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New Approach to the Linear-Combination-of-Atomic-Orbitals Method for Cubic Crystals

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A method of the linear combinations of atomic orbitals for cubic crystals with an *s* orbital on each atom is proposed, in which the Bloch wave functions (equivalent to the basis functions of the one-dimensional representations of the subgroup of lattice translations) are replaced by basis functions of the irreducible representations of the cubic point group. The coefficient functions of the atomic orbitals which enter into the new wave functions are solutions of the Wannier-Slater equation for a given type of lattice and for interactions between atomic neighbors. These functions meet the requirement that they vanish at the crystal boundary. For a pure crystal, the electron density need only be analyzed at one representative atomic site. Since a site like this can be put in the center of the system of coordinates, the needed coefficient functions can be the basis functions of only one irreducible representation, viz., that of the total symmetry of the cubic point group. They can be approximated in terms of a few cubic harmonics belonging to the irreducible representation mentioned and in terms of spherical Bessel functions equal in order to the cubic harmonics. Unlike the theory of Bloch, where the wave functions and energies depend on a three-component vector parameter, the present scheme introduces only one scalar parameter for the quantization of the electron states. This enables one to reduce the integration generating the Green's function to a one-dimensional one. The energies can be expressed as sums of powers of the quantum parameter and the band is obtained as a set of states which give the nonvanishing contribution to the electron density of the crystal. The band structure obtained from *approximate* solutions for the face-centered cubic lattice is compared with that obtained from Bloch's method. In the tight-binding approach these solutions and Bloch's method give the energy dependencies of the density of states which are close to each other over about two-thirds of the bandwidth. For almost-free electrons, these dependencies are nearly coincident within the interval of the energy between the band bottom and a certain level below the critical one in Bloch's band. With the same solutions we obtain bandwidths which are identical with Bloch's in the tight-binding case, but nearly double Bloch's in the case of almost-free electrons.

I. INTRODUCTION

The LCAO (linear-combination-of-atomic-orbitals) method of Bloch is a well-known approach to electron wave functions and energies in crystals.[1] For the sake of simplicity, let us consider the crystal as built up of one kind of atom distributed periodically in space, each atom with only one atomic orbital of spherical (*s*-type) symmetry. The wave function is

$$\Psi=\sum_i A(\vec{R}_i)\phi(\vec{r}-\vec{R}_i)\ , \tag{1}$$

where ϕ denotes the atomic *s* orbital and

$$A(\vec{R}_i)=N_B\, e^{i\vec{k}\cdot\vec{R}_i}. \tag{2}$$

N_B is the normalization coefficient, $\vec{k}$ is the vector in the reciprocal space, and $\vec{R}_i$ is the position vector of the atomic nucleus i in the crystal. The function Ψ fulfills the periodic, or Born–von Karman, conditions at the boundary and is the eigenfunction of the operator of the lattice translations [cf. Eq. (6)]. The energy of the electron is that of the atomic state plus simple trigonometric functions of the components of the three-dimensional vector $\vec{k}$, which are modulated by the integrals

$$\beta_{\mu\nu}=\int\phi^*(\vec{r}-\vec{R}_\mu)[V(\vec{r})-U(\vec{r}-\vec{R}_\nu)]\,\phi(\vec{r}-\vec{R}_\nu)\,d\tau\ ; \tag{3}$$

$V(\vec{r})$ is the crystal potential, $U(\vec{r}-\vec{R}_i)$ is the atomic potential at $\vec{R}_i$. The integrals (3) are the constant terms for all the electron states defined by the values k_x, k_y, and k_z. The energy E oscillates between two limiting values determined by the relation $E(k_x, k_y, k_z)$. Examples of the energy expressions for different lattices are given in textbooks.[1] We can assume that

$$\int\phi^*(\vec{r}-\vec{R}_\mu)\,\phi(\vec{r}-\vec{R}_\nu)d\tau=\delta_{\mu\nu}. \tag{4}$$

Then we find

$$N_B=N^{-1/2}, \tag{5}$$

where N is the number of atoms in the lattice.

The purpose of the present paper is to develop a method which although based on the approximation expressed by Eq. (1) seems to differ in its framework from that of Bloch. The method to be presented here is limited to crystals of cubic symmetry and involves only the sum of one kind of atomic orbital, i.e., those of spherical symmetry. Also, for the sake of simplicity, in a large part of the paper the nearest-neighbor interaction, or the tight-binding approximation, is assumed, i.e., (3) vanishes unless μ and ν are the same atom or nearest-neighbor atoms, although this limitation is inessential for the development of the method. The main idea of the approach is the following.

First, we drop the requirement that the wave functions of the crystal are the basis functions of the one-dimensional irreducible representations of the translations subgroup, but require them to be the basis functions of the irreducible representations of the subgroup equal to the symmetry point group of the crystal potential [in a special case equal to that of a cube (O_h)]. Then, assuming that the LCAO approximation holds, i.e., that Eq. (1) is valid and the atomic orbitals of spherical symmetry are repeated in each lattice site, the wave functions of the symmetry of the cubic point group can be arrived at when A of such a symmetry are given. Thus, instead of the A in Eq. (2) which fulfill the eigenequation for the translation operator

$$\hat{T}A = tA, \tag{6}$$

the eigenvalue t being $e^{i\vec{k}\cdot(\vec{R}_a - \vec{R}_b)}$, we seek such A as will be the basis functions of the irreducible representations of the cubic point group

$$\hat{P}A_m = \sum_k (P)_{mk} A_k ; \tag{7}$$

$\hat{P}$ in an operator of the group, $(P)_{mk}$ are the matrix elements of this operator with respect to the basis functions, and the indices m and k run over the number of dimensions of a given irreducible representation; see, e.g., Ref. 2.

Second, the above requirement for A implies that the boundary conditions for the wave function may be different from the periodic ones, which are characteristic of the function of Eqs. (1) and (2). The new conditions that satisfy the A of the present paper are introduced in Sec. III. Third, the periodic potential of the lattice has to be taken into account. According to Sec. II this requirement is met if the eigenequation

$$\hat{W}A = EA \tag{8}$$

is fulfilled. $\hat{W}$ in (8) is the Wannier-Slater differential operator for a given lattice[3,4] and E is equal—with an accuracy to a constant term—to the energy of the electron state represented by the approximate wave function (1). We seek instead of (2) such solutions for (8) as fulfill (7), with the new boundary conditions holding for Ψ and consequently also for A.

II. EQUATION

The usual assumption is that the Wannier-Slater (WS) equation presented in Eq. (8) holds in the absence of a perturbation of the periodic potential of the crystal only when A fulfills the periodic boundary conditions, i.e., when A is (2) for $V_p = 0$, where V_p is the potential change due to the perturbation. This assumption is based on the fact that the matrix elements of the energy operator commonly used for deriving Eq. (8) are the Fourier coefficients for the periodic function of the energy in the space of the vector $\vec{k}$, and are thus related directly to the solution of the eigenproblem with periodic conditions at the boundary.[4] This, however, seriously restricts the problem represented by Eq. (8), which can be derived—at least for all the cases we are concerned with—without requiring the wave function (1) to have specialized symmetry properties and conditions at the boundary. The proof—suggested by Friedel and exemplified by the case of a simple-cubic lattice with the tight-binding approximation for the crystal potential and one kind (s) of atomic orbital—is the following.

We consider A as the continuous function of the position $\vec{R}$ of the lattice sites. One side of the equation is obtained by developing the A in a Taylor series. We start from an atomic site $\vec{R}_n$ in the crystal and express the sum of A in the sites $\vec{R}_{vn}$, which are the nearest neighbors of $\vec{R}_n$, in terms of $A(\vec{R}_n)$:

$$\sum_{vn} A(\vec{R}_{vn}) = \sum_{vn} \left\{ A(\vec{R}) + (\vec{a}_{vn} \circ \nabla) A(\vec{R}) + \frac{(\vec{a}_{vn} \cdot \nabla)^2}{2!} A(\vec{R}) + \cdots \right\}_{\vec{R} = \vec{R}_n} . \tag{9}$$

The summation in (9) covers all $\vec{R}_{vn}$. The symbol $\vec{a}_{vn}$ denotes the vector $\vec{R}_{vn} - \vec{R}_n$. The differential operator (9) can be represented in a more condensed form. Since the lattice is symmetrical with regard to inversion, all odd-power terms vanish in (9). For the simple cubic lattice, Eq. (9) becomes

$$\sum_{vn} A(\vec{R}_{vn}) = \frac{q}{3} \left\{ \left[\sum_{m=0}^{m=\infty} \frac{a^{2m}}{(2m)!} \left(\frac{\partial^{2m}}{\partial X^{2m}} + \frac{\partial^{2m}}{\partial Y^{2m}} + \frac{\partial^{2m}}{\partial Z^{2m}} \right) A(\vec{R}) \right\}_{\vec{R} = \vec{R}_n} \right. , \tag{10}$$

where q—the number of the nearest atomic neighbors—is 6; $a = |\vec{a}_{vn}|$ is the same for all vn and equal to the lattice parameter. Using the series expansion for cosine we have

$$\sum_{\nu n} A(\vec{R}_{\nu n}) = \frac{q}{3}\left\{\left[\cos\left(ia\frac{\partial}{\partial X}\right) + \cos\left(ia\frac{\partial}{\partial Y}\right) + \cos\left(ia\frac{\partial}{\partial Z}\right)\right] A(\vec{R})\right\}_{\vec{R}=\vec{R}_n} . \qquad (11)$$

The other side of the equation for A is obtained from the tight-binding approximation. First, we substitute Eq. (1) for Ψ in the Schrödinger equation $\hat{H}\Psi = E\Psi$, where $\hat{H}$ is $-(\hbar^2/2m_e)\Delta + V(\vec{r})$, and $V(\vec{r})$ in the area near any $\vec{R}_i$ can as usual be considered as $U(\vec{r}-\vec{R}_i) + V(\vec{r}) - U(\vec{r}-\vec{R}_i)$. Next, we multiply the equation by the atomic orbital of $\vec{R}_n$ and integrate it over the crystal volume; we obtain

$$\begin{aligned} A(\vec{R}_n)[E - E^0 - \gamma(n)] &= \sum_{\nu n} \beta(\nu n) A(\vec{R}_{\nu n}) \\ &= \beta(n) \sum_{\nu n} A(\vec{R}_{\nu n}) , \end{aligned} \qquad (12)$$

where $\beta(\nu n)$ is the integral (3) for $\vec{R}_\mu = \vec{R}_{\nu n}$ and $\vec{R}_\nu = \vec{R}_n$, and $\gamma(n)$ is (3) for $\vec{R}_\mu = \vec{R}_\nu = \vec{R}_n$. Since spherical symmetry is assumed for ϕ, we have the same $\beta(\nu n)$ for all $\vec{R}_{\nu n}$, and thus the second equation in (12) is valid with $\beta(\nu n)$ abbreviated to a single $\beta(n)$. The usual approximation of Eq. (4) has been taken into account. E^0 is the eigenvalue of the atomic orbital ϕ. From (10) and (12) we obtain

$$\begin{aligned} &[E - E^0 - \gamma(n)] A(\vec{R}_n) \\ &\quad = \frac{q}{3}\beta(n)\left\{\left[\cos\left(ia\frac{\partial}{\partial X}\right) + \cos\left(ia\frac{\partial}{\partial Y}\right) \right.\right. \\ &\qquad \left.\left. + \cos\left(ia\frac{\partial}{\partial Z}\right)\right] A(\vec{R})\right\}_{\vec{R}=\vec{R}_n} . \end{aligned} \qquad (13)$$

This is a Wannier-Slater equation which determines A in the case of a (perfect) simple cubic lattice. It is repeated for each $\vec{R}_n$ inside the lattice and the index n can be omitted because $\gamma(n)$ and $\beta(n)$ are the same for all n beyond the regions close to the crystal surface.

An equation analogous to (13) can be established in the same way for other lattices. For example, for the face-centered cubic (fcc) lattice with s atomic orbitals we obtain

$$\begin{aligned} (E - E^0 - \gamma) A(\vec{R}_n) &= \frac{q}{3}\beta\left\{\left[\cos\left(ia\frac{\partial}{\partial X}\right)\cos\left(ia\frac{\partial}{\partial Y}\right) \right.\right. \\ &\quad + \cos\left(ia\frac{\partial}{\partial Y}\right)\cos\left(ia\frac{\partial}{\partial Z}\right) \\ &\quad \left.\left. + \cos\left(ia\frac{\partial}{\partial Z}\right)\cos\left(ia\frac{\partial}{\partial X}\right)\right] A(\vec{R})\right\}_{\vec{R}=\vec{R}_n} , \end{aligned} \qquad (14)$$

where q is 12 and a, β, and γ are, respectively, the value of the lattice parameter and the corresponding integrals for the fcc lattice. The WS equation for lattices with interaction between atomic neighbors more distant than the nearest ones can be obtained in the same way.

