \ x$	y through $-\pi/2$	+	+	−	−	0	0	0	0	0	0
C_4	$y\ \ x\ \ -z$	$x=y$ through π	+	+	−	−	+	+	−	−	+	+
	$z\ \ -y\ \ x$	$x=z$ through π	+	+	−	−	0	0	0	0	0	0
	$-x\ \ z\ \ y$	$y=z$ through π	+	+	−	−	0	0	0	0	0	0
	$-y\ \ -x\ \ -z$	$x=-y$ through π	+	+	−	−	+	+	−	−	+	+
	$-z\ \ -y\ \ -x$	$x=-z$ through π	+	+	−	−	0	0	0	0	0	0
	$-x\ \ -z\ \ -y$	$y=-z$ through π	+	+	−	−	0	0	0	0	0	0
C_5	$z\ \ x\ \ y$	$x=y=z$ through $+2\pi/3$	+	+	+	+	0	0	0	0	0	0
	$y\ \ z\ \ x$	$x=y=z$ through $-2\pi/3$	+	+	+	+	0	0	0	0	0	0
	$z\ \ -x\ \ -y$	$x=-y=z$ through $+2\pi/3$	+	+	+	+	0	0	0	0	0	0
	$-y\ \ -z\ \ x$	$x=-y=z$ through $-2\pi/3$	+	+	+	+	0	0	0	0	0	0
	$-z\ \ -x\ \ y$	$x=-y=-z$ through $2\pi/3$	+	+	+	+	0	0	0	0	0	0
	$-y\ \ z\ \ -x$	$x=-y=-z$ through $-2\pi/3$	+	+	+	+	0	0	0	0	0	0
	$-z\ \ x\ \ -y$	$x=y=-z$ through $2\pi/3$	+	+	+	+	0	0	0	0	0	0
	$y\ \ -z\ \ -x$	$x=y=-z$ through $-2\pi/3$	+	+	+	+	0	0	0	0	0	0
J	$-x\ \ -y\ \ -z$	none	+	−	−	+	+	−	−	+	+	−
JC_2	$x\ \ y\ \ -z$	z through π	+	−	−	+	+	−	−	+	+	−
	$-x\ \ y\ \ z$	x through π	+	−	−	+	+	−	+	−	−	+
JC_3	$y\ \ -x\ \ -z$	z through $\pm\pi/2$	+	−	+	−	+	−	+	−	−	+
	$-x\ \ z\ \ -y$	x through $\pm\pi/2$	+	−	+	−	0	0	0	0	0	0
JC_4	$-y\ \ -x\ \ z$	$x=y$ through π	+	−	+	−	+	−	+	−	+	−
	$-z\ \ y\ \ -x$	$x=z$ through π	+	−	+	−	0	0	0	0	0	0
JC_5	$-z\ \ -x\ \ -y$	$x=y=z$ through $2\pi/3$	+	−	−	+	0	0	0	0	0	0

for each order l. One of us[8] has derived this and the results are: for: $l=0$, one α type; $l=1$, one δ; $l=2$, one each of γ and ϵ; $l=3$, one each of β, δ, ϵ'; $l=4$, one each of α, γ, ϵ, δ'; $l=5$, one each of γ', ϵ' and two δ; $l=6$, one each of α, γ, β', δ' and two ϵ.

Construction of the Group Table

The behavior of each type of *KH* under the transformations of the crystal group is shown (for one function of a set of each type) in Table I. This is obtained by a study of the lower order *SH* using the above results as a guide. For $l=0$ there is the non-degenerate type α and there is one *SH* which is spherically symmetrical and remains invariant under all transformations. The behavior of this type is shown in column 4. For $l=1$ there is the triply-degenerate δ type. The three *SH* are x/ρ, y/ρ, z/ρ. The latter one transforms according to column 10, and only into either itself or one of the remaining two *SH*. For $l=2$ there are the doubly degenerate γ type and the triply degenerate ϵ type. The *SH* are $[z^2-1/2(x^2+y^2)]/\rho^2$; $(y^2-x^2)/\rho^2$; zx/ρ^2, zy/ρ^2 and xy/ρ^2. The behavior of the first of these is shown in column 8. In those cases in which it does not transform into itself it transforms only into a linear combination of itself and the second listed

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[8] H. Bethe, Ann. d. Physik 3, 133 (1929).

above. It is therefore double degenerate and is identified with the γ type. The behavior of xy/ρ^2 is shown in column 12; it is degenerate with the remaining two, and is identified with the ϵ type. For $l=3$, there is among others the non-degenerate β type. Among the *SH* of $l=3$ there is found the function xyz/ρ^3. This obviously satisfies the requirements for a non-degenerate function and its behavior is listed in column 6. The remainder of the table corresponding to the behavior of the α', β', γ', δ', ϵ' types can now be determined with ease by observing that their behavior differs only in sign from corresponding unprimed types whenever an inversion is involved.

Construction of Characteristic Polynomials

For this purpose it is noted that any power of ρ is invariant under the transformation of each element of the cubic group. Thus not only the *SH* x/ρ, y/ρ, z/ρ form functions of type δ but also the first order polynomials x, y, z or the third order polynomials $x\rho^2$, $y\rho^2$, $z\rho^2$. All sets which differ only by a power of ρ are therefore considered "identical" for the present purposes.

