ELECTRONIC BANDS IN SODIUM CHLORIDE

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I.

INTRODUCTION

The purpose of this thesis has been to extend the methods of calculation of wave functions in solids and to investigate the applications of these wave functions. The point of view has been that of the modified Hartree-Fock scheme of calculating wave functions developed by Wigner and Seitz,* together with the Slater* method of calculating excited states.

In particular, detailed computations have been made for the highest filled band in crystalline sodium chloride (rock salt), which originates from the completed 3p shell of the Cl^- ion. In the process of this work new methods were required in order to treat the type of boundary conditions arising for the case of two different kinds of atoms. Three different approximations, which may be characterized by the joining conditions, have been investigated. The most exact of these involves satisfying the Slater boundary conditions (continuity of ψ , and the component of $\nabla\psi$ along the interatomic line) at the midpoint of both the 110 type inter-chlorine line and the 100 type chlorine-sodium line. The approximation obtained by using the Cl-Na points alone differs markedly from this in its energy contours and is unsatisfactory for various

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*E. Wigner and F. Seitz, Phys. Rev. <u>46</u>, 509 (1934).
J. C. Slater, Phys. Rev. <u>45</u>, 794 (1934).

other reasons. Another approximation is obtained by neglecting the Na-Cl points and using the Cl-Cl points alone. Although this formulation would obviously be inadequate for the bands arising from Na levels, its results are quite close to those of the most complete method where that method has been worked out. It also has the advantage of leading to the face-centered lattice conditions which have already been investigated by Krutter.*

In the course of investigating the face-centered lattice, several new methods of increasing the information concerning the energy contours have been developed. It has been found possible to make calculations for small values of the wave vector, k, for cases in which it is impractical to carry out the details of the Slater method for larger values of k. Several new reductions of the general Slater determinant have been found which allow the energy contours to be drawn throughout space with a good deal more confidence than before.

It is possible to test the adequacy of the Slater method by applying it to the one case for which the correct solution is actually known: that of the case of zero potential which gives rise to plane waves. This test has been carried out for the important directions in body and face-centered lattices. For momenta within the first Brillouin zone the agreement is excellent. For the outer zones it is quite unsatisfactory and indicates definitely that some other

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*H. M. Krutter, Phys. Rev. <u>48</u>, 664 (1935).

method must be employed there to obtain accurate results.

II.

THE FOCK EQUATIONS AND THE HARTREE APPROXIMATION

If we are willing to neglect the motion of the nuclei, as in the method of the "clamped" molecule, the Hamiltonian for the electrons is

$$(2.1) \qquad H = \sum_j \frac{1}{2m}\left(\frac{\hbar}{i}\right)^2 \nabla_j^2 + V(x_j) + \sum_{j<k}\sum \frac{e^2}{r_{ij}} \quad .$$

Here j is the index of the electrons and runs from 1 to n, the total number of electrons. x_j is the coordinate of electron j, and ∇_j is the gradient in these coordinates. $V(x_j)$ is the potential energy of an electron at x_j in the field of the nuclei. Although this potential is infinite for an infinite crystal, the potential on any electron is rendered finite by the presence of the interaction term $\sum\sum e^2/r_{ij}$.

The Fock method consists of setting up a determinental wave function of the form

$$(2.2) \qquad \chi = \frac{1}{\sqrt{n!}} \begin{vmatrix} \psi_1(x_1, \xi_1) & \cdots & \psi_1(x_n, \xi_n) \\ \cdot\ \cdot\ \cdot & \cdot\ \cdot\ \cdot & \cdot\ \cdot\ \cdot \\ \psi_n(x_1, \xi_1) & \cdots & \psi_n(x_n, \xi_n) \end{vmatrix} \quad .$$

The ξ_i are spin coordinates and the one electron wave functions $\psi_j(x , \xi) = \psi_j(x)\ \delta_{m_j \xi}$ are assumed to satisfy the equations

$$(2.3) \qquad \sum_{\xi} \int \bar{\psi}_j(x , \xi)\ \psi_k(x, \xi) dx = \delta_{jk}$$

This orthonormal condition introduces no lack of generality. If we attempt to minimize the mean value of H

$$(2.4)\quad \bar{H} = \sum_{\xi's} \cdots \sum \int \cdots \int_{x's} \bar{\chi} H \chi \, dx_1 \cdots dx_n \quad ,$$

we find that the functions ψ must satisfy the well-known Fock equations.*

If atomic units are used, these equations may be written in the form

$$(2.5)\quad \left[-\nabla^2 + V(x) + B(x)\right] \psi_i(x\xi) + \sum_k \left[-A_{ki}(x) - \lambda_{ki}\right]\psi_k(x\xi) = 0$$

Here $B(x) = \sum_k \sum_{\xi'} \int \left|\psi_k(x'\xi')\right|^2 \frac{2}{r(xx')} \, dx'$

is the electrostatic potential of the electron distribution represented by χ. $V + B$ is then the electrostatic potential of a neutral lattice of plus point charges imbedded in the negative charge distribution of electrons.

The A_{ki} are the exchange terms:

$$(2.6)\quad A_{ki}(x) = \sum_{\xi'} \int \bar{\psi}_k(x'\xi')\psi_i(x'\xi') \frac{2}{r(xx')} \, dx' \quad .$$

In order to understand the effect of the exchange terms, we shall assume that the ψ_k are functions of the

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*The notation and treatment of the Fock equations given here is taken in an abbreviated form from Frenkel "Wave Mechanics Advanced General Theory", pages 428 to 431.

Bloch type. Let us suppose that we have a parallelepiped of material whose edges are parallel to a set of three fundamental lattice translations a_1, a_2, a_3 . Let there be n_1 atoms along the first edge, etc., so that the total number of atoms $N = n_1 n_2 n_3$.

Bloch Functions for One Kind of Atom

When the atoms are so far apart that atomic wave functions can be used, the Bloch functions satisfy the Fock equations. Let the normalized wave function around atom α , whose position is $R_\alpha = \sum_s m_{\alpha s} a_s$, be $\psi_\alpha (x)$. We shall assume that ψ's for different atoms do not overlap. The Bloch functions will be

$$(2.7) \qquad \Psi_k = \frac{1}{\sqrt{N^3}} \sum_\alpha e^{2\pi i \beta_k \cdot R_\alpha} \psi_\alpha$$

If we express β_k in terms of the reciprocal vectors b_s of the a_s , $\beta_k = \sum_s \ell_{ks} b_s$,* then the conditions of periodicity for the entire parallelepiped require that

$$(2.8) \qquad \ell_{ks} = \frac{h_{ks}}{n_s} \qquad \text{where} \qquad h_{ks} = 0, 1, 2 \cdots, n_s - 1 .$$

Thus there will be $n_1 n_2 n_3$ choices of the triplets $(\ell_{k1}, \ell_{k2}, \ell_{k3})$,

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*The reciprocal vectors are defined by $b_s \cdot a_t = S_{st}$; these equations are satisfied by $b_1 = (a_2 x a_3)/[a_1 \cdot a_2 x a_3]$ etc.

or just as many Bloch functions as there are atomic functions. To establish the orthonormal properties of the ψ_k , consider

$$\int \overline{\psi}_{k'}(x)\, \psi_k(x)\, dV$$

$$(2.9) \qquad = \sum_{\alpha'} \sum_{\alpha} \frac{1}{N}\, e^{2\pi i(\beta_k \cdot R_\alpha - \beta_{k'} \cdot R_{\alpha'})} \int \overline{\psi}_{\alpha'} \psi_\alpha \, dV$$

$$= \frac{1}{N} \sum_{\alpha} e^{2\pi i(\beta_k - \beta_{k'}) \cdot R_\alpha} = \begin{matrix} 1 & \beta_k = \beta_{k'} \\ 0 & \beta_k \neq \beta_{k'} \end{matrix}$$

Hence the ψ_k are related to the ψ_α by a unitary transformation and the reciprocal transformation can be written down at once.

$$(2.10) \qquad \psi_\alpha = \frac{1}{\sqrt{N}} \sum_k e^{-2\pi i \beta_k \cdot R_\alpha} \psi_k$$

Next consider

$$(2.11) \qquad S = \sum_k A_{ki}(x) \psi_k(x) = \sum_k \int \overline{\psi}_k(x') \frac{2}{r(xx')} \psi_i(x')\, dx'\, \psi_k(x)$$