III. BOUNDARY CONDITIONS AND ELECTRON DENSITY

The boundary condition we assume is that the electrons are enclosed in a large spherical crystal block of the radius R_d, i.e.,

$$\Psi(\vec{r}) = 0 \qquad (15)$$

for $|\vec{r}| = R_d$. Then Ψ will be much like the standing waves in a spherical potential box. Since Ψ in (1) is modulated everywhere by the same atomic functions ϕ, the condition of standing waves is valid for A; we have

$$A(\vec{R}) = 0 \qquad (16)$$

for $|\vec{R}| = R_d$. This raises the problem of the spatial distribution of the electron density determined by the new Ψ and A. The answer is offered by the general theorem, given for the free particles (electrons) by von Laue[5] and extended to the electrons in the field of the periodic lattice by Friedel,[6] which states that the electron density per unit energy range is practically independent of the form of the conditions at the boundary providing that the distance from the boundary is greater than the electron wavelength characteristic of the considered energy range and that there is a sufficiently large number of electron states within the energy range. This density is constant in the free-electron case and is periodic with the lattice in the case of a crystal.

Now let ΔE be the energy interval. When Eq. (4) is used the electron charge within ΔE will be

$$\sum_\omega \int \Psi^*_\omega \Psi_\omega \, d\tau = \sum_\omega \sum_i A^*(\vec{R}_i, \omega) A(\vec{R}_i, \omega), \qquad (17)$$

where the summation over ω runs over all the wave functions having energies within the chosen interval. According to the theorem of von Laue and Friedel we expect also in the case of A of Eqs. (7) and (16)

$$\begin{aligned} \sum_\omega A^*(\vec{R}_1, \omega) A(\vec{R}_1, \omega) &\approx \sum_\omega A^*(\vec{R}_2, \omega) A(\vec{R}_2, \omega) \\ &\approx \sum_\omega A^*(\vec{R}_3, \omega) A(\vec{R}_3, \omega), \quad \text{etc.}, \end{aligned} \qquad (18)$$

providing $\vec{R}_1$, $\vec{R}_2$, $\vec{R}_3$, etc., are not too close to the surface of the crystal, and ΔE covers a sufficiently large number of states.

Equation (18) offers an important simplification. Because, when it is fulfilled, we can obtain the density of electron states in the crystal without calculating the solutions of the WS equation in the *whole* crystal area. We can leave it at calculating the electron charge only at one atom, the situation at this atom being repeated throughout the crystal. For example, we can choose this atom at the center of the coordinate system and then investigate

$$\sum_{\omega} A^{*}(\vec{0}, \omega) A(\vec{0}, \omega) \tag{19}$$

and its dependence on E. Then, of the functions A belonging to different irreducible representations of the cubic point group, we need only such solutions as are the basis functions for the total symmetry representation (Γ_1) of the group, because only they can give a nonvanishing contribution to (19) (cf. Sec. IV).

IV. CONSTRUCTION OF FUNCTIONS *A*

A. Method

This section presents the technique of solving the WS equation. Our attention is focused on solutions belonging to the irreducible representation Γ_1 (cf. Sec. III and the following notes). Mathematically, the problem is to solve the eigenequation

$$\hat{W} A(\vec{R}, \kappa) = \mathrm{E}(\kappa) A(\vec{R}, \kappa), \tag{20}$$

where κ is a parameter and A should be continuous, should have the required symmetry, and should fulfill certain conditions at the boundary and be normalized; $\hat{W}$ is the differential operator given for two cubic lattices in Eqs. (13) and (14), and

$$\mathrm{E}(\kappa) = (E - E^0 - \gamma)/q\beta \tag{21}$$

in each case. The function A can be constructed similarly for all cubic lattices. For simplicity, we put the lattice parameter a as equal to the unit distance.

In general, A can be considered as a polynomial composed of the infinite number of terms arranged as follows ($R^2 = X^2 + Y^2 + Z^2$):

$$\begin{array}{lllll}
\mathit{const}; & \kappa^2; & \kappa^4; & \kappa^6; & \text{etc.};\\
\kappa^2 R^2; & \kappa^4 R^2; & \kappa^6 R^2; & \kappa^8 R^2; & \text{etc.};\\[1ex]
\kappa^4 R^4; & \kappa^6 R^4; & \kappa^8 R^4; & \kappa^{10} R^4; & \text{etc.};\\
\kappa^4 (X^4+Y^4+Z^4); & \kappa^6 (X^4+Y^4+Z^4); & \kappa^8 (X^4+Y^4+Z^4); & \kappa^{10} (X^4+Y^4+Z^4); & \text{etc.};\\[1ex]
\kappa^6 R^6; & \kappa^8 R^6; & \kappa^{10} R^6; & \kappa^{12} R^6; & \text{etc.};\\
\kappa^6 R^2 (X^4+Y^4+Z^4); & \kappa^8 R^2 (X^4+Y^4+Z^4); & \kappa^{10} R^2 (X^4+Y^4+Z^4); & \kappa^{12} R^2 (X^4+Y^4+Z^4); & \text{etc.};\\
\kappa^6 (X^6+Y^6+Z^6); & \kappa^8 (X^6+Y^6+Z^6); & \kappa^{10} (X^6+Y^6+Z^6); & \kappa^{12} (X^6+Y^6+Z^6); & \text{etc.};\\[1ex]
\kappa^8 R^8; & \kappa^{10} R^8; & \kappa^{12} R^8; & \kappa^{14} R^8; & \text{etc.};\\
\kappa^8 R^4 (X^4+Y^4+Z^4); & \kappa^{10} R^4 (X^4+Y^4+Z^4); & \kappa^{12} R^4 (X^4+Y^4+Z^4); & \kappa^{14} R^4 (X^4+Y^4+Z^4); & \text{etc.};\\
\kappa^8 R^2 (X^6+Y^6+Z^6); & \kappa^{10} R^2 (X^6+Y^6+Z^6); & \kappa^{12} R^2 (X^6+Y^6+Z^6); & \kappa^{14} R^2 (X^6+Y^6+Z^6); & \text{etc.};\\
\kappa^8 (X^8+Y^8+Z^8); & \kappa^{10} (X^8+Y^8+Z^8); & \kappa^{12} (X^8+Y^8+Z^8); & \kappa^{14} (X^8+Y^8+Z^8); & \text{etc.};\\[1ex]
\text{etc.}; & \text{etc.}; & \text{etc.}; & \text{etc.}; & \text{etc.};
\end{array} \tag{22}$$

It is clear how the further terms can be added. Rows having the same powers of κ and equal orders $d = a + b + c$ of the polynomials expressed in terms of $X^a Y^b Z^c$ form multiple rows. The exception is the first multiple row, which is made up of the terms κ^p and $\kappa^{p+2} R^2$.

The polynomials which depend on X, Y, and Z and enter into a given multiple row are completely analogous to the characteristic polynomials of type Γ_1 of Von der Lage and Bethe.[7] They are so chosen as to enable any polynomial of type Γ_1 and the order characteristic of this row to be represented as a linear combination of the polynomials in this row.[8] Only the polynomials of type Γ_1 are important because other irreducible representations of the cubic point group give exclusively terms which vanish at $\vec{0}$.

The action of $\hat{W}$ on any of the polynomials of the type in (22) gives a linear combination of polynomials of the same type. From this point of view, the polynomials form a complete set and can be combined to fulfill Eq. (20) to the arbitrary degree of the approximation for the solution. This approximation is the better the larger the number of differential operators of different orders we include in our $\hat{W}$ and the larger the number of polynomials (22) which fit (20). However, for the normalization and the establishment of the boundary conditions the approximate behavior of A at large distances from the origin of the coordinate system should be suitable and known. Thus we choose the following combinations of (22):

$$j_0(\kappa R) \tag{23}$$

and

$$\begin{array}{llll}
\cdots; & \cdots; & \cdots; & \cdots; \\
(KH)_4^{\Gamma_1} j_4(\kappa R); & \kappa^2 (KH)_4^{\Gamma_1} j_4(\kappa R); & \kappa^4 (KH)_4^{\Gamma_1} j_4(\kappa R); & \text{etc.}; \\
\cdots; & \cdots; & \cdots; & \cdots; \\
(KH)_6^{\Gamma_1} j_6(\kappa R); & \kappa^2 (KH)_6^{\Gamma_1} j_6(\kappa R); & \kappa^4 (KH)_6^{\Gamma_1} j_6(\kappa R); & \text{etc.}; \\
\cdots; & \cdots; & \cdots; & \cdots; \\
\cdots; & \cdots; & \cdots; & \cdots; \\
(KH)_8^{\Gamma_1} j_8(\kappa R); & \kappa^2 (KH)_8^{\Gamma_1} j_8(\kappa R); & \kappa^4 (KH)_8^{\Gamma_1} j_8(\kappa R); & \text{etc.}; \\
\cdots; & \cdots; & \cdots; & \cdots; \\
\cdots; & \cdots; & \cdots; & \cdots; \\
\cdots; & \cdots; & \cdots; & \cdots; \\
\text{etc.}; & \text{etc.}; & \text{etc.}; & \text{etc.};
\end{array} \qquad (24)$$

$(KH)_l^{\Gamma_1}$ is a cubic harmonic of symmetry Γ_1 and order l and j_l is a spherical Bessel function of order l. We seek such coefficients in the combination of (23) and (24)

$$A^{\Gamma_1} = N^{\Gamma_1}(\kappa) \sum_l \sum_t \sum_m c_{l,t,m} (KH)_{l,t}^{\Gamma_1} j_l(\kappa R)\, \kappa^{2m} \qquad (25)$$

and such

$$\alpha_0,\ \alpha_1,\ \alpha_2,\ \ldots,\ \text{etc.}, \qquad (26)$$

in the expression

$$\mathrm{E}(\kappa) = \alpha_0 + \alpha_1 \kappa^2 + \alpha_2 \kappa^4 + \alpha_3 \kappa^6 + \cdots \qquad (27)$$

as will make a possibly large number of columns and multiple rows of polynomials in (22) satisfy Eq. (20).[9] $N^{\Gamma_1}(\kappa)$ in (25) is the normalization coefficient of the wave function which has coefficient function A^{Γ_1}. In the present, use is made only of the orders l for which one cubic harmonic occurs in the combination of (25), which permits us to drop the index t.[10]

Practically, we calculate the coefficients $c_{l,m}$ and α_i in the following way. First, we make all the polynomials of the first column of (22) satisfy (20). This is achieved with $\alpha_0 = 1$, and holds for arbitrary combinations of functions (24). The same can be done with the second column of (22) if we consider that all $(KH)_{l,t}^{\Gamma_1} j_l(\kappa R)$ are the eigenfunctions of the Laplace operator with the same eigenvalue $-\kappa^2$. Then, α_1 is the negative value of the coefficient of the Laplace operator in $\hat{W}$. With the sc lattice as an example, this gives—with Eq. (21)—α_1 equal to $-\frac{1}{6}$.

Now the matter becomes less simple. For example, the four polynomials at the top of the third column in (22) (two multiple rows) cam be made to satisfy (20) by choosing the right α_2 and coefficient $c_{4,0}$ for $(KH)_4^{\Gamma_1} j_4$; so can the seven polynomials at the top of this column (three multiple rows) by suitably choosing α_2 (which will be different from the previous) and the coefficients for $(KH)_4^{\Gamma_1} j_4$ and $(KH)_6^{\Gamma_1} j_6$; and so can also the 11 polynomials at the top of the column by choosing the right α_2 and the coefficients for $(KH)_4^{\Gamma_1} j_4$, $(KH)_6^{\Gamma_1} j_6$, and $(KH)_8^{\Gamma_1} j_8$, etc. In all the cases ($d \leqslant 10$) examined in the present paper the number of the functions $(KH)_l^{\Gamma_1} j_l$ with $l > 0$ needed in combination (25) to make Eq. (20) satisfied by the polynomials taken from the top of the third column in (22) equals the number of the multiple rows less unity taken into account in the column; a case in which the polynomials of Ref. 8 occur has to be classified separately because two different $(KH)_{12}^{\Gamma_1}$ have to be considered when we seek to satisfy Eq. (20) for a complete multiple row which has $d = 12$. The coefficient for the term j_0 in (25) need not be determined; we put it as equal to unity in each combination.