The problem of constructing *CP* is the problem of finding linear combinations of terms of the form $x^p y^q z^r$ $(l=p+q+r)$ which are linearly independent of other chosen polynomials of the same order (or identical polynomials of lower order) and which behave according to their type (Table I). The results of reference 8 quoted above aids in pointing out types for which a search is instituted.

As an example, the procedure for obtaining the *CP* of order four is briefly outlined, assuming *CP* of lower order have already been obtained. This order contains one set each of types α, γ, ϵ and δ'. These are nine linearly independent functions to be constructed from the fifteen linearly independent polynomials: three of form x^4, six of form xy^3, three of form x^2yz, and three of form x^2y^2. However, these fifteen are effectively reduced to nine because of the six fourth order polynomials obtained by multiplying identical lower order polynomials by powers of ρ^2 *viz*:

α type, P_1: ρ^4,
γ type, P_2: $\rho^2(x^2-y^2)$, $\rho^2(y^2-z^2)$,
ϵ type, P_3: ρ^2xy, ρ^2yz, ρ^2zx.

With an eye on the Table I there are constructed the following:

Polynomials obviously of the α type

P_4: $x^4+y^4+z^4$
P_5: $x^2y^2+y^2z^2+z^2x^2$ is not new but is equal to $\frac{1}{2}(P_1-P_4)$

Polynomials of γ type

P_6: x^4-y^4, y^4-z^4
P_7: $(x^2-y^2)z^2$, $(y^2-z^2)x^2$ not new *viz.* P_2-P_6

Polynomials of ϵ type

P_8: xyz^2, yzx^2, zxy^2
P_9: x^3y+xy^3, y^3z+yz^3, z^3x+zx^3 not new *viz.* P_3-P_8

Polynomials of the δ' type

P_{10}: x^3y-xy^3, y^3z-yz^3, z^3x-zx^3

These exhaust the possible number of fourth order linearly independent functions. The three fourth powers are exhausted in the three function P_4 and P_6, the six of form x^3y in P_9 and P_{10}, the three of form x^2yz in P_8, and the three of form x^2y^2 in P_5 and P_7.

Construction of Kubic Harmonics from the Characteristic Polynomials

Dividing the *CP* of order l by ρ^l yields functions of the angles alone. These functions, F_{ls}, have the correct symmetry properties of type s but do not obey Legendre's differential equation of order l. However, from their nature it follows that they are linear combinations of *SH* of order l and lower. In order to eliminate all lower order harmonics F_{ls} can be made orthogonal to all *SH* of order less than l. Because of the orthogonality of functions belonging to different irreducible representations, it is only necessary to make F_{ls} orthogonal to all *KH* of type s and lower l. This is done by expanding F_{ls} in terms of *KH* of the same type and orders l and lower, and obtaining the *KH*, K_{ls}, in the usual way. One of us[9] has obtained all the *KH* up to $l=6$; these are listed in Table II.

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[9] H. A. Bethe, unpublished paper (1935).

TABLE II. List of the Kubic Harmonics classified according to symmetry properties. All functions normalized to 4π. Factors of ρ^{-l} are omitted throughout, i.e., x, y, z are written for x/ρ, y/ρ, z/ρ. Functions in square brackets indicate functions with normalization factors omitted.