The three ψ_k's involve three summations over the ψ_α 's. It is clear that the only non-vanishing terms occur when the terms in $\overline{\psi}_k(x')$ and $\psi_i(x')$ come from the same atom. Hence S reduces to

$$(2.12) \qquad \frac{1}{\sqrt{N^3}} \sum_k \sum_\alpha \sum_{\alpha'} e^{2\pi i\left[\beta_k \cdot (R_\alpha - R_{\alpha'}) + \beta_i \cdot R_{\alpha'}\right]} \int |\psi_{\alpha'}(x')|^2 \frac{2}{r(xx')}\, dx'\, \psi_\alpha(x)$$

$$= \frac{1}{\sqrt{N}} \sum_\alpha \sum_{\alpha'} \delta_{\alpha\alpha'}\, e^{2\pi i \beta_i \cdot R_{\alpha'}} \int |\psi_{\alpha'}(x')|^2 \frac{2}{r(xx')}\, dx'\, \psi_\alpha(x)$$

If we put this expression in Equation (2.5) and suppose that x is near R_α, we get

$$(2.13)\quad \frac{1}{N^{1/2}} e^{2\pi i \beta_i \cdot R_\alpha}\left[-\nabla^2 + V(x) + B(x) + \int |\psi_\alpha(x')|^2 \frac{2}{r(xx')}\,dx' - \lambda_{ii}\right]\psi_\alpha - \sum_{k} \frac{\lambda_{ki}}{N^{1/2}} \times e^{2\pi i \beta_k \cdot R_\alpha}\psi_\alpha(x) = 0 \quad .$$

The λ_{ki} will be zero, as can be seen by multiplying by $e^{-2\pi i \beta_i \cdot R_\alpha}$ and summing over α. The first term is just the Fock equation for one type of atom and λ_{ii} is the energy of the solution.

As a matter of fact, this result could have been seen without calculation. The single atom ψ_α's are related to the Bloch ψ_k's by a unitary transformation, and it is well-known that a unitary transformation leaves the Fock equations satisfied. However, the method of derivation used above is suggestive of what may be true where the isolated atom picture breaks down. In that case, single atom wave functions cannot be used for outer shell electrons and ψ_k must be represented by

$$(2.14)\qquad \psi_k = \frac{1}{N^{1/2}} \sum e^{2\pi i \beta_k \cdot R_\alpha}\psi_{k\alpha}(x)$$

where the $\psi_{k\alpha}$ for different atoms may overlap and in general will be dependent on k. If the dependence on k is not too extreme, we should expect that in the summation over k in Equation (2.12) the term for $\alpha = \alpha'$ would be quite large compared with those for $\alpha \neq \alpha'$ and that the value of the terms would decrease rapidly as $|R_\alpha - R_{\alpha'}|$ increases from zero. From (2.13) we saw that as the electron moved about the lattice in state ψ_k, it always found itself upon an atom lacking one electron in the same state as itself. We could then think of the electron as carrying a hole about with it, and pushing other electrons out of this hole as it moved around. We would expect to find this property preserved, probably to a lesser extent, in the exact solution.

Free Electron Wave Functions

This view is confirmed in another case in which a solution of the Fock equations is known. That is the case of free electrons where the $\psi_k = e^{2\pi i \beta_k \cdot x}$. For this we find that the exchange expression can be integrated out and again represents a hole which the electron carries about with it. We find on the average that this hole represents an absence of one electron in the lattice cell surrounding the electron under consideration.* Hence, at both extremes, that of separated atoms and that of plane waves, there is an effective hole of roughly the volume of one cell which follows each electron through the lattice. This further confirms the argument above that there should be an effective hole in intermediate cases.

Another feature is discovered in the plane wave pic-

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*J. Bardeen, Phys. Rev. 49, 656 (1936).

ture. The values of the exchange term for a given electron is found to depend upon the momentum of the electron.* By a straightforward calculation, it can be shown that this term is largest for an electron with zero momentum and becomes negligible for highly excited electrons. This behavior becomes reasonable in consideration of the Thomas-Fermi picture. An electron with small momentum finds that all adjacent values in momentum space are occupied; therefore, in order to possess its allotted volume h^3 of phase space, it must have a large volume of configuration space. This produces the hole about the electron. On the other hand, an electron with almost the maximum momentum -- that is, one near the surface of the occupied sphere in momentum space -- is conscious of the wide open spaces near it and therefore is not so greedy of configuration space or so repulsive to other electrons as the electron from the center of the densely populated region. It has therefore a much smaller hole. It is interesting to see if this type of effect is present in case of Bloch-like functions.

Excited Bloch Functions

Let us see what the effect of exciting one electron would be in the Bloch approximation. Excitation of one electron

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*J. Bardeen, Phys. Rev. 49, 653 (1936).

would be represented by replacing a Bloch function,

$$(2.15) \qquad \psi_{k_0} = \frac{1}{\sqrt{N}} \sum_{\alpha} e^{2\pi i \beta_{k_0} \cdot R_\alpha} \psi_\alpha \quad ,$$

in the determinental wave function χ , by a Bloch function for an excited state,

$$(2.16) \qquad \eta = \frac{1}{\sqrt{N}} \sum_{\alpha} e^{2\pi i \beta_0 \cdot R_\alpha} \eta_\alpha$$

Now this change will effect a negligible alteration in the Fock equations for ψ_k . This follows from the fact that the density of charge introduced by any one wave function into B or A is proportional to $1/N$. However, the A term for η itself may be greatly altered. This term, using the same type of calculation as used in (2.12), reduces to

$$(2.17) \quad S = \frac{1}{N^{1/2}} \sum_{\alpha} \sum_{\alpha'} e^{2\pi i \beta_0 \cdot R_\alpha} \int \overline{\psi_{\alpha'}}(x') \eta_\alpha (x') \frac{2}{r(xx')} dx' \psi_\alpha (x) \quad .$$

In this case the exchange integral may be very small. On the atomic picture $\int \overline{\psi_\alpha}(x') \eta_\alpha(x') dx' = 0$. The presence of the $1/r$ term will spoil the orthogonality of the functions. However, we should expect the effective hole due to the $\overline{\psi} \eta$ exchange to be much smaller than that for the $|\psi^2|$ exchange.

Behavior of the Hole for Several Filled Bands

So far in the discussion, except for η , only one type of atomic function has been used. Actually there is a double set of Bloch functions from each atomic level, one with each spin. These other terms have already been included in the description of B, and we must now see how they will enter in A. In the Fock equation for ψ_k, the A terms will be of the form

$$\sum_{\xi'} \int \overline{\varphi}_i(x'\xi')\psi_k(x'\xi')\frac{2}{r(xx')}dx'\ \varphi_i(x\xi) \quad . \tag{2.18}$$

It is seen at once that there is no exchange between functions of different spins. For functions of the same spin, we must consider all the atomic levels. By the same argument that was used with η, we conclude that the most important term is the $|\psi|^2$ one. If we neglect the other terms entirely, it is quite simple to specify the type of field in which the electron moves. For a given electron moving in a filled band, the field is that of the entire lattice and the electrons, B+V, minus the potential due to one electronic charge distributed according to the wave function of the given electron. This potential follows the electron about so as to be on the same atom as the electron. If the electron is in an unfilled band, then the potential is just B+V, the hole being negligible.

This neglect of the hole for excited states is not as well justified as the presence of the hole for filled states. In fact, for the case where free atom functions are correct, it is distinctly incorrect. In that case, the excited states of the lattice obviously correspond to excitation of single atoms or waves of excitation, such as are used by Frenkel* and

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*J. Frenkel, Phys. Rev. 37, 17 and 37, 1276 (1931)

Wentzel.* Our method would not give these states, because the correct excited atom wave function is a solution of the wave equation in a field with a complete hole (atomic picture), whereas the lattice method does not give this field. The question arises, why do the lattice and Bloch methods agree perfectly for the lowest state but not for excited states? The reason for this is that the lowest state determinantal wave function is actually the same for both pictures. On the other hand, the single determinantal function for an excited state handled on the lattice basis is not equal to any corresponding determinant of the single atom functions with one excited atom; in fact, cannot be expressed as a linear combination of these at all. Hence, it appears that the Bloch type of function was definitely bad for the calculation of excited states. There are other reasons in connection with polarization forces in the theory of dispersion which argue against the lattice treatment.