Coefficients can be similarly chosen to make the polynomials in the columns following the third satisfy (20). For the nth column in (22) ($n > 3$), this is done by calculating the coefficient α_{n-1} in Eq. (27) and those for such functions $\kappa^{2m} (KH)_l^{\Gamma_1} j_l$ of Eq. (24) as have the power exponent $m = n - 3$. Then the coefficient α_p with $p < n - 1$ as well as those of the functions (24) with $m < n - 3$, calculated in the preceding steps, are put as constants into the equations for α_{n-1} and $c_{l,n-3}$. The number of $\kappa^{2(n-3)} (KH)_l^{\Gamma_1} j_l$ used in this operation was found to be the same as for the third ($n = 3$) column.

A characteristic point is that the number of the parameters [the coefficients for the functions $\kappa^{2m} (KH)_l^{\Gamma_1} j_l$ and those in Eq. (27)] used in the calculations is clearly less than the number of the polynomials in (22) which we seek to make satisfy (20). This number of polynomials equals the number of component rows times the number of the columns after the second one. We can increase accordingly the number of the parameters by replacing the dots in Eq. (24) with additional functions. For example, we can choose the following combinations of the polynomials in (22):

$$\begin{array}{cccc}
\kappa^2 j_2(\kappa R); & \kappa^4 j_2(\kappa R); & \kappa^6 j_2(\kappa R); & \text{etc.}; \\
\cdots\,; & \cdots\,; & \cdots\,; & \cdots\,; \\
\kappa^2 j_4(\kappa R); & \kappa^4 j_4(\kappa R); & \kappa^6 j_4(\kappa R); & \text{etc.}; \\
\cdots\,; & \cdots\,; & \cdots\,; & \cdots\,; \\
\kappa^2 j_6(\kappa R); & \kappa^4 j_6(\kappa R); & \kappa^6 j_6(\kappa R); & \text{etc.}; \\
\kappa^2\left[\left(\frac{X}{R}\right)^4+\left(\frac{Y}{R}\right)^4+\left(\frac{Z}{R}\right)^4\right] j_6; & \kappa^4\left[\left(\frac{X}{R}\right)^4+\left(\frac{Y}{R}\right)^4+\left(\frac{Z}{R}\right)^4\right] j_6; & \kappa^6\left[\left(\frac{X}{R}\right)^4+\left(\frac{Y}{R}\right)^4+\left(\frac{Z}{R}\right)^4\right] j_6; & \text{etc.}; \\
\cdots\,; & \cdots\,; & \cdots\,; & \cdots\,; \\
\kappa^2 j_8(\kappa R); & \kappa^4 j_8(\kappa R); & \kappa^6 j_8(\kappa R); & \text{etc.}; \\
\kappa^2\left[\left(\frac{X}{R}\right)^4+\left(\frac{Y}{R}\right)^4+\left(\frac{Z}{R}\right)^4\right] j_8; & \kappa^4\left[\left(\frac{X}{R}\right)^4+\left(\frac{Y}{R}\right)^4+\left(\frac{Z}{R}\right)^4\right] j_8; & \kappa^6\left[\left(\frac{X}{R}\right)^4+\left(\frac{Y}{R}\right)^4+\left(\frac{Z}{R}\right)^4\right] j_8; & \text{etc.}; \\
\kappa^2\left[\left(\frac{X}{R}\right)^6+\left(\frac{Y}{R}\right)^6+\left(\frac{Z}{R}\right)^6\right] j_8; & \kappa^4\left[\left(\frac{X}{R}\right)^6+\left(\frac{Y}{R}\right)^6+\left(\frac{Z}{R}\right)^6\right] j_8; & \kappa^6\left[\left(\frac{X}{R}\right)^6+\left(\frac{Y}{R}\right)^6+\left(\frac{Z}{R}\right)^6\right] j_8; & \text{etc.}; \\
\cdots\,; & \cdots\,; & \cdots\,; & \cdots\,.
\end{array} \tag{28}$$

The behavior of these combinations at large distances from the origin of the coordinate system is also suitable for our purpose. Then the combination for A^{Γ_1} is supplemented with

$$S^{\Gamma_1}=N^{\Gamma_1}(\kappa)\sum_{l}\sum_{t'}\sum_{m}\bar{c}_{l,t',m}(KP)_{l,t'}\,j_l(\kappa R)\,\kappa^{2m+2}\,, \tag{29}$$

where KP is the angle-dependent term in a given function (28), and t' indicates the component row into which the function belongs. [For example, the coefficient for $\kappa^2 j_8(\kappa R)$ is $\bar{c}_{8,1,0}$.] But the introduction of functions (28) is superfluous if we consider that the coefficients $\bar{c}_{l,t',m}$ are exactly zero, as was shown by numerical calculations made for all the considered sets of multiple rows and columns in the upper left corner of what would be the complete Eq. (22) and for all kinds of cubic lattices,[11] and also in the case of the interactions between atomic neighbors more distant than the first ones. This reduces the number of independent equations to that of the coefficients in (25) and (27) and, by simplifying the calculations, provides a powerful tool for checking them.

Another characteristic point is that the equations for the coefficients which make the polynomials of the third column in (22) satisfy Eq. (20) are not linear. The degree of the algebraic equation to which the problem is reduced equals the *total* number of the components $(KH)^{\Gamma_1}_{l,t}\,j_l$ introduced into the development. Thus—after the equation has been solved—the number of combinations in (25) equals the number of the functions $(KH)^{\Gamma_1}_{l,t}\,j_l$ used in it. Hereafter, we give the index λ to different combinations of the same $(KH)^{\Gamma_1}_{l,t}$. The inclusion in calculations of more than three columns of the polynomials does not increase the number of A^{Γ_1}, because the equations for the coefficients needed for the polynomials in the columns beyond the third are linear. The consequences will be important in Secs. IV B–VII.

The cubic harmonics of Γ_1 used in the calculations are those in Ref. 7 with the normalization factors omitted, excepting $(KH)^{\Gamma_1}_6$, which is three times the non-normalized expression in Ref. 7. Table I gives the coefficients in (25) and (27) for four multiple rows and various numbers of columns considered in (22) for the fcc lattice. The detailed data for $c_{l,t,m}$ and α_l for the sc lattice, and some for the bcc lattice, will be published elsewhere.[11a]

B. Problem of Convergence

The problem of the convergence of the method can be examined in two aspects. First, we may ask to what extent the individual solutions of (25) and (27) can be considered as accurate. This—with the whole problem confined to site $\vec{0}$—is reduced to an examination of the accuracy of

$$N^{\Gamma_1}(\kappa)=A^{\Gamma_1}(\vec{0},\,\kappa) \tag{30}$$

TABLE I. Coefficients $c_{l,m}$ and α_i of Eqs. (25) and (27) for the fcc lattice when only $l=0$, 4, 6, and 8 are taken into account. All coefficients $\bar{c}_{l,t',m}$ of Eq. (29) vanish for all λ. The coefficient $\alpha_1=-\frac{1}{3}$ is used in the establishment of all equations for $c_{l,m}$, α_i and $\bar{c}_{l,t',m}$.

	$\lambda=1$		$\lambda=2$		$\lambda=3$		$\lambda=4$	
α_2	3.612 657	10^{-2}	3.448 426	10^{-2}	3.241 209	10^{-2}	2.890 003	10^{-2}
$c_{4,0}$	−6.599 012		−2.719 073		2.176 445		1.047 368	10^{1}
$c_{6,0}$	−5.715 378	10^{1}	7.346 275	10^{1}	1.015 794	10^{1}	−3.530 344	10^{1}
$c_{8,0}$	2.273 779	10^{1}	7.994 031	10^{1}	−1.308 137	10^{2}	1.094 105	10^{2}
α_3	−1.684 30	10^{-3}	−1.858 61	10^{-3}	−1.505 67	10^{-3}	−1.083 19	10^{-3}
$c_{4,1}$	−3.336 87	10^{-2}	−3.988 56	10^{-2}	−5.495 37	10^{-2}	−3.041 13	10^{-2}
$c_{6,1}$	−1.039 53		−8.127 91	10^{-1}	2.695 77	10^{-2}	4.188 97	10^{-1}
$c_{8,1}$	2.365 47	10^{-1}	−1.670 10	10^{-1}	−1.925 27	10^{-1}	−1.448 25	
α_4	4.377 00	10^{-5}	5.980 17	10^{-5}	4.039 18	10^{-5}	2.281 83	10^{-5}
$c_{4,2}$	4.875 69	10^{-3}	3.993 31	10^{-3}	−2.509 77	10^{-3}	−3.416 69	10^{-3}
$c_{6,2}$	1.411 21	10^{-1}	1.838 91	10^{-1}	1.776 84	10^{-2}	2.358 43	10^{-2}
$c_{8,2}$	6.913 13	10^{-2}	1.150 45	10^{-1}	−2.617 68	10^{-2}	−9.996 01	10^{-2}
α_5	−7.450 47	10^{-7}	−1.232 97	10^{-6}	−6.966 45	10^{-7}	−3.156 00	10^{-7}
$c_{4,3}$	−6.854 37	10^{-4}	−1.028 63	10^{-3}	−1.998 20	10^{-4}	−2.413 60	10^{-4}
$c_{6,3}$	−2.346 52	10^{-2}	−2.976 84	10^{-2}	1.368 37	10^{-3}	1.341 60	10^{-3}
$c_{8,3}$	−1.076 27	10^{-2}	−1.064 60	10^{-2}	−6.306 77	10^{-4}	−5.950 13	10^{-3}
α_6	1.521 19	10^{-8}	1.493 03	10^{-8}	8.906 02	10^{-9}	2.920 81	10^{-9}
$c_{4,4}$	1.170 79	10^{-4}	1.581 67	10^{-4}	−1.548 32	10^{-5}	−1.531 52	10^{-5}
$c_{6,4}$	3.907 82	10^{-3}	5.715 38	10^{-3}	1.133 32	10^{-3}	8.080 41	10^{-5}
$c_{8,4}$	1.837 92	10^{-3}	2.964 17	10^{-3}	4.822 31	10^{-5}	−3.486 39	10^{-4}
α_7	−6.680 03	10^{-10}	4.070 53	10^{-10}	−6.863 86	10^{-11}	−3.278 83	10^{-11}
$c_{4,5}$	−1.950 05	10^{-5}	−3.111 76	10^{-5}	−1.166 4	10^{-6}	−9.573	10^{-7}
$c_{6,5}$	−6.530 57	10^{-4}	−1.001 24	10^{-3}	1.001 9	10^{-5}	4.828	10^{-6}
$c_{8,5}$	−3.036 19	10^{-4}	−4.322 64	10^{-4}	1.137 8	10^{-5}	−1.991	10^{-5}
α_8	−1.040 4	10^{-10}	−1.018 1	10^{-10}	9.7	10^{-13}	−5.3	10^{-13}
$c_{4,6}$	3.249 2	10^{-6}	5.381	10^{-6}	−9.21	10^{-8}	−5.83	10^{-8}
$c_{6,6}$	1.086 7	10^{-4}	1.837	10^{-4}	8.87	10^{-7}	2.84	10^{-7}
$c_{8,6}$	5.060 6	10^{-5}	8.826	10^{-5}	1.60	10^{-6}	−1.09	10^{-6}

and of $E(\kappa)$ within a certain interval of κ. It is found in Sec. VI that only solutions with κ below a certain constant value, usually much smaller than 10, are important for our purposes. In this case, relatively good individual $[N^{\Gamma_1}(\kappa)]^2$ and $E(\kappa)$ can be obtained even with the aid of only a few terms in (25) and (27). This can be checked by calculating $[N^{\Gamma_1}(\kappa)]^2$ and $E(\kappa)$ in terms of a certain number of the powers of κ used in (27) and (30), and by comparing the results with those obtained in the next (more developed) approximation. The convergence is usually very good for small κ (2–2.5 or less); for larger κ it is the better the larger not only the number of the powers of κ but also the number of the terms $(KH)_l^{\Gamma_1} j_l$ used in the calculations.

In the second step, we may ask how many of the solutions of (25), or of the components $(KH)_{l,t}^{\Gamma_1}$, have to be taken into account. Their number can be established by finding how many $(KH)_{l,t}^{\Gamma_1} j_l$ are needed for a fairly satisfactory approach to the total electron charge in the crystal; see Sec. VI. For fcc solutions having large powers of κ, we find this number to be larger than 4, but probably not very much so.