type α	$\alpha_0=1$
	$\alpha_4=\frac{5(3\cdot7)^{\frac{1}{2}}}{4}\left(x^4+y^4+z^4-\frac{3}{5}\rho^4\right)$
	$\alpha_6=\frac{3\cdot7\cdot11(2\cdot13)^{\frac{1}{2}}}{8}\left(x^2y^2z^2+\frac{1}{22}[\alpha_4]\rho^2-\frac{1}{105}\rho^6\right)$
	$\alpha_8=\frac{5\cdot13(3\cdot11\cdot17)^{\frac{1}{2}}}{16}\left(x^8+y^8+z^8-\frac{28}{5}[\alpha_6]\rho^2-\frac{210}{143}[\alpha_4]\rho^4-\frac{1}{6}\rho^8\right)$
type β	$\beta_3=(3\cdot5\cdot7)^{\frac{1}{2}}xyz$
	$\beta_7=\frac{11(3\cdot5\cdot7\cdot13)^{\frac{1}{2}}}{4}xyz\left(x^4+y^4+z^4-\frac{5}{11}\rho^4\right)$
type γ	$(\gamma_2)_1=5^{\frac{1}{2}}(z^2-\tfrac{1}{2}(x^2+y^2))$; $(\gamma_2)_2=\frac{(3\cdot5)^{\frac{1}{2}}}{2}(x^2-y^2)$
	$(\gamma_4)_1=\frac{7(3\cdot5)^{\frac{1}{2}}}{2}\left(z^4-\tfrac{1}{2}\left(x^4+y^4\right)-\frac{6}{7}[\gamma_2]_1\rho^2\right)$; $(\gamma_4)_2=\frac{3\cdot7(5)^{\frac{1}{2}}}{4}\left(x^4-y^4-\frac{6}{7}[\gamma_2]_2\rho^2\right)$
	$(\gamma_6)_1=\frac{11(2\cdot7\cdot13)^{\frac{1}{2}}}{4}\left(z^6-\tfrac{1}{2}(x^6+y^6)-\frac{15}{11}[\gamma_4]_1\rho^2-\frac{5}{7}[\gamma_2]_1\rho^4\right)$;
	$(\gamma_6)_2=\frac{11(2\cdot3\cdot7\cdot13)^{\frac{1}{2}}}{8}\left(x^6-y^6-\frac{15}{11}[\gamma_4]_2\rho^2-\frac{5}{7}[\gamma_2]_2\rho^4\right)$
type δ†	$(\delta_1)_z=3^{\frac{1}{2}}z$
	$(\delta_3)_z=\frac{5(7)^{\frac{1}{2}}}{2}\left(z^3-\frac{3}{5}z\rho^2\right)$
	$(\delta_5)_z=\frac{3^2\cdot7(11)^{\frac{1}{2}}}{8}\left(z^5-\frac{10}{9}[\delta_3]_z\rho^2-\frac{3}{7}[\delta_1]_z\rho^4\right)$
	$(\delta_5')_z=\frac{3(5\cdot7\cdot11)^{\frac{1}{2}}}{2}z\left(x^4+y^4-\frac{3}{4}(x^2+y^2)^2\right)$
type ϵ	$(\epsilon_2)_z=(3\cdot5)^{\frac{1}{2}}xy$
	$(\epsilon_4)_z=\frac{3\cdot7(5)^{\frac{1}{2}}}{2}xy\left(z^2-\frac{1}{7}\rho^2\right)$
	$(\epsilon_6)_z=\frac{3\cdot11(2\cdot3\cdot5\cdot7\cdot13)^{\frac{1}{2}}}{16}xy\left(z^4-\frac{6}{11}z^2\rho^2+\frac{1}{33}\rho^4\right)$
	$(\epsilon_6')_z=\frac{(2\cdot3\cdot7\cdot11\cdot13)^{\frac{1}{2}}}{2}xy(x^4+y^4-\frac{5}{8}(x^2+y^2)^2)$
type α'	$\alpha_9'=\frac{(6\cdot5\cdot7\cdot11\cdot13\cdot17\cdot19)^{\frac{1}{2}}}{8}xyz(x^4(y^2-z^2)+y^4(z^2-x^2)+z^4(x^2-y^2))$
type β'	$\beta_6'=\frac{(2\cdot3\cdot5\cdot7\cdot11\cdot13)^{\frac{1}{2}}}{8}(x^4(y^2-z^2)+y^4(z^2-x^2)+z^4(x^2-y^2))$
type γ'	$(\gamma_5')_1=(3\cdot5\cdot7\cdot11)^{\frac{1}{2}}xyz(z^2-\tfrac{1}{2}(x^2+y^2))$; $(\gamma_5')_2=\frac{3(5\cdot7\cdot11)^{\frac{1}{2}}}{2}xyz(x^2-y^2)$
	$(\gamma_7')_1=\frac{13(3\cdot5\cdot7\cdot11)^{\frac{1}{2}}}{2}xyz\left(z^4-\tfrac{1}{2}(x^4+y^4)-\frac{10}{13}(z^2-\tfrac{1}{2}(x^2+y^2))\rho^2\right)$
	$(\gamma_7')_2=\frac{3\cdot13(5\cdot7\cdot11)^{\frac{1}{2}}}{4}xyz\left(x^4-y^4-\frac{10}{13}(x^2-y^2)\rho^2\right)$
type δ'	$(\delta_4')_z=\frac{3(5\cdot7)^{\frac{1}{2}}}{2}xy(x^2-y^2)$
	$(\delta_6')_z=\frac{3\cdot11(7\cdot13)^{\frac{1}{2}}}{4}xy(x^2-y^2)\left(z^2-\frac{1}{11}\rho^2\right)$
type ϵ'	$(\epsilon_3')_z=\frac{(3\cdot5\cdot7)^{\frac{1}{2}}}{2}z(x^2-y^2)$
	$(\epsilon_5')_z=\frac{3(3\cdot5\cdot7\cdot11)^{\frac{1}{2}}}{4}(z^3-\tfrac{1}{3}z\rho^2)(x^2-y^2)$

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† For types δ and ϵ, which are triply degenerate, the other two functions are found by cyclic interchange of coordinates.

BOUNDARY CONDITIONS AT THE SURFACE OF THE CRYSTAL CELL

The *BC* on the surfaces of the crystal cell are fixed by the periodicity of the eigenfunction which in turn is the property of its wave vector. A translation from a point *A* on one face to the point *B* perpendicularly opposite on a parallel second face is a translation of a lattice-point vector **T**. It is well known[6] that $\psi(\boldsymbol{\rho}+\mathbf{T})=\psi(\boldsymbol{\rho})\exp i\mathbf{k}\cdot\mathbf{T}$ so that, in general

$$\psi_B=\psi_A\exp i\mathbf{k}\cdot\mathbf{T}. \tag{2}$$

These *BC* can be put into a generally more usable form by employing the symmetry properties (listed in a group table) of the eigenfunction type. For the *KH* this is now done.