On the other hand, the tighter the lattice is squeezed, the worse the free atomic picture becomes (especially for excited states, which generally have greater spatial extention than the normal state) and consequently the better the free electron picture becomes and the more nearly correct are the Fock lattice equations. In the intermediate region both methods are inadequate, and it is not unlikely that the Fock method itself is not good enough. This is in harmony with the findings

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*G. Wentzel, Helv. Physica Acta <u>6</u>, 89 (1933).

of Wigner* in connection with the somewhat similar problem of the correlation hole between electrons of antiparallel spin in monovalent metals. Actually it is not of great practical interest that neither free atom nor lattice Fock approximation is adequate. Satisfactory mathematical methods have yet to be evolved for obtaining good solutions for excited states on either picture.

For practical purposes, the Fock approximation is replaced by a Hartree scheme. The exchange term is actually considered to be a part of the potential according to the above procedure, and the total potential is then averaged over all angles according to the Hartree method. The resultant equation for ψ can then be resolved according to the spherical harmonics, and the radial equation solved numerically. The values of λ_{kk} will give the energies of the one electron functions.

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*E. Wigner, Phys. Rev. 46, 1002 (1934).

The Fock Approximation for the Case of Two Atom Types

So far in our investigation we have supposed that there was only one type of atom. This made it possible to write down Bloch functions which were sums over a single set of lattice points. In general, the situation will be more complicated. For NaCl, in particular, there are two types of atoms, each forming a face-centered lattice with every atom at a symmetry center. For this case, we must consider each Bloch type function as being formed of two parts: one part giving the behavior around the Cl, the other around the Na. For the levels arising from inner atomic shells, the wave functions will not be very different from the free atom wave functions, and for them Bloch functions using only one lattice type will be satisfactory. For the upper levels, however, the wave functions will extend over both Cl and Na atoms, being considerably larger about the atoms from which they originated as atomic levels than about the other atoms, but being appreciable, nevertheless, about both types.

In order to investigate the type of hole which is associated with one of these electrons, let us build up a Bloch type wave function. Let the atomic type wave function about the chlorine atom at R_α be ψ_α, and about the Na atom at R_γ be φ_γ. Then the Bloch type functions would be

$$(2.19) \qquad \psi_k = \frac{1}{N^{1/2}} \left[\sum_\alpha e^{2\pi i k \cdot R_\alpha} \psi_\alpha + \sum_\gamma e^{2\pi i k \cdot R_\gamma} \varphi_\gamma \right]$$

(A proof that the correct one electron wave functions are actually of this type is given in Theorem II of a later section.)

We will neglect the overlapping of ψ_α and φ_γ and suppose that $\int |\psi_\alpha + \varphi_\gamma|^2 \, dx = 1$. The components of the exchange terms will be of four types:

$$(1) \qquad \int \overline{\psi_\alpha}(x')\psi_\alpha(x')\frac{2}{r(xx')}dx' \; \psi_{\alpha'}(x)$$

$$(2) \qquad \int \overline{\psi_\alpha}(x')\psi_\alpha(x')\frac{2}{r(xx')}dx' \; \varphi_\gamma(x)$$

$$(3) \qquad \int \overline{\varphi_\gamma}(x')\varphi_\gamma(x')\frac{2}{r(xx')}dx' \; \psi_\alpha(x)$$

$$(4) \qquad \int \overline{\varphi_\gamma}(x')\varphi_\gamma(x')\frac{2}{r(xx')}dx' \; \varphi_{\gamma'}(x)$$

(Terms of the form

$$\int \overline{\psi_\alpha}(x')\varphi_\gamma(x')\frac{2}{r(xx')}dx' \; \varphi_{\gamma'}(x)$$

will not occur, since $\overline{\psi_\alpha}(x')\varphi_\gamma(x')$ is always zero.)

The effect of (1) and (4) will be the same as that found for the one atom type case. They will lead to a hole of the type $|\psi_\alpha|^2$ or $|\varphi_\gamma|^2$ when the electron is on a ψ-type or a φ-type atom respectively. (2) and (3) are similar, so that only one of them need be investigated.

Consider the terms of type (2) occurring in

$$(2.20)\qquad S = \sum_{k} A_{ki}\,\psi_k$$

$$= \frac{1}{N^{3/2}} \sum_{k}\sum_{\alpha}\sum_{\gamma} e^{2\pi i(-\beta_k\cdot(R_\gamma - R_\alpha) + \beta_i\cdot R_\alpha)} \int |\psi_\alpha(x')|^2 \frac{2}{r(xx')} dx'\,\varphi_\gamma(x)$$

In evaluating this term in the Fock equation for ψ_i, we shall assume that the electron is located on atom γ, and calculate the contribution of the integral when the electron x' is on atom α. If we call this term

$U_{\alpha\gamma i}(x)\,\frac{1}{\sqrt{N}}\,e^{2\pi i\beta_i\cdot R_\gamma}\varphi_\gamma(x)$, so as to have it resemble

a potential energy term, we find

$$(2.21)\qquad e^{2\pi i\beta_i\cdot R_\gamma}U_{\alpha\gamma i}(x) = \frac{1}{N}\sum_{k} e^{2\pi i[\beta_k\cdot(R_\gamma - R_\alpha) + \beta_i\cdot R_\alpha]} \int |\psi_\alpha(x')|^2 \frac{2}{r(xx')} dx$$

and

$$S = \sum_{\alpha}\sum_{\gamma} U_{\alpha\gamma i}(x)\,\frac{1}{\sqrt{N}}\,e^{2\pi i\beta_i\cdot R_\gamma}\,\varphi_\gamma(x) \qquad .$$

We are interested in seeing how $U_{\alpha\gamma i}$ behaves and whether or not it can be interpreted as a hole in the charge distribution about the neighboring atoms α when the electron is on atom γ.

In order to investigate this, we need the value of the coefficient of

$$\int |\psi_\alpha(x')|^2 \frac{2}{r(xx')} dx'$$

in $U_{\alpha\gamma i}(x)$. A value of unity for the coefficient would correspond to a hole on atom α with charge distribution $|\psi_\alpha{}^2|$. This is

$$(2.22)\quad \frac{1}{N}\, e^{2\pi i \beta_i \cdot (R_\alpha - R_\gamma)} \sum_k e^{2\pi i \beta_k \cdot (R_\gamma - R_\alpha)} \quad .$$

For the sodium chloride lattice, the unit vectors are

$$a_1 = \frac{a}{2}(011) \quad , \quad a_2 = \frac{a}{2}(101) \quad , \quad a_3 = \frac{a}{2}(110) .$$

The reciprocal vectors will be

$$b_1 = \frac{1}{a}(\bar{1}11) \quad , \quad b_2 = \frac{1}{a}(1\bar{1}1) \quad , \quad b_3 = \frac{1}{a}(11\bar{1}) \quad .$$

The displacement between nearest Na's and Cl's will be

$$\rho = (1/2)a(100) = \frac{1}{2}(a_1 + a_2 - a_3) \quad .$$

Then $R_\alpha - R_\gamma$ will be a whole number of lattice vectors plus ρ and can be written as

$$R_\gamma - R_\alpha = (m_1 + \tfrac{1}{2})a_1 + (m_2 + \tfrac{1}{2})a_2 + (m_3 + \tfrac{1}{2})a_3 \quad .$$

Now

$$\beta_k = \sum_S \frac{\ell_{ks}}{n_s}\, b_s \qquad \text{where} \quad \ell_{ks} = 0, 1, 2, \cdots n_s \quad .$$

Therefore,

$$\beta_k \cdot (R_\gamma - R_\alpha) = \sum_s \frac{\ell_{ks}}{n_s}(m_s + \tfrac{1}{2}) \quad .$$

Hence, the sum over k becomes

$$\sum_{\ell_1} e^{2\pi i \ell_1 (m_1+1/2)} \sum_{\ell_2} e^{2\pi i \ell_2 (m_2+1/2)} \sum_{\ell_3} e^{2\pi i \ell_3 (m_3+1/2)}$$

$$= \frac{e^{2\pi i (m_1+1/2)} - 1}{e^{2\pi i \frac{(m_1+1/2)}{n_1}} - 1} \quad \frac{e^{2\pi i (m_2+1/2)} - 1}{e^{2\pi i \frac{(m_2+1/2)}{n_2}} - 1} \quad \frac{e^{2\pi i (m_3+1/2)} - 1}{e^{2\pi i \frac{(m_3+1/2)}{n_3}} - 1} \; .$$