For the case of the sc crystal, in which the interval of κ corresponding to the electron states is evidently larger than in the fcc crystal (see Sec. VI; Ref. 16), more individual solutions as well as more terms in each of them are necessary for a good approximation.

V. ELECTRON STATES AND THEIR DENSITY

According to Eq. (16) we require that A^{Γ_1} vanish at the surface of a crystal block equal to a sphere with the radius R_d.[12] Since R_d is large—e.g., ~ 10^8 when expressed in terms of the lattice parameter taken as the unit distance—we have with good approximation

$$A^{\Gamma_1}(\kappa\,,\,\theta\,,\,\varphi\,,\,R_d)$$

$$=\sum_l F_l^{\Gamma_1}(\kappa\,,\,\theta\,,\,\varphi)\,\frac{\sin(\kappa R_d-\frac{1}{2}l\pi}{\kappa R_d}\;, \qquad (31)$$

providing the relation

$$\kappa R_d > \tfrac{1}{2}l(l+1) \qquad (32)$$

is valid. If the number of the spherical Bessel functions used for A^{Γ_1} and consequently also the values of l in (31) are small, the relations (32) and (31) do not hold only when κ is very small. For the larger κ, which fill a much larger interval because the electrons in a crystal block are very numerous,[13] the expression (31) can be considered as exact.[14] The zeros of the whole function (31) coincide with the zeros of the component functions j_l and are identical for all l, considering that the l in the combination (31) are of the same (even) parity. Hence, the quantization of A^{Γ_1} can be replaced by that of a single component of A^{Γ_1}, e.g., $j_0(\kappa R)$. The quantum condition is then

$$\kappa R_d = n\pi, \quad n = 1, 2, 3, \ldots, \text{etc.}, \tag{33}$$

and the density of states per unit κ is[15]

$$\frac{dn}{d\kappa} = \frac{R_d}{\pi} . \tag{34}$$

A similar reasoning can be applied to the functions for $\Gamma_i \neq \Gamma_1$, providing they can be considered as sufficiently accurate when composed of not too large a number of j_l.

Now we normalize the relevant Ψ; using Eq. (4) we obtain

$$\int \Psi^* \Psi d\tau = \textstyle\sum_i A^{\Gamma_1 *}(\vec{R}_i, \kappa) A^{\Gamma_1}(\vec{R}_i, \kappa) = 1 \tag{35}$$

for any κ. Providing A does not change too rapidly along the distance between two neighboring atoms, the summation in (35) over the lattice sites can be replaced by integration over the volume of the crystal sphere. Then

$$\textstyle\sum_i A^{\Gamma_1 *}(\vec{R}_i, \kappa) A^{\Gamma_1}(\vec{R}_i, \kappa) = (1/v_a) \int [A^{\Gamma_1}(\vec{R}, \kappa)]^2 d\Omega \tag{36}$$

because A^{Γ_1} is real; v_a is the volume of the atomic cell and $\Omega = \frac{4}{3}\pi R_d^3$. In view of the orthogonality relation between $(KH)^{\Gamma_1}_{l,t}$ having different l, or the same l and different t, any component of the integral (36) is proportional to

$$\int_0^{R_d} j_l^2(\kappa R) R^2 \, dR . \tag{37}$$

The integral (37) vanishes at the lower limit owing to the behavior of j_l at small R. At the upper limit—R_d being very large—all j_l can be approximated by $[\sin(\kappa R)]/\kappa R$ (we notice that all l in A^{Γ_1} are even numbers). We obtain

$$\int \frac{\sin^2 \kappa R}{\kappa^2 R^2} R^2 \, dR = \frac{1}{2\kappa^2}\left(R - \frac{\sin 2\kappa R}{2\kappa}\right),$$

which at $R = R_d$ gives $(1/2\kappa^2)R_d$ because $\sin\kappa R_d = 0$ at the boundary. Thus the right-hand side of Eq. (36) is

$$\{[N^{\Gamma_1}(\kappa)]^2 / 2\kappa^2 v_a\} \times 4\pi R_d [1 + \textstyle\sum_l \sum_t (\sum_m c_{l,t,m} \kappa^{2m})^2 I_{l,t}] , \tag{38}$$

where the summation over l and t includes all the (non-normalized) cubic harmonics in Γ_1 except that whose $l = 0$, and $I_{l,t}$ is

$$I_{l,t} = (4\pi)^{-1} \int_0^{\pi} d\theta \int_0^{2\pi} d\varphi \sin\theta \, [(KH)^{\Gamma_1}_{l,t}]^2 .$$

The density of crystal states, $D^c(\kappa)$, per unit range of κ and per volume of one crystal cell, can be obtained by multiplying Eq. (34) by the number of the electron charge provided by the cell at the central atom, thus 1, times this atom's contribution

$$[A^{\Gamma_1}(\vec{0}, \kappa)]^2 \tag{39}$$

to the total charge carried by an orbital having the quantum parameter κ. In view of (30)—and owing to the requirement that (36) or (38) be unity—we have

$$D^c(\kappa) = [N^{\Gamma_1}(\kappa)]^2 R_d/\pi = \{\cdots\}^{-1} (1/2\pi^2) \kappa^2 v_a , \tag{40}$$

where the expression within the square braces is that given in Eq. (38); v_a is 1 for the sc crystal and 2 for the fcc crystal, if the primitive translations from Sec. II are used and the lattice parameter a is put equal to the unit distance (cf. also Secs. IV A and VI A).

The density of states $D^c(\mathrm{E})$ as a function of energy and per unit of volume (e.g., v_a further below) can be obtained from the relation

$$D^c(\mathrm{E}) = (\Delta\mathrm{E})^{-1} \int_{\Delta\mathrm{E}} D^c(\kappa) \, d\kappa . \tag{41}$$

The integration in (41) is extended over this interval (or intervals) of κ for which the energies are within the interval

$$(\mathrm{E} - \tfrac{1}{2}\Delta\mathrm{E}, \; \mathrm{E} + \tfrac{1}{2}\Delta\mathrm{E}) . \tag{42}$$

It should be noted that Eqs. (40) and (41) are related to only *one* A^{Γ_1} solution. But we have many A^{Γ_1} (see Sec. IV and Sec. VI) for any κ and each can contribute to the electron density at $\vec{0}$. Thus the total crystal density of states per unit range of κ and per unit of volume is

$$D(\kappa) = \textstyle\sum_\lambda D^{c,\lambda}(\kappa) , \tag{40$'$}$$

where the components are (40)'s for different λ. In the same way the total density of states in the crystal as a function of E and per unit of volume is

$$D(\mathrm{E}) = \textstyle\sum_\lambda D^{c,\lambda}(\mathrm{E}) , \tag{41$'$}$$

where the components are those of Eq. (41). The results of the calculations of $D^{c,\lambda}(\kappa)$ are discussed in the Sec. VI; those for $D(\mathrm{E})$ in Sec. VII.

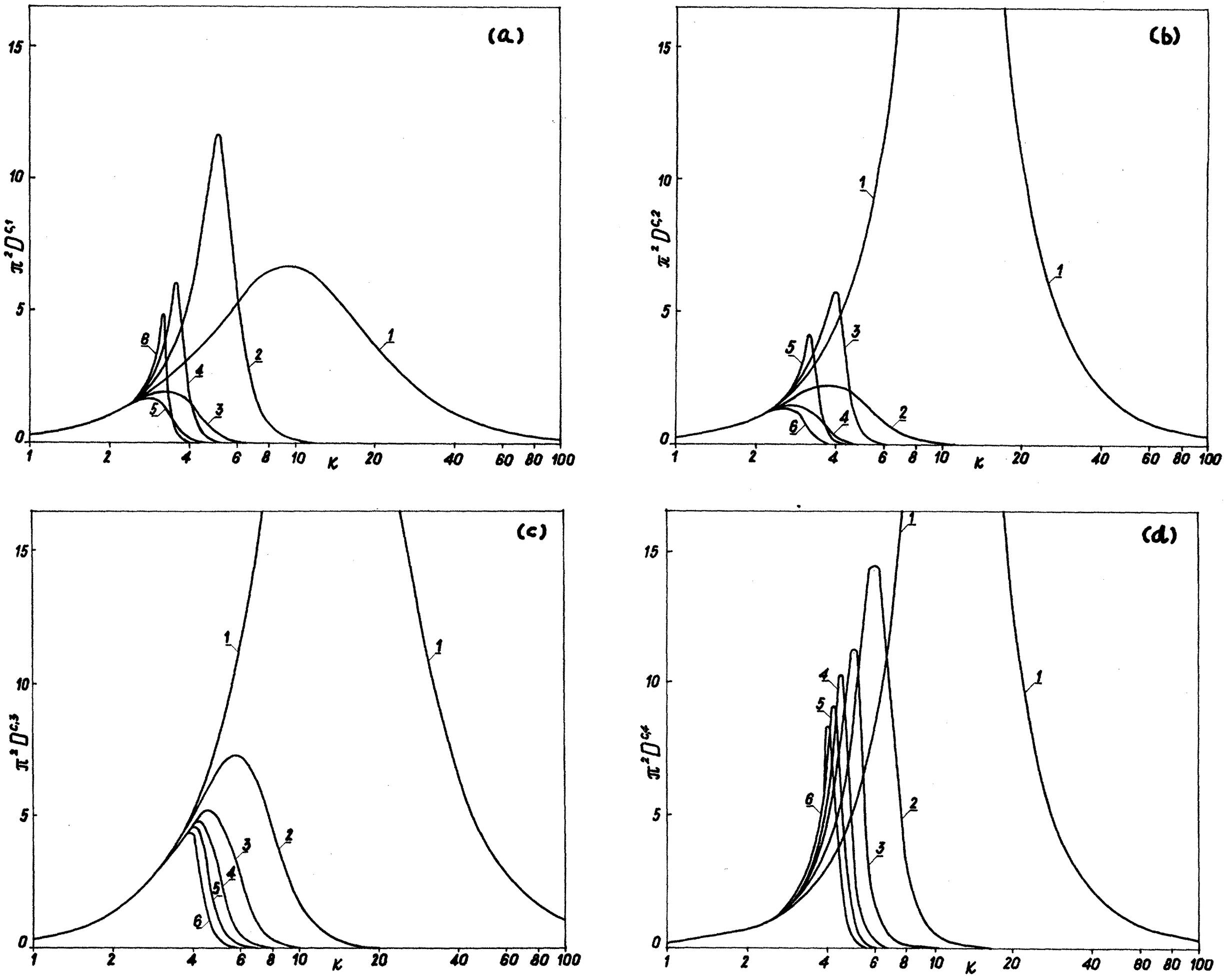

FIG. 1. Densities of states $D^{c,\lambda}$ times π^2 vs κ for (a) $\lambda=1$, (b) $\lambda=2$, (c) $\lambda=3$, (d) $\lambda=4$ (case of $l=0$, 4, 6, and 8 taken into account) as a semilogarithmic plot; fcc lattice. The integers indicate the largest value of m used in the development of Eq. (25) in each case. The abscissas of the inflection points of curves 1–6 are given in Table II. The maxima of curves 1 for λ from 2 to 4 occur, respectively, at κ equal to about 11.2, 12.6, and 11.2 and attain approximately the values 35.5, 30.5, and 41.5. For the largest $m=0$ (a case not shown in the figures) all $D^{c,\lambda}$ are propotional to κ^2 tending towards infinity with κ.