The unit crystal cell for the body centered cubic lattice is shown in Fig. 1. It has two non-equivalent face forms: six square faces on planes $x=\pm a$, $y=\pm a$, $z=\pm a$; and eight hexagonal faces whose normal vectors are $(\pm a/2,\ \pm a/2,\ \pm a/2)$. The translations between pairs of square faces are $(0,0,2a)$, $(0,2a,0)$, and $(2a,0,0)$ and those between the hexagonal faces are $(\pm a,\pm a,a)$. For the wave vectors $(0,0,0)$ and $(0,0,\pi/a)$ (to which the *KH* belong) the periodicity conditions are particularly simple. From (2) they are:

for $k=0,0,0$	Eigenfunctions are periodic with the periods of all pairs of parallel faces of the cell	(3a)
for $k=0,0,\pi/a$	Eigenfunctions are periodic with the period of pairs of square faces	(3b)
	Eigenfunctions are anti-periodic with the period of pairs of hexagonal faces	(3c)

(By "anti-periodic" is here meant that the function changes sign only upon a displacement by the "period" stated.) Correspondingly, eigenfunctions belonging to $\mathbf{k}=0,0,0$ are here said to be periodic; those belonging to $\mathbf{k}=0,0,\pi/a$, anti-periodic.

As an example, the working *BC* are now derived for the anti-periodic δ-type function with z axis preferred. Non-equivalent pairs of faces are considered separately. For the square faces $z=\pm a$: Periodicity, (3*a*), and symmetry operator $x,\ y,\ -z$ (Table I), give successively

$$\psi(x,y,a)=\psi(x,y,-a)=-\psi(x,y,a)$$

so that the eigenfunction vanishes over this face. For the square faces $x=\pm a$ (or $y=\pm a$): Periodicity and symmetry operator $-x,\ y,\ z$ gives

$$\psi(a+\epsilon,y,z)=\psi(-a+\epsilon,y,z)=\psi(a-\epsilon,y,z)$$

so that the normal derivative $\partial\psi(a,y,z)/\partial x$, vanishes over this surface. For the hexagonal surfaces $\pm x\pm y+z=\pm(3/2)a$: Anti-periodicity, (3c), and symmetry operator $-y,\ -x,\ -z$ gives

$$\begin{aligned}\psi(x,y,z)&=-\psi(x-a,y-a,z-a)\\&=+\psi(a-y,a-x,a-z)\end{aligned}$$

so that the function is symmetrical about the line $\zeta=0$ (Fig. 1). Similarly, the normal derivative is anti-symmetric about the same line. Table III lists working *BC* similarly obtained for all types of functions for that function of a type which has its z axis preferred.

Fitting of the Boundary Conditions—Empty Lattice Test

In the notation of Kubic Harmonics the candidates for eigenfunctions (1), have the form

$$\psi_s=\Sigma_{lt}A_{lt}K_{slt}R_l(E,\rho), \tag{4}$$

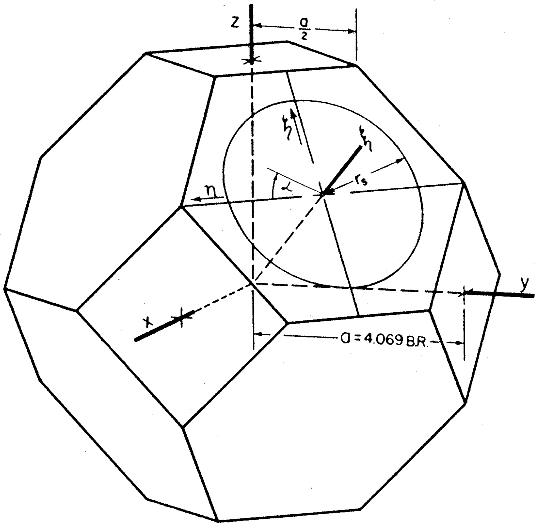

FIG. 1. Unit lattice cell for the cubic body centered crystal lattice. The lattice constant, 2*a*, for sodium, is shown as 8.138 Bohr radii. The circle on the hexagonal face is the trace of an equal volume sphere and it was over this circle that the boundary conditions were approximately satisfied.

TABLE III. Boundary conditions on ψ and its normal derivative on the faces of the unit cell. For degenerate types the BC on that eigenfunction is listed which has its z axis preferred. 0 = function vanishes over surface; a = antisymmetric; s = symmetric.

Type	Square faces (Either periodic or anti-periodic functions)				Hexagonal faces Symmetry about line $\zeta=0$			
	$x=\pm a$ (or $y=\pm a$)		$z=\pm a$		Periodic		Anti-periodic	
	ψ	$\frac{\partial\psi}{\partial\eta}$	ψ	$\frac{\partial\psi}{\partial\eta}$	ψ	$\frac{\partial\psi}{\partial\xi}$	ψ	$\frac{\partial\psi}{\partial\xi}$
α		0		0	s	a	a	s
β	0		0		a	s	s	a
γ		0		0	s	a	a	s
δ		0	0		a	s	s	a
ϵ	0			0	s	a	a	s
α'	0		0		s	a	a	s
β'		0		0	a	s	s	a
γ'	0		0		s	a	a	s
δ'	0			0	a	s	s	a
ϵ'		0	0		s	a	a	s

where l is summed over those orders containing the type s, and t is summed over the multiple sets of a type which may occur for the higher orders of l. Because the Kubic Harmonics contain all the requirements imposed by the symmetry of the lattice, (4) already satisfy proper BC at many points on the surfaces of the cell. It remains to satisfy the remaining BC imposed by periodicity shown in Table III.