Each factor here is of the form

$$\frac{-2}{e^{2\pi i \frac{(m_1+1/2)}{n_1}} - 1} \; .$$

Since the size of the crystal is arbitrary, we may choose n_1 as large as we wish and expand these terms in inverse powers of n_1. This gives

$$\frac{-2}{e^{2\pi i \frac{(m_1+1/2)}{n_1}} - 1} = - \frac{2n_1}{2\pi i (m_1+1/2)} \left(1 - \frac{2\pi i (m_1+1/2)}{n_1} + \qquad \right).$$

Recalling that $n_1 n_2 n_3 = N$, we find that (2.22) becomes

$$(2.23) \qquad - \frac{i \, e^{2\pi i \beta_i \cdot (R_\alpha - R_\gamma)}}{\pi^3 (m_1+1/2)(m_2+1/2)(m_3+1/2)} + \text{terms in } \frac{1}{n_1} \text{ etc.}$$

This factor will in general be complex. In particular, for $\beta_i = 0$, it is pure imaginary. This means that the potential of the hole induced on atom α due to the presence of the electron on atom γ is pure imaginary. Such a potential has no straightforward interpretation in quantum mechanics. In making calculations, it is necessary to approximate the field by one of spherical symmetry. This suggests that we should consider the α atoms in pairs, α and α', such that $R_\alpha - R_\gamma = -(R_{\alpha'} - R_\gamma)$. If we add the potentials of these pairs, we find the net potential is real. This follows from the reversal of sign of the terms $m_1 + 1/2$, etc., which make the coefficients for α and α' complex conjugates. For $\beta_1 = 0$, these terms just cancel in the spherical approximation, and the exchange potential vanishes. For values of β_1 and R_α such that

$$e^{2\pi i \beta \cdot (R_\alpha - R_\gamma)} = \pm 1 ,$$

the potential of atom pairs α and α' on the electron at atom γ will be

$$\pm \frac{2}{\pi^3(m_1+1/2)(m_2+1/2)(m_3+1/2)} \int \left|\psi_\alpha(x')\right|^2 \frac{2}{r(xx')}\, dx' .$$

An exchange potential of such peculiar characteristics as those given above is definitely without physical significance. What the calculations indicate is that the Fock method is not appropriate for wave functions of the type (2.19).

In fact, we are inclined to think that physical intuition about these potentials is more reliable than the information obtained above. For example, in the Cl-3p band, the Cl wave functions ψ are much larger than the Na functions φ. When an electron of this band is around a Cl, there will be a defect of almost one electron about that atom. On the other hand, when it moves onto an adjacent Na, the hole which it makes in the φ distribution there is much less than one electron. It is not reasonable to suppose that a certain amount of the larger hole remains on the adjacent Cl atoms. We have no basis at present for making a satisfactory guess as to what fraction of the hole does remain. We find, however, in Sections X and XI, that the results for the 3p band are not very dependent upon the value estimated for this fraction.

The correct method of procedure in regard to this matter would probably be similar to that of Wigner.* He was interested in a "correlation hole" between electrons of antiparallel spin, however, whereas we are concerned with the case of parallel spin.

Energy of an Excited State

The value of the energy H for the wave function χ (2.2) is

$$\bar{H} = \sum_{\xi'} \int \bar{\chi}\, H \chi \, dx \tag{2.24}$$

(where dx' stands for $dx_1 dx_2 \cdots dx_n$ and ξ' for $\xi_1 \cdots \xi_n$)

$$= \sum_k \int \bar{\psi}_k \left[-\nabla^2 + V \right] \psi_k \, dx$$

$$+ \sum_k \sum_{> i} \int \left| \psi_k(x) \right|^2 \left| \psi_i(x') \right|^2 \frac{2}{r(xx')} dx dx'$$

$$- \sum_k \sum_{> i} \int \bar{\psi}_k(x) \psi_i(x) \bar{\psi}_i(x') \psi_k(x') \frac{2}{r(xx')} dx dx'$$

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*E. Wigner, Phys. Rev. 46, 1002 (1934).

If ψ_k is replaced by φ and the difference between the new $\overline{H}'$ and the old $\overline{H}$ is found, we get

$$
\begin{aligned}
\overline{H}' - \overline{H} = {} & \int \bar{\varphi} \left[-\nabla^2 + V \right] \varphi \, dx - \int \bar{\psi}_k \left[-\nabla^2 + V \right] \psi_k \, dx \\
& + \sum_{i \neq k \text{ or } \varphi} \int \bar{\psi}_i(x) \ ^2 \left(|\varphi(x)|^2 - |\psi_k(x)|^2 \right) \frac{2}{r(xx')} \, dx dx' \\
& - \int \bar{\varphi}(x) \sum_{i \neq k \text{ or } \varphi} \int \bar{\psi}_i(x') \ \varphi(x') \frac{2}{r(xx')} dx' \psi_i(x) dx \\
& + \int \bar{\psi}_k(x) \sum_{i \neq k \text{ or } \varphi} \int \overline{\psi_i}(x') \ \psi_k(x') \frac{2}{r(xx')} dx' \ \psi_i(x) dx \\
= {} & \int \bar{\varphi} \left[(-\nabla^2 + V + B)\varphi - \sum_i A_{i\varphi} \psi_i \right] dx \\
& - \int \bar{\psi}_k \left[(-\nabla^2 + V + B)\psi_k - \sum_i A_{ik} \psi_i \right] dx
\end{aligned}
$$

From equations (2.5) and (2.13) we conclude

$$
\overline{H'} - \overline{H} = \psi_{\varphi\varphi} - \lambda_{kk} \qquad .
$$

Hence, the energy difference between states in the Fock lattice scheme is just the difference in energy values of the states involved in the excitation. If several electrons are excited, the energies will be additive. This will hold so long as the cross terms between excited functions are negligible, which they will be if the number of excited states is very small compared to the unexcited states, a condition which will be generally fulfilled.

III.

GENERAL REMARKS ABOUT THE POTENTIALS

After the potential field in which an electron moves has been determined, the problem is to find a solution of the Fock equation, or, rather, the Hartree approximation of it. We are interested in solutions of the type

$$\psi_k = \sum_{\alpha} e^{2xi\beta_k \cdot R_\alpha} \psi_{k\alpha}$$

where $_k$ is defined for the cell centered around $\dot{R}$ and is zero outside. The whole function $_k$ is finite and continuous with a continuous gradient throughout the entire lattice. The problem is to solve the wave equation inside of any cell subject to boundary conditions on the surface of the cell which insure the fulfilment of the continuity requirements.

The Na-Cl lattice is face-centered and has exactly the same symmetry as it would have if the Na atoms were removed. The fundamental cell is formed by assigning to a chlorine atom all the space which is nearer it than any other chlorine. Such a cell will contain one chlorine atom at its center and one-sixth of each of the nearest six sodium atoms: one NaCl molecule in all. Fig. 3 shows this cell. The space in the center of the cell is assigned to the Cl; the pyramids at the corners to the Na. Since the Cl^- ionic radius, 1.8Å, is much larger than the Na^+, 1.0Å, a larger space is allowed to it. This