VI. FURTHER PROPERTIES OF ELECTRON STATES

A. Bands of States and Their Limits

Considering the density of states per unit range of κ and per unit of volume, we find a profound difference between free electrons and those in the crystal. The free electron $D(\kappa)$ is

$$D^f(\kappa)=\frac{dn}{d\kappa}\,[N^f(\kappa)]^2=\frac{\kappa^2}{2\pi^2} \tag{43}$$

because again one point, that of $|\vec{R}|=0$, can be considered as representative of the system and the normalization coefficient of the free-electron solution which does not vanish at $|\vec{R}|=0$, viz., $j_0(\kappa R)$, is $\kappa(2\pi R_a)^{-1/2}$. The $D^f(\kappa)$ starts at zero and tends towards infinity with κ. At the same time all $D^{c,\lambda}(\kappa)$—except with very undeveloped solutions—first increase from zero (at $\kappa=0$) similarly to $D^f(\kappa)$, and then decrease to extremely small values (see Fig. 1), usually the more rapidly the more extended $A^{\Gamma_1,\lambda}$ are used. In the limiting case of a very extended $A^{\Gamma_1,\lambda}$ a very abrupt decrease may be expected. Thus, at a chosen crystal point, e.g., $\vec{0}$ the electron density is built up only by the states with $\kappa>0$ [cf. Eq. (33) and—concerning the states with negative κ—the end of Sec. VI C] but less than a certain limiting value; when κ exceeds this value, the states do not contribute to the density. The zone for the one-dimensional quantum parameter has its counterpart in the theory of Bloch. Since to any interval of κ there corresponds [via Eq. (27)]

TABLE II. Positions of inflection points of $D^{c,\lambda}(\kappa)$ for fcc and sc lattices in different approximations. The m figure at the top of each column indicates the largest power exponent used in the development of Eq. (25).

fcc lattice; $l=0$ and 4 taken into account							
λ	$m=0$	$m=1$	$m=2$	$m=3$	$m=4$	$m=5$	$m=6$
1	no	15	7.1	5.8	5.2	5.0	4.9
2	inflection points	13	10.6	7.2	8.7	6.7	7.1
fcc lattice; $l=0$, 4, and 6 taken into account							
λ	$m=0$	$m=1$	$m=2$	$m=3$	$m=4$	$m=5$	$m=6$
1	no	14	6.0	4.9	4.1	3.9	3.6
2	inflection	21	6.9	5.0	4.6	4.0	4.0
3	points	44	13	8.1	6.4	5.6	5.2
fcc lattice; $l=0$, 4, 6, and 8 taken into account							
λ	$m=0$	$m=1$	$m=2$	$m=3$	$m=4$	$m=5$	$m=6$
1	no	14.5	5.7	4.2	3.8	3.4	3.3
2	inflection	13	5.1	4.2	3.5	3.4	3.1
3	points	19	7.6	5.7	4.9	4.5	4.3
4		14	6.7	5.3	4.8	4.5	4.3
sc lattice: $l=0$ and 4 taken into account							
λ	$m=0$	$m=1$	$m=2$	$m=3$	$m=4$	$m=5$	$m=6$
1	no	54	24	21	18	14	12
2	inflection points	36	23	34	15	13	11
λ	$m=7$	$m=8$	$m=9$	$m=10$	$m=11$	$m=12$	$m=13$
1	11	11	10	10	9.8	9.6	9.4
2	11	10	10	9.6	9.4	9.2	9.1
sc lattice; $l=0$, 4, and 6 taken into account							
λ	$m=0$	$m=1$	$m=2$	$m=3$	$m=4$	$m=5$	$m=6$
1	no	52	18	13	12	11	10.5
2	inflection	76	18	13	11	10	9.2
3	points	158	17	11	10	9.0	8.5

an interval or intervals of energy, there is also in the present method a zone for the energies of electron states.

We can distinguish on $D^{c,\lambda}(\kappa)$ inflection points to the right of which the decrease of $D^{c,\lambda}$ becomes very rapid for developed $A^{\Gamma_1,\lambda}$. The abcissas $\kappa_i{}^\lambda$ of these points calculated in successive approximations, as well as $D^{c,\lambda}$ themselves, exhibit a tendency to converge [see respectively, Table II and Figs. 1(a)–1(d)]. When, for the fcc lattice, the approximation for $A^{\Gamma_1,\lambda}$ and convergence of κ_i^λ are rather satisfactory, we have

$$\kappa_i^1=3.3;\quad \kappa_i^2=3.1;\quad \kappa_i^3=4.3;\quad \kappa_i^4=4.3. \tag{44}$$

Let us note that the maximum value in (44) is not far from the maximum value of $|\vec{k}|$ for the first Brillouin zone of the fcc lattice

$$(\tfrac{1}{2}\sqrt{5})\pi=3.51\,, \tag{45}$$

which holds if (1, 1, 0); (1, 0, 1) and (0, 1, 1) are taken as the primitive translations. This is the expected result if we take into account that (a) the functions of Eq. (24) are—similarly to Eq. (2)—the free-electron eigenfunctions with

$$\kappa=|\vec{k}| \tag{46}$$

[cf. Eqs. (56) and (58)]; (b) the functions $A^{\Gamma_1,\lambda}$ responsible for Eq. (44) have been calculated with the same primitive translations as those used for (45) (cf. the beginning of Sec. IV A); and (c) Eq. (45) denotes the limiting value of $|\vec{k}|$ or κ, which can be accepted quasicontinuously by the electron states in the fcc crystal of Bloch starting from $|\vec{k}|=0$. In the idealized case of very accurate $A^{\Gamma_1,\lambda}$ we may expect the maximum value of κ_i^λ for the fcc crystal to come close to that of Eq. (45).[16]

The above reasoning is supported also by the correspondence between the meaning of the maximum of $|\vec{k}|$ and the maximum of κ for the behavior of A, respectively, in the theory of Bloch and the present one. The existence of a certain maximum κ which can be accepted by electron states implies that the wavelength $\Lambda=2\pi\kappa^{-1}$ of the coefficient function $A^{\Gamma_1,\lambda}$ at large distances $\vec{R}$ cannot be less than a certain critical length. This prevents $A^{\Gamma_1,\lambda}$ from oscillating too rapidly, in agreement with the assumption made in deriving the equation and the properties for $A^{\Gamma_1,\lambda}$ (cf. also Sec. VI B). But this result also is fully consistent with the LCAO theory of Bloch. For, an arbitrary vector $\vec{k}'$ in the reciprocal space can be represented as the sum $\vec{k}+\vec{K}_j$, where $\vec{K}_j$ is the vector of the reciprocal lattice and $\vec{k}$ is the vector inside the first Brillouin zone, or on its surface. The property $\vec{K}_j\cdot\vec{R}_i=2\pi\delta_{ji}$ gives

$$e^{i\vec{k}'\cdot\vec{R}_i}=e^{i(\vec{k}\cdot\vec{R}_i+2\pi\delta_{ji})}=e^{i\vec{k}\cdot\vec{R}_i}\,, \tag{47}$$

and thus (2) or (47) cannot have a wavelength shorter than that obtained from the maximum value of $\vec{k}$ on the surface of the first Brillouin zone.[17]

The next point of importance is the maximum which a single atom at $\vec{R}_i$ and the band of the crystal states can contribute to the total electron charge of the crystal. If the atomic orbitals fulfill Eq. (4), this value is given in the LCAO theory of Bloch simply as[18]

$$Q(\vec{R}_i)=\sum_{\vec{k}}(1/N)\,e^{-i\vec{k}\cdot\vec{R}_i}\,e^{i\vec{k}\cdot\vec{R}_i}\times\int\phi^*(\vec{r}-\vec{R}_i)\,\phi(\vec{r}-\vec{R}_i)\,d\tau \tag{48}$$

equal to

$$(1/N)\sum_{\vec{k}}1=1 \tag{49}$$

because the summation is extended over all the states of the Brillouin zone. Equation (49) is fundamental for an explanation of the experimental data for solids. In our calculations—confined to Γ_1 and related to site $\vec{0}$—we should have the same result for Q and we consider the discrepancy of $Q(\vec{0})$ from 1 as the measure of the inaccuracy of the set of solutions used for it.

The maximum contribution to the electron density can be calculated when all quantum states whose

TABLE III. Values of $Q(\vec{0})$ [see Eq. (50)] for fcc and sc lattices in different approximations. The figures m have the same meaning as in Table II.

fcc lattice; $l=0$ and 4 taken into account						
$m=0$	$m=1$	$m=2$	$m=3$	$m=4$	$m=5$	$m=6$
∞	187	21.6	7.30	15.8	8.60	10.9
fcc lattice; $l=0$, 4, and 6 taken into account						
$m=0$	$m=1$	$m=2$	$m=3$	$m=4$	$m=5$	$m=6$
∞	857	76.2	15.8	7.88	5.15	4.02
fcc lattice; $l=0$, 4, 6, and 8 taken into account						
$m=0$	$m=1$	$m=2$	$m=3$	$m=4$	$m=5$	$m=6$
∞	218	12.6	5.40	3.71	2.89	2.50
sc lattice; $l=0$ and 4 taken into account						
$m=0$	$m=1$	$m=2$	$m=3$	$m=4$	$m=5$	$m=6$
∞	2560	302	671	99.6	49.1	33.9
$m=7$	$m=8$	$m=9$	$m=10$	$m=11$	$m=12$	$m=13$
26.7	22.6	19.9	18.2	16.9	15.8	15.0
sc lattice; $l=0$, 4, and 6 taken into account						
$m=0$	$m=1$	$m=2$	$m=3$	$m=4$	$m=5$	$m=6$
∞	20100	132	50.1	32.1	24.9	21.0

wave functions do not vanish at $\vec{0}$ are taken into account. Thus

$$Q(\vec{0})=\sum_{\lambda}\int_0^{\infty} D^{c,\lambda}(\kappa)\,d\kappa \tag{50}$$

since, in principle, the densities of all states—also those of very large κ—can add up significantly to Q. This is so in the case of free electrons for which $Q(\vec{0})$ is infinity. The values of $Q(\vec{0})$ in different approximations for $A^{\Gamma_1,\lambda}$ are given in Table III. We see that for little developed $A^{\Gamma_1,\lambda}$ ($m=0$) the values for (50) are still infinite. However, when the terms with $m>0$ are introduced in (25), we have a zonal (band) structure, i.e., Eq. (50) can be written

$$Q(\vec{0})=\sum_{\lambda}\int_0^{\kappa_m^{\lambda}} D^{c,\lambda}(\kappa)\,d\kappa\ , \tag{51}$$

where κ_m^{λ} are finite values.

From Figs. 1(a)–1(d) it is evident that for well developed $A^{\Gamma_1,\lambda}$ these values should not be much larger than the abcissas of the inflection points discussed at the beginning of this section. In fact, when κ_i^{λ} of Eq. (44) are put as the upper limits of the integrals (51), the difference between (51) and (50), calculated for the case of solutions corresponding to (44), is only about 12% of (50). For κ_m^{λ} somewhat larger than κ_i^{λ}, viz.,

$$\kappa_m^1=3.7\ ;\quad \kappa_m^2=3.5\ ;\quad \kappa_m^3=4.55\ ;\quad \kappa_m^4=4.8\ , \tag{52}$$

this difference diminishes to about 1.5%. Another characteristic point is that for well developed $A^{\Gamma_1,\lambda}$ the difference between (51), or (50), and (49) decreases distinctly (Table III), and $E^{\lambda}(\kappa)$ also can be rather accurate within the intervals $(0,\ \kappa_m^{\lambda})$, which enables the density of states per energy unit to be calculated from Eqs. (41) and (41′). The limits of the energy band can be obtained as the extreme values of E^{λ} within the intervals $(0,\ \kappa_m^{\lambda})$. This is done in Sec. VII for the fcc lattice as an example.

B. Property of Orthogonality

Two LCAO functions, either (i) with different κ, or (ii) with the same κ and different λ, are orthogonal. Owing to Eq. (4) and the assumptions characteristic for the derivation of Eq. (36), the orthogonality of Ψ becomes equivalent to that of $A^{\Gamma_1,\lambda}$. The property (i) can be deduced from the behavior of $j_l(\kappa R)$ at very small and very large R and is valid for any approximate $A^{\Gamma_1,\lambda}$. The property (ii) is due to the operator $\hat{W}$ being Hermitian[19]; this orthogonality can be fulfilled rather accurately by the approximate solutions for rather small κ only. For example, for the developed $A^{\Gamma_1,\lambda}$ of the present paper (the fcc lattice) calculations show it to be well fulfilled for all λ only for $\kappa \lesssim 2$.

C. Total Number of States in the Crystal

The multitude of $A^{\Gamma_1,\lambda}$ for the same κ is important not only for the accurate calculation of $Q(\vec{0})$ (see Table III),[20] but also when the total number of the electron states in the crystal is considered. Since j_l with $l \gg 0$—which may dominate in the developed $A^{\Gamma_1,\lambda}$ (see Ref. 20)—have a smaller number of zeros in a given interval for κR_d than has j_0, we can expect that quantization of very developed $A^{\Gamma_1,\lambda}$ according to the boundary condition (16) will not give more states than will give the quantization of a single component j_0. Therefore, for an average macroscopic crystal ($R_d \sim 10^8$) the number of states for an individual λ is at most of the order of about 10^8, because, as has been pointed out, only κ not exceeding several units in magnitude contribute to the electron density of the crystal.[21] The remainder of about 10^{23} electron states in the crystal should originate from the multiplicity of solutions $A^{\Gamma_1,\lambda}$ for the same κ as well as from A belonging to the irreducible representations different from Γ_1.