The radial functions R_l can in general only be obtained by numerical integration (see next section) and depend on the special potential V used in the Schrödinger equation. Obviously, the coefficients A_{lt} will also depend on the special problem and cannot be determined analytically. To keep the labor within limits, only a finite number of terms in (4) must be used. Actually at most, four terms were used in which case three[10] constant coefficients A_{lt} and the eigenvalue E can be determined. This allows, in principle, the BC on at most[11] four distinct (not symmetrically equivalent) points to be satisfied, aside from those points whose BC are automatically satisfied by the KH. Eigenvalues obtained by various choices of sets of points yielded results 10–100 percent in error[12] for an empty lattice. It became evident that some method must be developed to produce a better "average" fit. This is now described.

To simplify arithmetic and to put (4) in a generally more convenient form, polynomials related to the Kubic Harmonics are defined

$$P_{lt}=\rho^l K_{lt}$$

so that (4) becomes

$$\psi=\Sigma_{lt}A_{lt}P_{lt}(x,\,y,\,z)S_l(E,\,\rho),\tag{5}$$

with

$$S_l=R_l\rho^{-l}.\tag{5a}$$

The functions S_l are obtained by mechanical integration. The form (5) or its normal derivative is used directly to fit BC on chosen points of a square face (actually at most only one point on squares, a central point, was fitted).

On the hexagonal surfaces an "average" fit was desired. For this purpose, a more complicated method had to be used: Eq. (5) was transformed to cylindrical coordinates, r, α, ξ ($\alpha=0$ in direction $+\eta$, Fig. 1, and ξ normal to the surface). Each polynomial, P_{lt}, was expressed as a Fourier series in α whose coefficients, P_{ltn}, are homogeneous polynomials in ξ and r of order l. The result is

$$\psi=[\Sigma_{lt}A_{lt}S_l(E,\,\rho)\Sigma_n P_{ltn}\cos n\alpha]\\+[\Sigma_{lt}A_{lt}S_l\Sigma_m P_{ltm}\sin m\alpha]\tag{6}$$

wherein either n is summed over zero, and all positive even integers, and m over all positive odd integers or the reverse, depending upon the type. In either case, the first term in (6) is symmetrical, the second is anti-symmetrical about the axis $\alpha=0$ and correspondingly ψ is said to be composed of an even part, ψ_+, and an odd part, ψ_-, respectively. The BC on the hexagonal surfaces are completely satisfied when ψ_+ (or ψ_-) and the normal derivative of ψ_- (or ψ_+) vanish over the hexagonal surfaces corresponding to the BC (Table III) that ψ is antisymmetric (or symmetric).

For a symmetrical eigenfunction the exact boundary conditions on the hexagonal surfaces may be stated in the form.

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[10] The fourth coefficient is determined by normalization.

[11] Most points on the hexagonal faces have BC on both ψ and its normal derivative so that if such a point were included the number of points that can be fitted would be reduced.

[12] It is noteworthy that choices including the central point of the hexagonal faces used by Slater gave results which were particularly bad. This is understandable because the central point has a much smaller distance from the origin than an average point, and also has a much higher symmetry which makes the BC degenerate.

$$\text{For all } m \quad \Sigma_{lt}A_{lt}S_l(E,\rho)P_{ltm}(r,\xi)=0 \qquad (7)$$
$$\text{and for all } n \quad (\partial/\partial\xi)[\Sigma_{lt}A_{lt}S_lP_{ltn}]=0,$$

respectively. (When ψ is anti-symmetric m and n are interchanged in (7).) For fitting with the limited number of A_{lt} it was assumed, as an approximation that the radius, r_s, of the trace of the equal volume sphere on the hexagonal surface was a good "average" radius and that boundary requirements (7) corresponding to the higher harmonics in the expansion (6) could be neglected. The actual numerical procedure was, using the experimental lattice constant, Fig. 1, to make a likely choice of E and determine the disposable constant coefficients, A_{lt}, with a compatible number of BC, (7), of lowest m and n. The choice of E is then tested by use of a BC on a square surface, and then the procedure is repeated until the consistent value for E is found.

The method was tested using the *ELT* for each of the solutions carried out. In the limit of vanishing potential V, the radial functions S_l are functions akin to the Bessel's functions $J_{l+\frac{1}{2}}(K,\rho)/\rho^l$. Using these functions, the eigenvalues E are obtained from the above procedure of fitting the BC, and can then be compared with their known true values, $\mathbf{K}^2$. ($\mathbf{K}$ is the "free electron" wave vector which depends on $\mathbf{k}$ and on the number of the Brillouin zone.) The results are given in Table IV.