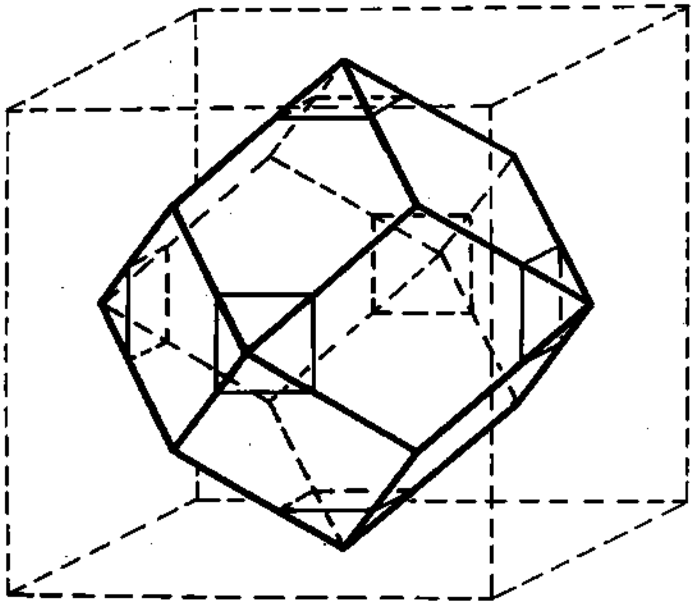


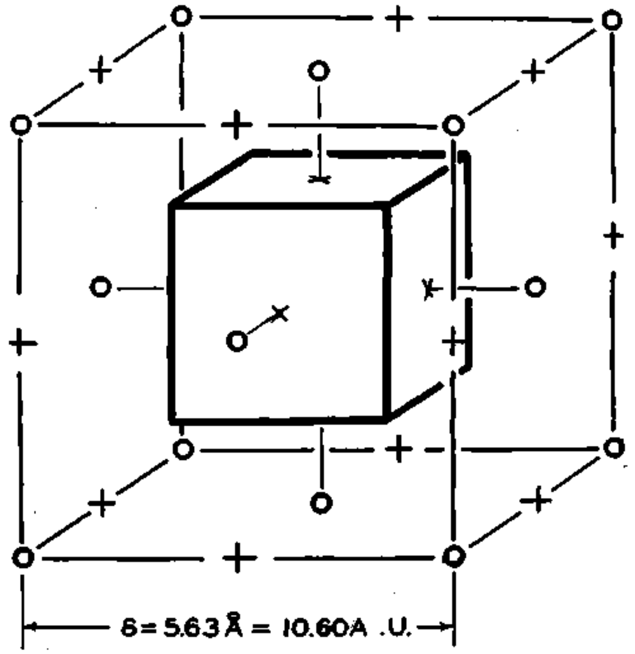
fig. 3

is schematic and the position of the Na-Cl dividing planes are not to scale.

Another cell could be formed by interchanging sodiums and chlorines; the difference between these cells is unessential: in the end both kinds lead to exactly the same conditions. For ease of visualization, the chlorine centered cell is better and will be used.

The method of solution, as stated on page 14, consists of approximating the wave equation near any atom by a spherically symmetric wave equation. In the case of a face or body-centered metal, the wave equation is very nearly spherically symmetrical. This is due to the fact that the atoms are neutral so that the electron is conscious of the field of the nearest one only and this is spherically symmetric. In the case of NaCl this is true, but to a lesser extent.

In order to get an idea of how much error there is in spherical symmetry, let us neglect the exchange hole for the moment and use an idealized model in which each ion is represented by a point charge at a lattice point. Next we surround each atom by a cubic box containing all points nearer it than any other atom. The planes which contain the faces of the cube are not reflection planes of the lattice; in order to be such, they would have to be placed so as to be perpendicular bisectors to lines connecting like


δ = 5.63 Å = 10.60 A.U.

atoms. Instead, they are perpendicular bisectors to the lines connecting atoms of opposite sign. This shows that any point in one of these planes is equidistant from pairs of positive and negative charges, and hence that it is at zero electrostatic potential. Therefore, the field inside one of these cubes is identical with that which would be produced by a point charge at the center of a grounded conducting cube. The zero potential of this field, of course, is far from spherical; however, the inner potential surfaces rapidly round out to become spheres. That this process will indeed occur can be seen by considering the edges and corners of the cube. At these places the field is zero, and the equipotentials are widely separated, so that the surfaces will move rapidly toward the center as the potential changes, thus becoming more nearly spherical.

Another indication of the validity of the spherical approximation may be obtained from consideration of the expansion of the potential in spherical harmonics. The cubic symmetry causes only certain of the harmonics to be allowed, the first three of these having ℓ values of 0, 4, 6. The higher harmonics will fall off as r^4 or r^6 as $r \rightarrow 0$, and will allow the $1/r$ term to dominate for distances only slightly within the cube. The surface harmonics for $\ell = 4,6$, etc. are unimportant for another reason. If the 0^{th} and 1^{st} order perturbation energy of these with s and p states -- those of the Cl^- ion -- is computed, it is seen that s,p states have no zeroeth order perturbation energy with these terms in the potential. The s state has first order perturbation energy with g and higher harmonics only, the p with f and higher.

There is yet one more justification for the method. So far, only the Madelung lattice potential has been considered. As is well-known, the ions are not point charges, but negative clouds of charge surrounding positive nuclei. As soon as the electron has penetrated through a small amount of the cloud, the nucleus exerts the predominant force, and the field becomes spherically symmetric.

The potential about any ion will then be considered to be of two parts; the potential of the ion itself and that of the surroundings. The former will be computed from existent atomic fields. The latter can be calculated by various methods.* However, since we are interested only in the zeroeth order spherical harmonic of this field, we need make use of Madelung's number only. Madelung's number is a pure number which occurs in the calculation of the electrostatic energy of ionic lattices. It enables one to calculate its energy per ion for a given type of lattice in terms of the charge on the ion and the lattice spacing, δ . For the NaCl lattice, we find that the electrostatic energy per cell (4 molecules) is

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*E. Madelung, Phys. Zs. 19, 524 (1918).
P. P. Ewand, Zs. f. Krist. 56, 129 (1921).
H. M. Evjen, Phys. Rev. 39, 675 (1932).

$$\varphi = \frac{-13.94\ e^2}{\delta}$$

The energy per molecule,

$$\varphi_{\text{per molecule}} = \frac{\varphi}{4} = \frac{-13.94\ e^2}{4 \times 4\ (\delta/4)} = -0.872\ \frac{e^2}{(\delta/4)} \quad ,$$

is 1/2 the electrostatic potential at the Cl^- ion times the charge on the ion plus a like quantity for the Na^+ ion. Due to the symmetry of the ions, this is equal to the charge at one ion times the electrostatic potential of all other ions at that ion.

It is interesting to note that the number 0.872 can be estimated roughly from the zero potential cube picture. The potential on the surface of the cube is $1/r$ due to the charge at the center, and therefore $-1/r$ due to the charges outside. What we are interested in, then, is the potential at the center of an empty cube whose surface is maintained at a potential $-1/r$. This value must lie between the extreme values on the surface (Gauss mean value theorem) which are $-1/(\delta/4)$ for the midpoint of the face and $-1/\sqrt{3}(\delta/4) = -0.58/\sqrt{3}(\delta/4)$ for a corner. However, the corner is certainly not as important as the center of the face. The correct value would probably be about halfway between the value at the middle of the face and the middle of the edge. This gives $\left[-1/(\delta/4) - 1/\sqrt{2}(\delta/4)\right]/2 = -0.85/(\delta/4)$ for the potential.

Hence the potential at an ion should be taken to be the potential of the ion plus $e^2(0.872)/(\delta/4)$ if the ion is Na^+, minus if it is Cl^-. In atomic units the e^2 is replaced by 2. After these potentials are known, and suitable allowances are made for the exchange hole, the wave equation can be solved for the radial functions associated with the various spherical harmonics. The next problem is to form a continuous solution in the elementary cell which satisfies the proper boundary conditions. Before doing this, there are three theorems to be proved about wave functions in a lattice with centers of symmetry.

IV.

CALCULATION OF THE POTENTIAL AND THE RADIAL FUNCTIONS FOR THE FILLED BANDS

If we consider the crystal to be essentially ionic, the sodium will be in the form of ions. The upper or valence wave functions will have practically zero charge density around these, and therefore no hole. The field that should be used around the positive ions will be just that of the positive ion or the same field as was used in metallic sodium. Wave functions for this field have been obtained by Slater.

The field around the chlorine is not the same as the ionic field, however, due to the fact that the atoms are squeezed together, changing the charge density. In order to correct for this effect, the volume of space belonging to a Cl^- ion was estimated. The volume of the cell belonging to a NaCl molecule (see figure of page 24). is $(530)^3 \times 2 =$ 300 At.U. This is, of course, the volume of the duodecahedron of page . However, a certain amount of this volume should be allowed for the sodium atom; exactly how much cannot be decided until a self-consistent solution of the entire problem is obtained. A rough estimate was made from the Na ionic radius, which is 1.9 At.U. If we allow $\frac{4}{3}\pi(1.9)^3 = 29$ to the sodium, the Cl volume is 271. This is the volume of a sphere of radius 4.1 At.U. A reasonable approximation would be to renormalize the ionic wave functions so as to have unit charge inside a sphere of radius 4.1.