Let us note that $A^{\Gamma_1,\lambda}(\vec{R},\kappa)=A^{\Gamma_1,\lambda}(\vec{R},-\kappa)$ and the corresponding $E^{\lambda}(\kappa)=E^{\lambda}(-\kappa)$, thus the states having κ are identical with those having $-\kappa$ and there is no degeneracy associated with the sign of κ.

VII. $D(E)$ DEPENDENCIES AND THEIR COMPARISON WITH THE RESULTS OF THE THEORY OF BLOCH

The method of the present paper can be compared in essence with that of Bloch when the energy dependence of the density of states is calculated by both. In the present paper we do this for the example of the fcc lattice and for two limiting cases: (i) nearest-neighbor interaction between atoms, or the tight-binding approximation; and (ii) almost-free electrons. Bloch's $D(E)$ for case (i) is approached in the following way. First, the volume

TABLE IV. Average density of states in different approximations versus E in the fcc lattice with the nearest-neighbor, or tight-binding, interaction.

Energy interval	D(E) of the present method calculated with $l=0$, 4, 6, and 8; $m=5$[a]	D(E) of the present method calculated with $l=0$, 4, 6, and 8; $m=6$[a]	D(E) of Bloch [cf. Eq. (54) for E and the relevant argument]
(1, 29/30)	0.032	0.032	0.033
(29/30, 28/30)	0.061	0.061	0.061
(28/30, 27/30)	0.082	0.082	0.078
(27/30, 26/30)	0.098	0.098	0.106
(26/30, 25/30)	0.115	0.115	0.110
(25/30, 24/30)	0.132	0.132	0.127
(24/30, 23/30)	0.146	0.146	0.152
(23/30, 22/30)	0.161	0.161	0.160
(22/30, 21/30)	0.179	0.179	0.177
(21/30, 20/30)	0.192	0.192	0.192
(20/30, 19/30)	0.214	0.214	0.215
(19/30, 18/30)	0.230	0.230	0.224
(18/30, 17/30)	0.247	0.247	0.256
(17/30, 16/30)	0.263	0.263	0.258
(16/30, 15/30)	0.295	0.295	0.301
(15/30, 14/30)	0.305	0.305	0.307
(14/30, 13/30)	0.335	0.335	0.320
(13/30, 12/30)	0.359	0.359	0.363
(12/30, 11/30)	0.386	0.386	0.399
(11/30, 10/30)	0.415	0.415	0.410
(10/30, 9/30)	0.456	0.456	0.457
(9/30, 8/30)	0.489	0.489	0.481
(8/30, 7/30)	0.531	0.531	0.533
(7/30, 6/30)	0.582	0.582	0.585
(6/30, 5/30)	0.632	0.632	0.632
(5/30, 4/30)	1.162	0.697	0.693
(4/30, 3/30)	1.785	0.777	0.777
(3/30, 2/30)	2.467	1.055	0.865
(2/30, 1/30)	3.19	1.64	1.01
1/30, 0)	4.07	2.25	1.16
(0, −1/30)	5.21	5.11	1.56
(−1/30, −2/30)	7.45	9.94	1.53
(−2/30, −3/30)	5.02	4.22	1.58
(−3/30, −4/30)	5.34	5.04	1.63
(−4/30, −5/30)	5.66	5.69	1.70
(−5/30, −6/30)	6.34	6.21	1.73
(−6/30, −7/30)	8.04	7.21	1.88
(−7/30, −8/30)	14.62	9.87	2.00
(−8/30, −9/30)	2.54	2.86	2.18
(−9/30, −10/30)	4.53	4.65	2.77
(−10/30, −11/30)	0	0	0
Total electron charge in the band per one atomic site	2.81[b]	2.47[b]	1.00[c]

[a] Figures l and m have the same meaning as in Table IV and V.

[b] These figures differ only by about 1.5–3% from those given in Table V.

[c] See Eq. (49).

TABLE V. Average density of states in the fcc lattice with nearest-neighbor, or tight-binding, interaction as produced by the contributions from different subbands. Case: $l=0$, 4, 6, and 8; $m=6$. Figures l and m have the same meaning as in Tables I–IV. For comparison with another approximation by the theory of Bloch see Table IV.

Energy interval	$D^{c,1}$(E)	$D^{c,2}$(E)	$D^{c,3}$(E)	$D^{c,4}$(E)	D(E)[a]
(1, 29/30)	0.009	0.008	0.011	0.005	0.033
(29/30, 28/30)	0.017	0.015	0.020	0.010	0.062
(28/30, 27/30)	0.022	0.020	0.027	0.013	0.082
(27/30, 26/30)	0.026	0.024	0.032	0.016	0.098
(26/30, 25/30)	0.030	0.028	0.038	0.019	0.115
(25/30, 24/30)	0.036	0.032	0.043	0.021	0.132
(24/30, 23/30)	0.040	0.036	0.047	0.023	0.146
(23/30, 22/30)	0.044	0.038	0.054	0.026	0.162
(22/30, 21/30)	0.048	0.044	0.058	0.029	0.179
(21/30, 20/30)	0.051	0.047	0.063	0.030	0.191
(20/30, 19/30)	0.057	0.053	0.071	0.034	0.215
(19/30, 18/30)	0.064	0.056	0.073	0.036	0.229
(18/30, 17/30)	0.068	0.060	0.081	0.038	0.247
(17/30, 16/30)	0.072	0.066	0.085	0.040	0.263
(16/30, 15/30)	0.081	0.072	0.096	0.046	0.295
(15/30, 14/30)	0.085	0.075	0.097	0.048	0.305
(14/30, 13/30)	0.095	0.081	0.108	0.050	0.334
(13/30, 12/30)	0.099	0.088	0.117	0.056	0.360
(12/30, 11/30)	0.110	0.098	0.121	0.057	0.386
(11/30, 10/30)	0.118	0.101	0.134	0.061	0.414
(10/30, 9/30)	0.131	0.112	0.144	0.068	0.455
(9/30, 8/30)	0.146	0.120	0.153	0.070	0.489
(8/30, 7/30)	0.156	0.128	0.170	0.078	0.532
(7/30, 6/30)	0.178	0.141	0.181	0.083	0.583
(6/30, 5/30)	0.196	0.155	0.192	0.088	0.631
(5/30, 4/30)	0.223	0.165	0.211	0.097	0.696
(4/30, 3/30)	0.260	0.181	0.232	0.103	0.776
(3/30, 2/30)	0.302	0.205	0.255	0.293	1.055
(2/30, 1/30)	0.38	0.22	0.28	0.76	1.64
(1/30, 0)	0.48	0.24	0.53	1.00	2.25
(0, −1/30)	2.64	0.28	0.79	1.40	5.11
(−1/30, −2/30)	6.66	0.31	1.05	1.93	9.95
(−2/30, −3/30)	···	0.35	1.41	2.46	4.22
(−3/30, −4/30)	···	0.40	1.86	2.78	5.04
(−4/30, −5/30)	···	0.47	2.37	2.85	5.69
(−5/30, −6/30)	···	0.52	3.04	2.65	6.21
(−6/30, −7/30)	···	0.56	4.15	2.50	7.21
(−7/30, −8/30)	···	0.47	6.97	2.43	9.87
(−8/30, −9/30)	···	0.19	···	2.67	2.86
(−9/30, −10/30)	···	0.01	···	4.64	4.65
Total electron charge in the band per one atomic site	0.43	0.21	0.84	0.99	2.47

[a] Some figures in this column differ by unity at the last decimal place from those of the corresponding column in Table IV in view of the rounded values for $D^{c,\lambda}$(E) in the present table.

of $\frac{1}{8}$ of the first Brillouin zone is cut out by xy, yz, and zx planes and approximated by that of 62 500 equal cubes. Then for $\mathrm{E}(k_x, k_y, k_z)$ of Bloch we have

$$\mathrm{E}(k_x, k_y, k_z) = (E^B - E^0 - \gamma)/q\beta \ , \tag{53}$$

where E^B is the Bloch energy and E^0, γ, q, and β have the same meaning as in Eq. (21), thus—in the case of the fcc lattice—

$$\mathrm{E}(k_x, k_y, k_z) = \tfrac{1}{3}(\cos k_x \cos k_y + \cos k_y \cos k_z + \cos k_z \cos k_x), \tag{54}$$

and the interval

$$\Delta \mathrm{E} = \tfrac{1}{30} \tag{55}$$

has been chosen. The value of (54) is between 1 attained for $k_x = k_y = k_z = 0$ and $-\frac{1}{3}$ obtained on the diagonals of the squares on the boundary of the first Brillouin zone corresponding to the primitive translations used in Eq. (54). Since β is usually considered as negative, the maximum value of (54) can be referred to the bottom, and the minimum to the top of the energy band. An approximation to Bloch's D(E) can be obtained when the number of cubes for which the Bloch energies are enclosed in any of the 40 intervals of (55) is calculated for the interval between 1 and $-\frac{1}{3}$.

The same magnitude of the energy interval as in (55) also is assumed in the (approximate) calculations of the D(E) of the present method. These D(E) are little affected by the value of the interval between two neighboring values of κ, assumed as 0.002. The number of the considered points of κ is determined by the magnitude of the intervals $(0, \kappa_m^\lambda)$. The inclusion of points with $\kappa > \kappa_m^\lambda$ will not change D(E) significantly providing Eq. (51) is a good approximation for $Q(\vec{0})$. Two D(E), calculated for rather developed approximations for $A^{\Gamma_1,\lambda}$ and E^λ, are given in Table IV. The contributions to one of these D(E) made by individual subbands are presented in Table V. D(E) can be considered as accurate only in the interval $1 > \mathrm{E} \gtrsim 0.15$, because the solutions with $\kappa < 2$ are the only ones which contribute to D(E) within this interval. For $\mathrm{E} \lesssim 0.15$—and for the approximations in Table IV—important contributions to D(E) come from states whose κ is much larger than 2. In this case the developments for $A^{\Gamma_1,\lambda}$ and E^λ are very inaccurate and the results given in Tables IV and V can only be considered as a very poor approximation to D(E).

The limits of the energy band for the fcc lattice can be obtained as the maximum and the minimum value of E^λ inside the intervals of κ between zero and (52), if—for example—the more accurate of the approximations in Table IV is used. One of these values is attained by all E^λ at $\kappa = 0$ and equals 1. The other is provided by E^4 at $\kappa = 3.2$ and equals -0.33. In the considered approximation, therefore, we obtain band limits identical with those given by the theory of Bloch.[22]

The present scheme can be compared more accurately with that of Bloch for almost-free electrons. This approximation assumes that $V(\vec{r})$ and $U(\vec{r})$ tend to zero, so that the electrons in the lat-

TABLE VI. Density of states $D(E)\pi^2$ in the fcc lattice for the almost-free electron approximation. Present theory in the case of $l=0$, 4, 6, and 8; $m=6$ (figures l and m have the same meaning as in Tables I–V) vs the theory of Bloch. Only the values corresponding to states below a critical point in the theory of Bloch [$|\vec{k}| = \frac{1}{2}\sqrt{3}\,\pi = 2.72$] are considered.