Discussion of the Method

Table IV lists the error in the computed empty lattice eigenvalues belonging to $\mathbf{k}=0,0,0$ and $0,0,\pi/a$ as a percentage of their true values for the lowest lying levels (not including the ground state for which the test is not applicable since $\psi=\text{constant}$ is an exact solution). The number of terms used in the expansion of each of the eigenfunctions is also listed. This was arbitrarily limited by including Kubic Harmonics only up to $l=6$.

The results of the empty lattice test are most gratifying. At the upper end of the first Brillouin zone ($\mathbf{k}=0,0,\pi/a$), the error in the energy is one quarter of a percent or less, as compared with errors up to 40 percent in Slater's method (see Fig. 2, reference 5). Even at the upper end of the second zone, the error does not exceed 1 percent (Slater's method 35 percent). This improvement has been achieved while taking, in each individual case, only 2 to 4 terms in the expansion while Shockley took 8 terms in testing Slater's method. Even considering the greater complication of our Kubic Harmonics as compared with Legendre polynomials, and of our average fitting of the BC as compared with Slater's fitting at a point, the total labor in our method is probably no greater than in his. In fact, it would not involve excessive labor to include a considerably greater number of terms in our expansion. This would permit an extension of the method to higher Brillouin zones.

Since the eigenvalues for the empty lattice are in error by one percent or less it seems likely that the accuracy for filled cubic lattices will be limited by the accuracy of the potential, V. It is believed, therefore, that, at least for the wave vectors here considered, this is a one-electron approximation for cubic solids which compares favorably with methods for treating atoms.

The method is not confined to the investigation of one-electron states belonging to $\mathbf{k}=0,0,0$ and $0,0,\pi/a$. It appears to be a straightforward problem to obtain the energy spectrum for other symmetrical wave vectors without recalculation of the radial functions. This would involve constructing appropriate harmonics corresponding to the new irreducible representations and applying the more general periodicity boundary conditions compatible with the new wave vectors. Once the energy spectra of a number of symmetrical wave vectors has been determined the eigenvalue hypersurfaces can be traced out by interpolation guided by the BSW compatibility tables.[6] Behavior near wave vectors of symmetry

TABLE IV. Percent error in eigenvalues for the empty lattice and eigenvalues for sodium belonging to the lowest lying levels for $\mathbf{k}=0,0,0$ and $0,0,\pi/a$. Fitting for α and δ types belonging to $\mathbf{k}=0,0,\pi/a$ by the authors; remainder by Bowers (see reference 13).

Type	No. of terms used in eigenfunction expansion	$\mathbf{k}$	K	E in Ry for sodium	*ELT* error in E
α	3	0,0,0	0	-0.608	——
γ	3	$0,0,\pi/a$	π/a	-0.036	0.16%
δ	4	$0,0,\pi/a$	π/a	-0.0135	0.07%
α	3	$0,0,\pi/a$	π/a	$+0.0935$	0.26%
γ	3	0,0,0	$2\pi/a$	$+0.525$	0.8%
δ	4	0,0,0	$2\pi/a$	$+0.563$	0.6%
ϵ'	2	0,0,0	$2\pi/a$	$+0.600$	1.0%