For his solution of the Cl^- ion, Hartree tabulates[++] the quantity $Z(r)$ which is the number of electronic charges outside the radius r. From these we find that 9.2% of the 3p electrons and 0.9% of the 3s electrons are outside of $r = 4.1$. Hence, the potential of the renormalized 3p is 1.101 times that of Hartree's 3p and the renormalized 3s potential is 1.009 times Hartree's.

The potentials due to Hartree's 3p and 3s wave functions were computed and also the potential of the $1s^2 2s^2 2p^6$ core configuration. These were computed separately so that the potentials due to a 3s type hole and a 3p type hole could be found.

If Z is the charge inside radius r, then $\frac{dV}{dr} = -\frac{Z}{r^2}$. This equation was integrated by Simpson's rule to get the 3s and 3p potentials. If the radial part of the wave function is P/r and $\int P^2 dr = \frac{1}{4\pi} \int (\frac{P}{r})^2 \, dV = 1$, then the radial charge density is $\frac{1}{4\pi}(\frac{P}{r})^2$. If the potential is written as $Z_p(r)/r$, then $\nabla^2 Z_p(r)/r = -4\pi\rho$ gives $Z_p = -\frac{P^2}{r}$. This equation for the core configuration $1s^2 2s^2 2p^6$ was integrated by the Hartree methods[*] for small r ($r = 0.0$ to 0.2) and the first order Z equation for larger r.

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[*] D. R. Hartree, Camb. Phil. Soc. 24, 89 (1928).
[++] D. R. Hartree, Proc. Roy. Soc. 141, 282 (1933).

The wave equation about one ion in atomic units is $-\nabla^2\psi + (V - \bar{\varepsilon})\psi = 0$, and if $\psi = \frac{P}{r} S_{\ell}(\theta, \varphi)$ then $-P'' + \left[V - \bar{\varepsilon} + \frac{\ell(\ell+1)}{r^2}\right]P = 0$. V is the <u>total potential of the ion</u> and is

$$-\frac{2Z}{r} + \text{potential due to the electrons.}$$

V was chosen so as to be zero at $r = 3.8$ which corresponds to a point half way between Cl atoms and should represent roughly the limit of the Cl ion. For s functions, V was computed for the configuration $1s^2 2s^2 2p^6 3s 3p^6$, and for p, d, and f from $1s^2 2s^2 2p^6 3s^2 3p^5$. That is, for 3s and 3p , the hole was made of the same type as the wave function for which it was to be used. For d and f , a 3p hole was considered more reasonable than a 3s .

The $\bar{\varepsilon}$ defined above is not the Fock equation parameter, since we have not taken into account the lattice potential. This is $2 \times \frac{0.871}{(2.65)} = 0.66$. The extra factor of 2 is required by the use of atomic units in which the potential energy of 2 electrons is taken as $2/r_{12}$. If we denote the Fock parameter by $\bar{\varepsilon}_{\ell}$ (ℓ for lattice), we have $\bar{\varepsilon}_{\ell} = \bar{\varepsilon} - 0.66$.

The wave equations were integrated with enough different values of $\bar{\varepsilon}$, to allow interpolations of P and P' for arbitrary $\bar{\varepsilon}$ to be made throughout the energy range.

For later use we shall represent the radial parts of the solutions for the two types of atoms and for various ℓ values by

	0	1	2	3	4
Radial function around Cl	Σ	Π	Δ	Φ	Γ
Radial function around Na	S	P	D	F	G

A solution of Schrödinger's equation about a single atom involving only one radial function, such as $(x - y)/r\,\Pi(r)$, will be called a spherical function.

The value of $\frac{d\psi(r)}{dr}/\psi(r)$ at $r = 3.8$, the Cl-Cl half distance, will be denoted σ, $\varkappa$, δ, φ, γ for the Cl functions. The corresponding quantities for the sodium functions at $r = 2.65$, the Na-Cl half distance, will be indicated by s, p, d, f, g; the values of $\psi(2.65)/\psi(3.8)$ for Cl functions, by σ_c, $\varkappa_c$, δ_c, φ_c, γ_c; the values of $\frac{d\psi(2.65)}{dr}/\psi(3.8$ by $\dot{\sigma}_c$, $\dot{\varkappa}_c$, $\dot{\delta}_c$, $\dot{\varphi}_c$, $\dot{\gamma}_c$.

V.

SOME THEOREMS INVOLVING CENTERS OF SYMMETRY

In the Slater method of handling excited states, it is assumed that the wave function in the cell at the origin consists of two parts: a real part which is an even function about the center of the cell, and an imaginary part which is odd. This assumption leads to considerable simplification in formulating the boundary conditions and it is worth while to prove that it will generally be justified.

Before proceeding with the proof, it is advantageous to introduce some new terms which will considerably shorten the discussion. First of all, let us call the part of the wave function in the cell about the atom at the origin the <u>cellular function</u> and denote it by $\psi(r)$, r being the position vector in respect to the origin. The corresponding wave function throughout the entire lattice will be

$$\psi_{\varkappa} = \sum_{\alpha} e^{i\varkappa \cdot R_{\alpha}} \psi(r - R_{\alpha})$$

where the R_{α} are lattice vectors. In the special case where the ψ's are formed of unperturbed atomic functions, $\psi_{\varkappa}$ is called a Bloch function; in general, we shall call it a <u>lattice function</u>. When the cellular part ψ of the lattice function $\psi_{\varkappa}$ is of the form $g + iu$ we shall refer to it as <u>moral</u>.. More generally, any function will be known as moral about a center of symmetry if it is of the form $g + iu$

around that center. A function which can be made moral by multiplication by a constant will be called a worthy function. It is worth pointing out that worthy functions are really a very restricted class; for example, $(1 - i)x^2 + (1 + i)(y + z)$ is a worthy function around the origin, whereas $x^2 + (1 + i)(y + z)$ is not.

We are interested in justifying the assumption that all lattice functions have moral cellular parts. Such functions and their multiples by a constant will be called worthy lattice functions.

THEOREM I.

Any lattice function can be resolved into worthy lattice functions.

Introductory Remarks

That is, if we have a non-worthy function which satisfies our boundary conditions, it can be resolved into one or two worthy functions which also satisfy the boundary conditions. So long as this is true, there is no need of dealing with other than worthy functions. Any more complicated lattice function will be merely a linear combination of these.

Proof

If $\psi_{\varkappa}$ is a lattice function, it is obvious that the complex conjugate $\overline{\psi_{\varkappa}}$ will be an equally good lattice function. Also, since the atom at the origin, like every atom, is at a center of symmetry in the lattice, the function obtained by changing x to -x , y to -y , and z to -z will also be a good lattice function. Let us denote the resultant transformation on the function ψ_κ by $A\psi_\kappa$. The result of performing both operations on a function will again give a good function.

Let
$$\psi_\kappa = \sum_\alpha e^{i\kappa\cdot R_\alpha}\,\psi(r - R_\alpha)$$
$$\bar{\psi} = \sum_\alpha \bar{e}^{i\kappa\cdot R_\alpha}\,\bar{\psi}(+r-R_\alpha)$$
$$A\psi = \sum_\alpha e^{i\kappa\cdot R_\alpha}\,\psi(-r - R_\alpha) \quad .$$

Since the set of lattice points $-R_\alpha$ is the same as R_α ,
$$A\psi = \sum_\alpha e^{-i\kappa\cdot R_\alpha}\,\psi(-r + R_\alpha) \quad .$$

Now $\psi(-r + R_\alpha)$ is the same cellular function around atom α as $\psi(-r)$ is around the origin. But $\psi(-r) = A\psi(r)$ by definition. Then $A\bar{\psi}_\kappa$ will be
$$A\bar{\psi}_\kappa = \sum_\alpha e^{i\kappa\cdot R_\alpha}\,A\bar{\psi}(r - R_\alpha) \quad .$$

Now $\psi_\kappa + A\bar{\psi}_\kappa$ is worthy
$$\psi_{W_1} = \psi_\kappa + A\bar{\psi}_\kappa = \sum_\alpha e^{i\kappa\cdot R_\alpha}\left[\psi(r - R_\alpha) + A\bar{\psi}(r - R_\alpha)\right] \quad .$$

To see this resolve ψ into its even and odd parts $\psi = G + U$.