	$\pi^2\kappa^{-1}D^{c,\lambda}(\kappa)$								Total value from columns with $\lambda=1$ to $\lambda=4$; cf. Eq. (59)		Bloch [cf. Eq. (57)]
κ	$\lambda=1$		$\lambda=2$		$\lambda=3$		$\lambda=4$				
0.05	1.377 142 12	10^{-2}	1.203 081 90	10^{-2}	1.647 212 02	10^{-2}	8.125 639 78	10^{-3}	5.000 000 02	10^{-2}	0.050 000 00
0.10	2.673 941 98	10^{-2}	2.406 362 21	10^{-2}	3.294 437 18	10^{-2}	1.625 258 67	10^{-2}	1.000 000 00	10^{-1}	0.100 000 00
0.15	4.010 059 66	10^{-2}	3.610 036 71	10^{-2}	4.941 688 36	10^{-2}	2.438 215 34	10^{-2}	1.500 000 00	10^{-1}	0.150 000 00
0.20	5.345 160 01	10^{-2}	4.814 295 82	10^{-2}	6.588 977 88	10^{-2}	3.251 566 35	10^{-2}	2.000 000 00	10^{-1}	0.200 000 00
0.25	6.678 914 79	10^{-2}	6.019 322 17	10^{-2}	8.236 317 34	10^{-2}	4.065 445 79	10^{-2}	2.500 000 00	10^{-1}	0.250 000 00
0.30	8.011 004 98	10^{-2}	7.225 288 01	10^{-2}	9.883 717 12	10^{-2}	4.879 990 05	10^{-2}	3.000 000 01	10^{-1}	0.300 000 00
0.35	9.341 122 54	10^{-2}	8.432 352 89	10^{-2}	1.153 118 64	10^{-1}	5.695 338 26	10^{-2}	3.500 000 00	10^{-1}	0.350 000 00
0.40	1.066 897 23	10^{-1}	9.640 661 81	10^{-2}	1.317 873 27	10^{-1}	6.511 633 19	10^{-2}	3.999 999 99	10^{-1}	0.400 000 00
0.45	1.199 427 38	10^{-1}	1.085 034 29	10^{-1}	1.482 636 17	10^{-1}	7.329 021 72	10^{-2}	4.500 000 01	10^{-1}	0.450 000 00
0.50	1.331 676 20	10^{-1}	1.206 150 58	10^{-1}	1.647 407 69	10^{-1}	8.147 655 47	10^{-2}	5.000 000 00	10^{-1}	0.500 000 00
0.55	1.463 618 93	10^{-1}	1.327 424 01	10^{-1}	1.812 187 92	10^{-1}	8.967 691 68	10^{-2}	5.500 000 03	10^{-1}	0.550 000 00
0.60	1.595 232 56	10^{-1}	1.448 861 38	10^{-1}	1.976 976 69	10^{-1}	9.789 293 84	10^{-2}	6.000 000 01	10^{-1}	0.600 000 00
0.65	1.726 495 96	10^{-1}	1.570 467 26	10^{-1}	2.141 773 52	10^{-1}	1.061 263 27	10^{-1}	6.500 000 00	10^{-1}	0.650 000 00
0.70	1.857 389 86	10^{-1}	1.692 243 85	10^{-1}	2.306 577 61	10^{-1}	1.143 788 68	10^{-1}	6.999 999 97	10^{-1}	0.700 000 00
0.75	1.987 896 91	10^{-1}	1.814 190 91	10^{-1}	2.471 387 80	10^{-1}	1.226 524 38	10^{-1}	7.499 999 98	10^{-1}	0.750 000 00
0.80	2.118 001 65	10^{-1}	1.936 305 70	10^{-1}	2.636 202 50	10^{-1}	1.309 490 13	10^{-1}	7.999 999 97	10^{-1}	0.800 000 00
0.85	2.247 690 52	10^{-1}	2.058 582 90	10^{-1}	2.801 019 75	10^{-1}	1.392 706 78	10^{-1}	8.499 999 92	10^{-1}	0.850 000 00
0.90	2.376 951 79	10^{-1}	2.181 014 57	10^{-1}	2.965 837 13	10^{-1}	1.476 196 43	10^{-1}	8.999 999 91	10^{-1}	0.900 000 00
0.95	2.505 775 49	10^{-1}	2.303 590 07	10^{-1}	3.130 651 69	10^{-1}	1.559 982 53	10^{-1}	9.499 999 77	10^{-1}	0.950 000 00
1.00	2.634 153 48	10^{-1}	2.426 296 03	10^{-1}	3.295 460 05	10^{-1}	1.644 090 00	10^{-1}	9.999 999 53	10^{-1}	1.000 000 00
1.05	2.762 079 21	10^{-1}	2.549 116 20	10^{-1}	3.460 258 27	10^{-1}	1.728 545 51	10^{-1}	1.049 999 92		1.050 000 00
1.10	2.889 547 79	10^{-1}	2.672 031 30	10^{-1}	3.625 041 77	10^{-1}	1.813 377 47	10^{-1}	1.099 999 83		1.100 000 00
1.15	3.016 555 95	10^{-1}	2.795 018 86	10^{-1}	3.789 805 56	10^{-1}	1.898 616 37	10^{-1}	1.149 999 67		1.150 000 00
1.20	3.143 102 13	10^{-1}	2.918 052 93	10^{-1}	3.954 543 86	10^{-1}	1.984 294 95	10^{-1}	1.199 999 38		1.200 000 00
1.25	3.269 186 40	10^{-1}	3.041 103 58	10^{-1}	4.119 250 50	10^{-1}	2.070 448 46	10^{-1}	1.249 998 89		1.250 000 00
1.30	3.394 810 78	10^{-1}	3.164 136 32	10^{-1}	4.283 918 47	10^{-1}	2.157 114 81	10^{-1}	1.299 998 03		1.300 000 00
1.35	3.519 979 44	10^{-1}	3.287 111 22	10^{-1}	4.448 540 31	10^{-1}	2.244 335 12	10^{-1}	1.349 996 61		1.350 000 00
1.40	3.644 699 24	10^{-1}	3.409 981 66	10^{-1}	4.613 107 93	10^{-1}	2.332 153 73	10^{-1}	1.399 994 25		1.400 000 00
1.45	3.768 980 45	10^{-1}	3.532 692 66	10^{-1}	4.777 612 59	10^{-1}	2.420 618 88	10^{-1}	1.499 990 46		1.450 000 00
1.50	3.892 837 82	10^{-1}	3.655 178 57	10^{-1}	4.942 044 99	10^{-1}	2.509 782 93	10^{-1}	1.499 984 43		1.500 000 00
1.55	4.016 292 10	10^{-1}	3.777 359 88	10^{-1}	5.106 395 67	10^{-1}	2.599 702 94	10^{-1}	1.549 975 06		1.550 000 00
1.60	4.139 371 98	10^{-1}	3.899 138 98	10^{-1}	5.270 654 22	10^{-1}	2.690 441 07	10^{-1}	1.599 960 62		1.600 000 00
1.65	4.262 117 18	10^{-1}	4.020 394 78	10^{-1}	5.434 810 31	10^{-1}	2.782 065 42	10^{-1}	1.649 938 77		1.650 000 00
1.70	4.384 582 29	10^{-1}	4.140 975 32	10^{-1}	5.598 853 53	10^{-1}	2.874 650 51	10^{-1}	1.699 906 16		1.700 000 00
1.75	4.506 841 75	10^{-1}	4.260 688 28	10^{-1}	5.762 773 23	10^{-1}	2.968 278 17	10^{-1}	1.749 858 14		1.750 000 00
1.80	4.628 996 62	10^{-1}	4.379 289 03	10^{-1}	5.926 559 19	10^{-1}	3.063 038 50	10^{-1}	1.799 788 33		1.800 000 00
1.85	4.751 183 47	10^{-1}	4.496 464 83	10^{-1}	6.090 201 57	10^{-1}	3.159 030 63	10^{-1}	1.849 688 05		1.850 000 00
1.90	4.873 585 65	10^{-1}	4.611 815 80	10^{-1}	6.253 691 60	10^{-1}	3.256 364 18	10^{-1}	1.899 545 72		1.900 000 00
1.95	4.996 447 71	10^{-1}	4.724 830 52	10^{-1}	6.417 021 55	10^{-1}	3.355 160 39	10^{-1}	1.949 346 02		1.950 000 00
2.00	5.120 094 34	10^{-1}	4.834 856 33	10^{-1}	6.580 185 44	10^{-1}	3.455 553 88	10^{-1}	1.999 069 00		2.000 000 00
2.05	5.244 953 67	10^{-1}	4.941 063 47	10^{-1}	6.743 179 91	10^{-1}	3.557 694 15	10^{-1}	2.048 689 11		2.050 000 00
2.10	5.371 587 18	10^{-1}	5.042 402 17	10^{-1}	6.906 003 90	10^{-1}	3.661 747 64	10^{-1}	2.098 174 08		2.100 000 00
2.15	5.500 727 71	10^{-1}	5.137 553 08	10^{-1}	7.068 660 52	10^{-1}	3.767 900 34	10^{-1}	2.147 484 16		2.150 000 00
2.20	5.633 327 12	10^{-1}	5.224 870 59	10^{-1}	7.231 157 46	10^{-1}	3.876 360 25	10^{-1}	2.196 571 54		2.200 000 00
2.25	5.770 616 75	10^{-1}	5.302 321 31	10^{-1}	7.393 507 66	10^{-1}	3.987 360 55	10^{-1}	2.245 380 63		2.250 000 00
2.30	5.914 184 32	10^{-1}	5.367 420 48	10^{-1}	7.555 730 81	10^{-1}	4.101 163 43	10^{-1}	2.293 849 90		2.300 000 00
2.35	6.066 072 04	10^{-1}	5.417 172 50	10^{-1}	7.717 854 55	10^{-1}	4.218 064 01	10^{-1}	2.341 916 30		2.350 000 00
2.40	6.228 902 45	10^{-1}	5.448 024 40	10^{-1}	7.879 915 41	10^{-1}	4.338 395 69	10^{-1}	2.389 523 79		2.400 000 00
2.45	6.406 042 00	10^{-}	5.455 847 83	10^{-1}	8.041 960 26	10^{-1}	4.462 535 66	10^{-1}	2.436 638 57		2.450 000 00
2.50	6.601 813 79	10^{-1}	5.435 970 03	10^{-1}	8.204 048 05	10^{-1}	4.590 911 88	10^{-1}	2.483 274 37		2.500 000 00
2.55	6.821 778 45	10^{-1}	5.383 283 53	10^{-1}	8.366 250 79	10^{-1}	4.724 011 23	10^{-1}	2.529 532 40		2.550 000 00
2.60	7.073 103 08	10^{-1}	5.292 469 93	10^{-1}	8.528 654 65	10^{-1}	4.862 388 57	10^{-1}	2.575 661 61		2.600 000 00
2.65	7.365 049 33	10^{-1}	5.158 377 10	10^{-1}	8.691 361 06	10^{-1}	5.006 678 44	10^{-1}	2.622 146 58		2.650 000 00
2.70	7.709 603 63	10^{-1}	4.976 582 75	10^{-1}	8.854 487 61	10^{-1}	5.157 608 28	10^{-1}	2.669 828 22		2.700 000 00

tice move in a field of an almost constant potential, and the coefficient functions—when considered as continuous functions in space—become the wave functions for the electrons. Then, in Bloch's case, we have the exact eigenenergies

$$E^f = (\hbar^2/2m_e)|\vec{k}|^2 \tag{56}$$

practically within the whole Brillouin zone and exact

$$D(E) \equiv D^f(E) = (\sqrt{E^f}/2^{1/2}\pi^2)v_a = (|\vec{k}|/2\pi^2)v_a \tag{57}$$

within the interval of the energies between the bottom of the band and the energy E_t for which the Fermi surface for free electrons touches the boundary of the first Brillouin zone; in Eq. (57) we have put $\hbar = m_e = 1$. For $E > E_t$ the relation $D(E)$ of Bloch declines sharply from the free electron $D(E)$ to zero; see, e.g., Ref. 23.

In our method we also know exactly the energies, since the wave functions, which in the case of the irreducible representation Γ_1 are equivalent to solutions (25), are the eigenfunctions for the Laplace, or kinetic-energy, operator. Thus $E(\kappa)$ are

$$E^f(\kappa) = (\hbar^2/2m_e)\kappa^2 \tag{58}$$

and identical with Eq. (56) providing Eq. (46) holds. The almost-free electron $D(E)$ can be obtained from $A^{\Gamma_1,\lambda}$ because the site $\vec{0}$ can be again considered as the representative point for the electron density. We then have for *all* energies ($E < E_t$ and $E > E_t$)

$$D(E) = \frac{dn}{d\kappa}\frac{d\kappa}{dE^f}\sum_{\lambda}\,[A^{\Gamma_1,\lambda}(\vec{0},\kappa)]^2 = \kappa^{-1}\sum_{\lambda} D^{c,\lambda}(\kappa)\ , \tag{59}$$

which takes account of Eq. (58) (with $\hbar = m_e = 1$); the formula for individual $D^{c,\lambda}$ is given in Eq. (40).

Equation (59) and the exact $D(E)$ in Bloch's Eq. (57) can be compared in the interval

$$0 < |\vec{k}| = \kappa < \tfrac{1}{2}\sqrt{3}\,\pi\ , \tag{60}$$

which corresponds to the interval $(0, E_t)$, because $\frac{1}{2}\sqrt{3}\,\pi$ is the shortest distance between the center and the boundary of the first Brillouin zone for the fcc lattice if the primitive translations used in Secs. IV A and VI A and in Eq. (54) are considered. This is done in Table VI where the corresponding approximate $D^{c,\lambda}$ and $v_a = 2$ are taken into account. In Fig. 2 we compare the almost-free electron $D(E)$ of the present method, calculated in different approximations, with that of Bloch in the wide range of energies (larger than that corresponding to $\kappa = |\vec{k}| = 1$). The discrepancy between the two kinds of D increases with the energy, and so the band width for almost-free electrons in the present method, when approximated similarly as was $D(E)$ in Tables IV–VI, is about twice that of Bloch. However, it may become close to that of Bloch in the case of very developed $A^{\Gamma_1,\lambda}$; see Sec. VI.