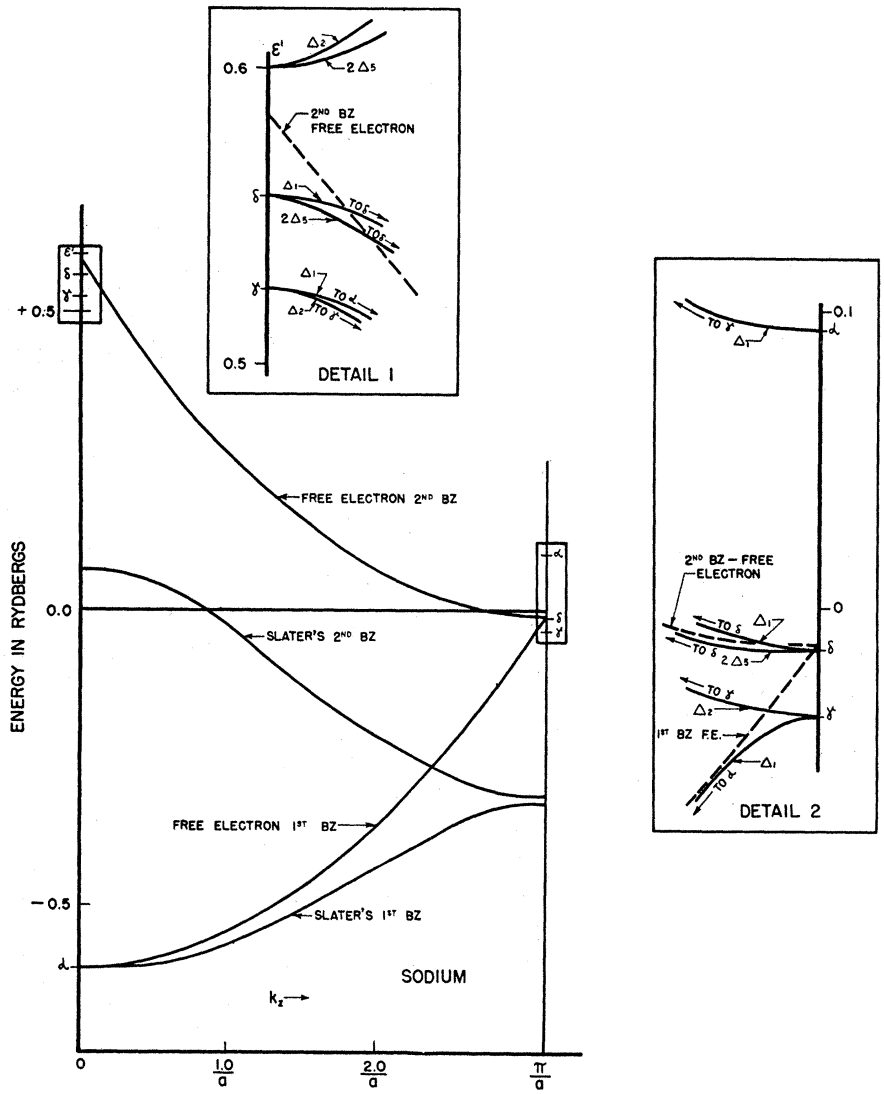

FIG. 2. This shows the eigenvalues at $\mathbf{k}=(0,0,0)$ and $(0,0,\pi/a)$ as computed for sodium by the present method. For comparison the eigenvalues in the 0,0,1 direction of the first two Brillouin zones for sodium as computed by Slater and for the free electron are shown. Detail 1 and Detail 2 sketch the BZ in the (0,0,1) direction which join up with the computed values (see BSW compatibility tables). Note that due to the degeneracy of the γ type at $\mathbf{k}=(0,0,\pi/a)$ there is no gap in the (0,0,1) direction between the first and second BZ.

can be investigated by perturbation methods with eigenfunctions obtained above; this has been done by Bowers.[13]

On the other hand, the harmonics and working relations are the same for all crystals having the same space group. Thus, having done the work for one substance, the problem for a substance having an identical lattice structure becomes one only of obtaining new radial functions and solving elementary sets of simultaneous algebraic equation. It must be admitted that thus far the method has been tested only for wave vectors of high symmetry. Accuracy of the method in general for crystals having a cell shape and symmetry departing widely from that of a sphere remains at present in doubt because of the basic approximation of separability of variables in the Schrödinger Equation.

RESULTS OF THE METHOD AS APPLIED TO SODIUM

When the method is to be applied to any problem other than the empty lattice, the potential V must be appropriately chosen. We have used the same potential[14] energy function

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[13] W. Bowers, Doctoral Thesis, Cornell University (1943).

[14] W. Prokofjew, Zeits. f. Physik **58**, 255 (1929).

V as W–S[2] and Slater.[3] The radial functions, R_l, were obtained by mechanical integration†† and checked by numerical integration using I.B.M. machines. The agreement was satisfactorily within the expected limits of error of the differential analyzer. Radial wave functions were obtained for $l=0$ to 6, and for energies $E=+0.6$, $+0.3$, $+0.1$, 0, -0.1, -0.3, and -0.6 Rydbergs. The eigenvalues were obtained by interpolation.

Table IV lists the seven lowest lying eigenvalues for $\mathbf{k}=0,0,0$ and $0,0,\pi/a$ as computed for sodium. For comparison Fig. 2 shows in addition the eigenvalues of the first and second Brillouin zones along the line 0,0,1 in $\mathbf{k}$ space, for the case of the free electron and that of sodium according to Slater's Fig. 3. Detailed sketches in Fig. 2 exhibit (for sodium) the variation from free electron eigenvalues near the center and boundary of the Brillouin zones. They also show the "sticking together" of the eigenvalue hypersurfaces at these points which was pointed out by BSW, and indicate the extremity eigenvalues to which the lower hypersurfaces join as determined by the BSW compatibility tables. The notations Δ_1, Δ_2, etc., indicate that the given eigenvalue belongs to the respective representation of the group of $\mathbf{k}$ (notation of BSW).

A very significant result of the present calculation is that for sodium in the 0,0,1 direction the electrons are essentially free. If the electrons were in fact free, the eigenvalue at the corner $(0,0,\pi/a)$ of the first Brillouin zone would be $-0.608+(\pi/a)^2=-0.012$ rydberg which is very close to the eigenvalue for the δ-type (-0.0135) actually found there and is in between the other two types. However, there is a slight deviation from freeness very close to this corner since the lowest lying energy hypersurface joins with the γ type with energy -0.036 rydberg. (The total width of the first Brillouin zone in the 0,0,1 direction is thus 4 percent less than for free electrons.) Bowers[13] has shown that this deviation extends only a very short distance from the corner. This essential freeness of the electron up to a point close to the corner of the first Brillouin zone is in agreement with the calculations of Bardeen,[15] wherein he obtained (near $\mathbf{k}=0,0,0$) the ratio of electronic mass to effective mass of 1.069 indicating a deviation in eigenvalues of 7 percent from those of the free electron.