Then
$$A\psi = G - U$$
$$A\bar{\psi} = \bar{G} - \bar{U}$$
$$\psi + A\psi = G + \bar{G} + U - \bar{U} = 2\,\mathrm{Re}\,G + 2i\,\mathrm{Im}\,U \quad .$$

This shows that from a given lattice function satisfying the boundary conditions we can construct a worthy function satisfying the conditions also. Another worthy function is

$$\psi_{w_2} = i(\psi_{\kappa} - A\bar{\psi}_{\kappa}) \quad .$$

In terms of these $\psi_{\kappa} = (\psi_{w_1} - i\psi_{w_2})/2$.

Q.E.D.

Corollary to Theorem I.

A worthy lattice function is a worthy function.

Although the cellular part of a worthy lattice function is worthy about the center of the cell, it is not obvious that the lattice function as a function throughout all space is worthy about this center. To prove the corollary, make the cellular part moral; this can be done in accordance with definition of the worthy lattice functions. Then, we find

$$\begin{aligned} A\bar{\psi}_{\kappa} &= \sum e^{i\kappa\cdot R_{\alpha}} A\bar{\psi}(r - R_{\alpha}) \\ &= \sum_{\alpha} e^{i\kappa\cdot R_{\alpha}} \psi(r - R_{\alpha}) = \psi_{\kappa} \quad , \end{aligned}$$

and $\psi_{\kappa} = \frac{1}{2}(\psi_{\kappa} + A\bar{\psi}_{\kappa})$. We have seen, however, that a function of this sort is moral. Hence, a constant times our worthy lattice function is a moral function which is what we wished to prove.

So far we have considered the functions worthy as regards their behavior about one of the sets of lattice points only. Since both sodiums and chlorines are at centers of symmetry, it is of interest to see if making the function worthy about one set of lattice points makes it worthy about the other set also.

THEOREM II.

In a lattice containing two sets of centers of symmetry, a function which is worthy for one set is worthy for the other set, and the phases of the moral functions are given by the same wave vector for both.

Proof

We first note that the method of setting up ψ insured that the function be moral about the point at the origin, actually moral throughout all space. We can then write ψ_{w_1} as $G_o + iU_o$. Let the displacement from the origin, which is a symmetry center of the first set, to a symmetry center of the second set be ρ. Then there is a symmetry center of the first set at 2ρ. About this second center

$$\psi_{w_1} = e^{i2\varkappa\cdot\rho}\left[G_{2\rho} + iU_{2\rho}\right] \quad . \quad \text{Therefore}$$

$$\psi_{w_1} = \tfrac{1}{2}\, e^{i\varkappa\cdot\rho}\left\{e^{-i\varkappa\cdot\rho}\left[G_o + iU_o\right] + e^{i\varkappa\cdot\rho}\left[G_{2\rho} + iU_{2\rho}\right]\right\}$$

$$= \tfrac{1}{2}\, e^{i\varkappa\cdot\rho}\left\{\cos\varkappa\cdot\rho\left[G_o + G_{2\rho}\right] - i\sin\varkappa\cdot\rho\left[G_o - G_{2\rho}\right] + \sin\varkappa\cdot\rho\left[U_o - U_{2\rho}\right] + i\cos\varkappa\cdot\rho\left[U_o + U_{2\rho}\right]\right\}$$

About the center at ρ , $G_0 + G_{2\rho}$ and $U_0 - U_{2\rho}$ are clearly even, whereas the other two functions are odd. Hence, the expression in the brackets is moral and the phase is $e^{i\kappa\cdot\rho}$.

Q.E.D.

This shows that we need only consider moral functions around each type of atom. The lattice functions are built up of these by summing over the cells.

There is one further theorem which reduces the number of boundary conditions considerably. If we look at the cell centered about the Cl, page 23, we see that there are three kinds of boundary surface: (1) Cl-Cl boundaries at the surface of the cell. (2) Na-Na at the surface. (3) Na-Cl inside the cell. The boundaries of type (1) are the same as those met with in metals and need not be discussed here. The type (2) boundaries are fictitious. If we make use of worthy functions, the wave function around a given Na will be the same, no matter from which cell we approach it, and, hence, these boundary surfaces do not actually exist. The boundaries of interest at the present time are those of type (3). In a given cell there are six of these, and, if we attempt to satisfy the Slater conditions (continuity of ψ and the normal component of grad ψ) at the midpoints of these, we will get 24 conditions. The extra factor of 2 is caused by the fact that the use of moral functions requires the fitting of real and imaginary parts separately. Fortunately, we can show that the actual number of conditions is only half this many, some of the faces being equivalent. Let us call these boundaries of type (3) internal faces.

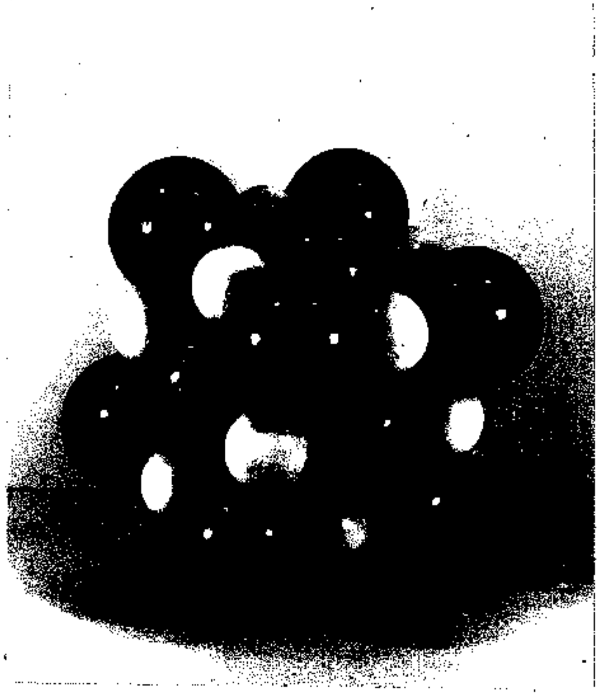
THEOREM III.

If worthy functions are used and the boundary conditions are satisfied on one internal face, they are satisfied on the other internal face paired with it by the center of symmetry.

Proof

The proof is very simple. Suppose the wave function ψ is worthy and satisfies the conditions on one internal face. Then the wave function $A\psi$ obtained by operating with the center of symmetry certainly satisfies the conditions on the other face, and so does the complex conjugate $A\overline{\psi}$ of $A\psi$. However, $A\overline{\psi} = \psi$, therefore ψ satisfies the conditions of both faces.

Q.E.D.



VI.

FORMULATION OF THE BOUNDARY CONDITIONS

So far we have discussed the method of calculating the wave functions for the various surface harmonics and the general aspects of the boundary conditions on the wave functions. The next problem is to see how we can utilize the results of the former to satisfy the requirements of the latter.

The general method of attack has been that discussed by Slater.* He required that the wave function and its normal derivative be continuous at the midpoint of each face separating two atoms. We shall demand that these continuity conditions be fulfilled at C-Cl and the NaCl midpoints. These midpoints are judged to be much more important than the NaNa midpoints on the basis of the ionic radii of the two atoms, which are such that the Na and Cl ions touch and the Cl-Cl ions almost touch one another, while the NaNa ions are quite far apart. A photograph of a model of Halite shows the relative sizes of the ions. From this it might appear reasonable to join Na and Cl at their ionic radii. In order to judge whether or not this was sensible, the total lattice potential was calculated along the NaCl line. For this calculation, Hartree's** fields of the Na^+ and Cl^- ions were used without

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*J. C. Slater, Phys. Rev. <u>45</u>, 794 (1934).

++ D. R. Hartree, Camb. Phil. Soc. <u>24</u>, 89 (1928).

alteration. It was found that the potential had a very flat maximu near the midpoint. From it we should be inclined to choose the NaCl midpoint for joining. This procedure is also suggested by the $\ell(\ell + 1)/r^2$ terms in the wave equation. By choosing the midpoint, these are made equal for both atoms.