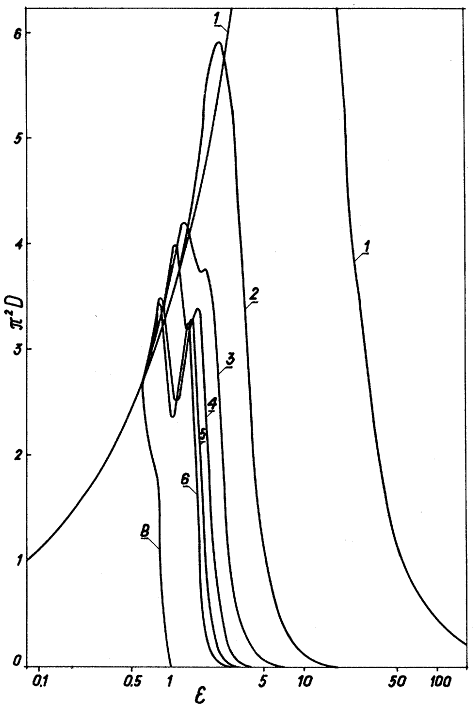

FIG. 2. $D(E)\pi^2$ for the almost-free electrons in the fcc lattice plotted in a semilogarithmic scale. Present theory in different approximations [case $l = 0$, 4, 6, and 8; the numbers of the curves have the same meaning as in Figs. 1(a)–1(d)] and the theory of Bloch (curve *B*). The width of the almost-free-electron band of Bloch has been taken as the unit of energy. A more detailed comparison between $D(E)$ of the present scheme and that of the theory of Bloch for $E < E_t$, where E_t is the energy at the critical point of $D(E)$ of Bloch, is given in Table VI.

Let us note that according to the von Laue–Friedel theorem the distribution of the electron density vs E does not depend on the position of the lattice site. Thus, the $D(E)$ curve for almost-free electrons calculated at site $\vec{0}$ is repeated in each crystal site not too close to the crystal boundary. Since the width of $D(E)$ is proportional to the square of the maximum value of κ for which the nonvanishing contribution to the electron density exists, this value of κ may be expected to be repeated in the crystal space in the same way as $D(E)$.

VIII. FINAL OBSERVATIONS

Apart from the factors discussed, the following points are characteristic of the solutions in the present method:

(i) Both the coefficient function and the energy depend on the structure of the crystal lattice and—when not only the nearest atomic neighbors are taken into account—the strength of the interaction between neighbors; in Bloch's theory only the energy varies between cases, whereas the coefficient function (2) for a single band is the same for all lattice types and all kinds of atomic interaction.

(ii) Unlike in Bloch's method, functions A are real; they meet the corresponding requirement of Ref. 24 for the coefficients in the best LCAO function for a given many-atomic system.

(iii) For the energy intervals for which the present method here affords accurate solutions, the distribution of the electron density in relation to energy (the density of states) is close, or very close, to that of Bloch. This holds both for the tight-binding and the almost-free electron approximations. It should be noted that for energy intervals corresponding to small κ the accurate density of states can be obtained already with fewer components λ than used in Tables IV–VI and Fig. 2, i.e., fewer than four.

(iv) Unlike the wave functions and energies of Bloch, which depend on the k_x, k_y, and k_z components of the vector $\vec{k}$, those in the present method depend only on one (scalar) parameter κ. Moreover, the energy can be expressed as a sum of the powers of this parameter. This may be expected to hold not only for the solutions of Γ_1 but also for those of the representations $\Gamma_i \neq \Gamma_1$. Then, for a perturbation problem, the integration generating the Green's function for (cubic) crystals is reduced to a one-dimensional one and—for solutions with energies within the band—we can classify the states into such as have wave functions which remain finite for large distances from the perturbation center and such as have those which fall off exponentially as these distances grow; both kinds of states may be important for the scattering problem.[25] The integration limit can be extended to infinity practically without loss of exactness (cf. Sec. VI). In the Bloch theory, the corresponding classification of states was possible only for the free-electron-like [$E^B(\vec{k})$ isotropic] systems; the Green's function for crystals and energies within the band could be reduced to a one-dimensional integral, and then calculated, only for a sc lattice with nearest-neighbor interaction.[26]

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[1] (a) J. R. Teitz, in *Solid State Physics*, edited by F. Seit F. Seitz and D. Turnbull (Academic, New York, 1955), Vol. 1; (b) J. C. Slater, in *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 19; (c) J. Callaway, *Energy Band Theory* (Academic, New York, 1964).

[2] J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1963), Vol. 1.

[3] G. Wannier, Phys. Rev. 52, 191 (1937).

[4] J. C. Slater, Phys. Rev. 76, 1592 (1949); *Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1967), Vol. 3: see also Ref. 1(b).

[5] M. von Laue, Ann. Physik 44, 1197 (1914); cf. also C. Kittel *Quantum Theory of Solids* (Wiley, New York, 1963).

[6] J. Friedel, Advan. Phys. 3, 446 (1954).

[7] F. C. Von der Lage and H. A. Bethe, Phys. Rev. 71, 612 (1947); cf. also D. D. Betts, A. B. Bhatia, and M. Wyman, Phys. Rev. 104, 37 (1956). See also the end of Sec. IV A.

[8] Let us note that, for example, in the sixth multiple row the number of polynomials (or of component rows) is not six but seven because in addition to R^{12}, $(X^4+Y^4+Z^4)R^8$, $(X^6+Y^6+Z^6)R^6$, $(X^8+Y^8+Z^8)R^4$, $(X^{10}+Y^{10}+Z^{10})R^2$, and $X^{12}+Y^{12}+Z^{12}$, the terms $X^4Y^4Z^4$ must be taken into account when *any* polynomial in X, Y, and Z of the order 12 and belonging to Γ_1 has to be expressed as a linear combination of the same polynomials.

[9] An idea of approaching the crystal wave functions in terms of the products of cubic harmonics and the functions which depend on the absolute value of the wave vector has already been suggested by Eyges [L. Eyges, Phys. Rev. 123, 1673 (1961); 126, 96 (1962)]. It relates, however, to such functions as fulfill Bloch's, or the periodic, boundary conditions.

[10] The number of cubic harmonics having the same l and belonging to Γ_1 is equal to the number of the solutions of the equation $l=4u+3w$, where u and w are positive integers or zero; see J. Moret-Bailly, Compt. Rend. 250, 990 (1960). Consequently, with $l<12$ no more than one $(KH)^{\Gamma_1}_{l,t}$ can exist.

[11] The result has been established by A. Wierzbicki. Extensive numerical calculations have been performed for the sc lattice with $d \leqslant 4$ and the number of columns in Eq. (22) equal to 16, for the fcc lattice with $d \leqslant 4$ and nine columns, and with the same number of columns for both sc and fcc lattices with $d \leqslant 6$ as well as $d \leqslant 8$. Only preliminary calculations have been made in the case of the bcc lattice and the results are qualitatively the same as those for sc and fcc lattices.

[11a] A. Wierzbicki, Acta Phys. Polon. (to be published).

[12] Quantization of this type has for the first time been introduced for solids by Friedel [J. Friedel, Nuovo Cimento Suppl. 7, 287 (1958)], who considered the free-electron approximation for the crystal wave functions. It has also been used for the coefficient function of the tight-binding approximation of Bloch for the case of the spherical symmetry of energy in the $\vec{k}$ space; see A. M. Clogston, Phys. Rev. 125, 439 (1962).

[13] The whole interval of κ for the crystal states is of the order of several units (see Sec. VI), and the interval of very small κ is—when $l \sim 10$—of the order of 10^{-6}.

[14] Moreover, the contribution to the electron density at $\vec{0}$ from a state which has a very small κ is exceedingly

small compared with that from any of the states within the range of $\kappa \gtrsim 1$, which alone contribute significantly to crystal electron density [cf., e.g., Eq. (40)]. Therefore, the errors in calculations of very small quantum parameters κ are completely negligible when a large number of electrons is considered.

[15] See Refs. 12 and 1(c).

[16] Table II shows that κ_i^λ are clearly larger for the sc lattice—the limiting value of $|\vec{k}|$ in the first Brillouin zone being $\sqrt{3}\pi$—than for fcc with the same approximation for $A^{\Gamma_1,\lambda}$. The convergence of the sc solutions is accordingly poorer.

[17] Another interpretation of the maximum value of κ, or $|\vec{k}|$, can refer to the energy at the top of the band in the almost-free-electron approximation; see Sec. VII.

[18] See, e.g., Ref. 1(a).

[19] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill, New York, 1960), Vol. 1, Appendix 7.

[20] This implies that greatly developed $A^{\Gamma_1,\lambda}$ have only a small admixture of j_0 and are dominated by the components with $l > 0$ which can enter $A^{\Gamma_1,\lambda}$ with large weights. These weights may cause the contributions of individual $A^{\Gamma_1,\lambda}$ to be small at $\vec{0}$ but important at other sites.

[21] This limitation on κ holds not only at $\vec{0}$ but seems to exist at any site not too close to the crystal boundary (cf. the end of Sec. VII).

[22] For the less accurate approximation in Table IV [with $\kappa_m^1 = 3.8$, $\kappa_m^2 = 3.9$, $\kappa_m^3 = 4.9$, and $\kappa_m^4 = 5.0$, which are not too far from the corresponding κ_i^λ in Table II and still provide more than 97% of $Q(\vec{0})$ (cf. Tables III and IV)] we have the same band limits: all $E^\lambda = 1$ at $\kappa = 0$ and the minimum value of E^λ inside $(0, \kappa_m^\lambda)$ is $E^4 = -0.33$ at $\kappa = 3.2$.

[23] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Clarendon, Oxford, 1936).

[24] C. C. J. Roothaan, Rev. Mod. Phys. 23, 69 (1951).

[25] G. F. Koster, Phys. Rev. 95, 1436 (1954).

[26] G. F. Koster and J. C. Slater, Phys. Rev. 96, 1208 (1954); T. Wolfram and J. Callaway, *ibid.* 130, 2207 (1963); J. Callaway, J. Math. Phys. 5, 783 (1964); D. Hone, H. Callen, and L. R. Walker, Phys. Rev. 144, 283 (1966); cf. also P. Soven, *ibid.* 178, 1136 (1969).

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K X-Ray Emission from KCl[†]

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Details of the *K* x-ray emission spectra of K^+ and Cl^- in KCl are discussed. It is shown that the valence hole is effectively localized to one atomic site during the lifetimes of both the potassium and chloride 1*s* holes. This localization is found to be an appreciable factor in the processes contributing to the emission. Calculations of the relative intensity of the cross-transition lines, of the type $1s_K^{-1} \rightarrow 3p_{Cl}^{-1}$, $K\beta_5$, are reported. The results of the calculations agree, to within 40%, with the observed values. The widths of the valence emission lines, due to the transitions $1s_K^{-1} \rightarrow 3p_{Cl}^{-1}$ and $1s_{Cl}^{-1} \rightarrow 3p_{Cl}^{-1}$, $K\beta_{1,3}$ are considered. Because of the localization of the final hole state, both initial and final hole states of the $K\beta_{1,3}$ transition see the same crystal potential, and thus there is no first-order broadening due to spatial variation of that potential. This is not the case for the cross-transition line $K\beta_5$. A model due to Dexter is then used to show that the corrected width of the $K\beta_5$ line should be about 0.5 eV greater than that for $K\beta_{1,3}$. This corresponds to the observations made by Deslattes.

INTRODUCTION

The *K* x-ray emission from the constituents of KCl have been among the most studied spectra in the field. One of the prime reasons for this is the ready accessibility of these spectra to present experimental techniques. Also playing a part in the motivation for these studies is the fact that KCl is a typical ionic crystal; understanding the emission processes from KCl is almost a prerequisite for unraveling the spectra from more complicated ionic crystals. In the interpretations, it has been helpful that the constituent ions are isoelectronic with argon, the most studied by x rays of the rare gases.

The room-temperature experimental data from KCl are reproducible and do not warrant further investigation at this time.[1-3] Also, the interpretation of the main features of the spectra are well substantiated. The present discussion uses that interpretation as a starting point for considering some details of the spectra.

The most intense line in each spectrum is $K\beta_{1,3}$, which is due to transitions $1s^{-1} \rightarrow 3p^{-1}$ essentially within each ion.[1,3-5] This line in the chlorine spectrum has a full width at half-maximum, referred to hereafter simply as width, of 0.4 ± 0.1 eV after instrumental, *K*-state, and spin-orbit