Actually, as shown in Fig. 2, the eigenvalues of the higher Brillouin zones also remain close to those for the free electron. However, there can be little doubt that the gap between the δ and γ states amounting to 0.022 rydberg is real because the empty lattice test indicates an uncertainty in calculated energies of only 0.26 percent of 0.6 Ry, that is, 0.0016 Ry, about 7 percent of the calculated difference between δ and γ states.

Figure 2 shows poor agreement with Slater's calculations for the 0,0,1 direction. It is suspected that these markedly different results are, in part, because of his choice of the centers of hexagons as fitting points. Experience gained in the present work indicates that these points were far from average points yielding particularly poor results in the case of the empty lattice.[12]

At $\mathbf{k}=0,0,\pi/a$ the lowest lying eigenvalue is the γ type ($E_\gamma=-0.036$ Ry) considerably below the lowest α type ($E_\alpha=+0.094$ Ry). The type Δ_1 (notation is that of BSW), belonging to the wave vectors lying on the line 0,0,1 is compatible with both the α and γ types at the line extremities. Thus, as we go along the line 0,0,1 in $\mathbf{k}$ space, the eigenvalues of the first Brillouin zone start at the α type ground state and end on this γ type at $\mathbf{k}=0,0,\pi/a$. Since the γ type is doubly degenerate it is also the lowest eigenvalue of the second Brillouin zone; if we then proceed again along the line 0,0,1 this eigenvalue emerges as a Δ_2 type from this γ type and ends on the low lying γ type at $\mathbf{k}=0,0,0$. Therefore, due to the "sticking together" effect of BSW, there is actually no gap in energy at all in the direction 0,0,1 between the eigenvalues of the first and second Brillouin zones. This condition of course does allow a change in density of states near the corner, and probably also gaps in other direction of $\mathbf{k}$ space, but at the corner of the first Brillouin zone there is no actual discontinuity.

No experimental verification of sufficient resolving power exists to support these results.

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†† In this connection the authors are indebted to Professor S. H. Caldwell of M.I.T. in making available the use of the mechanical Bush Differential Analyzer; to Mr. P. O. Crawford who as a graduate assistant (1940) made the work possible by operating the machine; to Dr. Martin Schwarzschild who ran an independent check on two of the functions at the Thomas Watson Computing Bureau at Columbia University.

[15] J. Bardeen, J. Chem. Phys. 6, 367 (1938).

X-ray absorption measurements of high resolving power for potassium, which is expected to show wider departure from free electrons, have been carried out by Platt.[16] The K edge investigated shows quite close agreement with his theoretically predicted absorption which was based on the assumption that the electrons are free. No evidence existed to show an energy gap. This, of course, is at best supporting evidence of the non-existence of a gap in potassium since gaps may exist which could be completely masked by the eigenvalue dependence upon wave vector direction.

ACKNOWLEDGMENTS

The authors are indebted to Dr. W. A. Bowers for permission to publish his results on the five additional states shown in Table IV and also wish to thank Dr. Bowers for continuing the application of the method when the war interrupted the work.

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[16] J. B. Platt, Phys. Rev. 69, 337 (1946).

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The Band Theory of Graphite

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The structure of the electronic energy bands and Brillouin zones for graphite is developed using the "tight binding" approximation. Graphite is found to be a semi-conductor with zero activation energy, i.e., there are no free electrons at zero temperature, but they are created at higher temperatures by excitation to a band contiguous to the highest one which is normally filled. The electrical conductivity is treated with assumptions about the mean free path. It is found to be about 100 times as great parallel to as across crystal planes. A large and anisotropic diamagnetic susceptibility is predicted for the conduction electrons; this is greatest for fields across the layers. The volume optical absorption is accounted for.

1. INTRODUCTION

The purpose of this paper is to develop a basis for the explanation of some of the physical properties of graphite through the band theory of solids. We shall be concerned primarily with a discussion of its electrical conductivity, but the treatment given makes possible the explanation not only of the electrical conductivity and its anisotropy but also the thermal conductivity, diamagnetic susceptibility, and optical absorption.

The electrical resistivity of single crystals of graphite is about 4 to 6×10^{-5} ohm-cm.[1] This corresponds to a conductivity of the order of that of a poor metal. The temperature coefficient of the conductivity is negative, as in the case of a metal. Polycrystalline graphite, on the other hand, has a much higher resistivity which varies very strongly according to the type of graphite used, and has a *positive* temperature coefficient of conductivity[2] to about 1400°C, and negative thereafter. Since the crystals of commercial graphites tend to be of the order of 10^{-6} cm, and it is quite porous (density ~ 1.6 as against 2.25 for single crystals), it seems reasonable to attribute the high resistivity of polycrystalline graphite to the crystal boundaries, on which may be lodged impurity atoms. The latter would tend to be driven off on heating, thus accounting for the observed temperature dependence. We shall show, however, that the band theory would seem to make possible the explanation of the conductivity properties of single crystals.

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[1] Given by E. Ryschewitsch, Zeits. f. Elektrochem. ang. physik. Chemie **29**, 474 (1923), as $3.9\text{–}6\times 10^{-5}$ ohm-cm.

[2] C. A. Hansen, Trans. Am. Electrochem. Soc. **16**, 329 (1909) gives 137.5×10^{-5} at 0°C 82.5×10^{-5} at 1400°C.