The next question is what these boundary conditions require of our worthy functions. Let the moral functions for two sorts of atoms be

$$(6.1)\qquad \begin{array}{ll} \text{Cl} & g(r) + iu(r) = \varphi(r) \\ \text{Na} & g_1(r) + iu_1(r) = \varphi_1(r) \end{array}$$

Then $$\psi = \sum_{\alpha} e^{i\mathbf{k}\cdot R_\alpha}\,\varphi(r - R_\alpha) + \sum_{\beta} e^{i\mathbf{k}\cdot R_\beta}\,\varphi_1(r - R_\beta)$$

where the R_α represent Cl lattice points and R_β, Na. The conditions required for continuity across the 110 Cl-Cl face, for example, are derived as follows. The wave function in the cell at $R = a(\frac{1}{2}\,\frac{1}{2}\,0)$ is $e^{i\mathbf{k}\cdot R}$ times the wave function in the 0^{th} cell. The midpoint is at $R/2 = \frac{1}{2}a(\frac{1}{2}\,\frac{1}{2}\,0)$. This point is $R/2$ in reference to the 0^{th} cell and $-R/2$ in reference to the $\frac{1}{2}a(110)$ cell. The values of the cellular functions at these points are thus $g(R/2) + iu(R/2)$ and $e^{i\mathbf{k}\cdot R}\left[g(R/2) - iu(R/2)\right]$. Similarly, the derivatives are $g'(R/2) + iu'(R/2)$ and $e^{i\mathbf{k}\cdot R}(-g'(R/2) + iu'(R/2))$ where g' means $\frac{d}{ds}$ along the line R. For spherical functions, then, $\frac{d}{ds}$ is the same as $\frac{d}{dr}$. Equating the values of ψ

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*See Slater "Energy Bands in Metals" for a more complete discussion.

and those of ψ' , we find the conditions

$$(6.2)\quad \begin{aligned} &-\tan(\varkappa\cdot R/2)\, g + u = 0 \\ &g' + \tan(\varkappa\cdot R/2) u' = 0 \end{aligned} \qquad .$$

For brevity, we denote $\tan(\varkappa\cdot R_{110}/2)$ by T_{110} , etc.

Along the NaCl lines the conditions are found in a similar way. Let a Cl atom be at 000 , and consider the midpoint at $R/2 = a(\frac{1}{4}\ 0\ 0)$. For the Na cell at $a(\frac{1}{2}\ 0\ 0)$, this is the point $-a(\frac{1}{4}\ 0\ 0)$. The moral function about the Na has the value $\varphi_1 = g_1(R/2) - iu_1(R/2)$ and the value of $\frac{d}{dx}\varphi_1(-R/2) = -g_1'(R/2) + iu_1'(R/2)$ at this point.

The boundary conditions are thus

$$(6.3)\quad \begin{aligned} g(R/2) + iu(R/2) &= e^{i\varkappa\cdot R}\left[g_1(R/2) - iu_1(R/2)\right] \\ g'(R/2) + iu'(R/2) &= e^{i\varkappa\cdot R}\left[-g_1'(R/2) + iu_1'(R/2)\right] \end{aligned}$$

These equations, as was noted in connection with Theorem II, must be separated into real and imaginary parts, since the functions of g and u are real.

It is well known that such boundary conditions as these are periodic in $\varkappa$ space. In order to see this, consider $\varkappa' = \varkappa + 2\pi b$, where b is a vector of the reciprocal lattice. Then in Equations (6.2),

$$\tan \varkappa'\cdot R/2 = \tan\left(\varkappa\cdot R/2 + \pi R\cdot b\right),$$

but $R\cdot b$ is an integer or zero, so that $\tan\varkappa'\cdot R/2 = \tan\varkappa\cdot R/2$.

To see that (6.3) is periodic, we must use the actual forms of the vectors R and b . The R's are of the form $a(\frac{1}{2}\ 0\ 0)$ and the b's of the form $1/a(\pm 1\ 1\ 1)$. Hence, $R \cdot b = \pm 1/2$. This introduces a factor $e^{\pm \pi i} = -1$ on the right side of 2 which is homogeneous in the Na functions and can thus absorb the real factor -1 .

The periodicity in $\varkappa$ space is not convenient for practical purposes, due to the fact fact that $2\pi b$ is not a simple vector. In order to have a simple periodicity, we replace by $2\pi k/a$. The lattice vectors in k space are then (1 1 1), (2 0 0), etc. (i.e., k space as body centered with lattice spacing 2.) The tangent vectors take on a particularly simple form,

$$T_{110} = \tan\tfrac{1}{2}\, 2\pi k \cdot (\tfrac{1}{2}\ \tfrac{1}{2}\ 0) \quad = \tan\tfrac{\pi}{2}(k_x + k_y) \text{ , for example.}$$

There are thus 24 equations to be satisfied: 12 of the Cl-Cl type for the 6 different 1 1 0 directions; 12 of the Na-Cl type for the 1 0 0, 0 1 0, and 0 0 1 directions. The $\bar{1}$ 0 0, 0 $\bar{1}$ 0, and 0 0 $\bar{1}$ midpoint conditions follow by Theorem III.

In order to satisfy these conditions, we shall expand the various g's and u's in terms of surface harmonics times the corresponding radial functions. 24 of these functions will be needed. When the g's and u's are expressed as linear combinations of these, the 24 equations give 24 conditions on the 24 expansion coefficients. The necessary and sufficient condition for a non-trivial solution of these equations is that the determinant of the system of equations vanishes. This determinant will be a function of the radial parts of the wave functions which are dependent upon the energy, $\bar{\varepsilon}_{\ell}$, and of the vector k . For a given energy there will be certain values of k for which the determinant vanishes. Real values of k correspond to lattice functions and complex values to damped waves, which are not of interest here.

The next problem is to choose the expansion function in terms of which to expres the g's and u's . There are several precautions which must be observed in choosing these. In the first place, we must have at least 12 Cl functions, in order to satisfy the 12 conditions of type 1 which do not involve the Na . Then we must choose 12 more functions to supplement these. Let us consider first the case where these are all chosen about the Na ion. For reasons indicated below, this will be called the Cl-Cl case.

Cl-Cl Case

For this case we have 12 functions around the Cl and 12 around the Na . The 12 Cl-Cl conditions are homogeneous in the Cl functions and give rise to a determinant in k and $\bar{\varepsilon}_{\ell}$. When this is solved for k , the function around the Cl will be fixed. The 12 Na-Cl conditions will not be homogeneous, but will relate the 12 Na function coefficients to the determined Cl function. The condition for solubility for the Na functions will be that the determinant for their coefficients in Equations (6.3) does not vanish. If this determinant does not vanish, the relation between $\bar{\varepsilon}_{\ell}$ and k is determined by the Cl functions only. The sodium functions are present merely to act as buffers and to give continuity across the Na-Cl faces.

If the determinant for the Na coefficients does vanish, then it is possible to obtain functions around the Na while the coefficients of the Cl functions are all zero. Since the boundary conditions for these functions are that φ_1 and φ_1' vanish at the Cl-Na midpoints, there are no restrictions placed on k . When the energy is such, then, that the Na determinant vanishes, we can get solutions for all values of k . Sets of wave functions like these, for which the energy is independent of k , are said to form "zero width bands." This treatment of the Na functions is obviously too crude. Nevertheless, it can easily be seen that the zero width bands give the correct wave functions and energy levels for the case of large separation of the atoms or for the inner electrons. Since no use is made of this fact, no proof will be given.

A suitable choice of the Cl functions has already been found by Krutter* for the face-centered Cu lattice. Since the Cu-Cu conditions are the same as the Cl-Cl conditions, these can be used here.

---

*H. M. Krutter, Phys. Rev. 48, 664 (1935).
Thesis (Ph.D.), Physics (1935).

A satisfactory set of Na functions are the following:

g type

$$S(r)\ ,\quad \frac{x^2 - y^2}{r^2}\,D(r)\ ,\quad \frac{x^2 - z^2}{r^2}\,D(r)$$

$$\frac{(35x^4 - 30x^2r^2 + 3r^4)}{r^4}\,G(r)\ ,\quad \frac{35y^4 - 30y^2r^2 + 3r^4}{r^4}\,G(r)$$

$$\frac{(35z^4 - 30z^2r^2 + 3r^4)}{r^4}\,G(r)$$

u type

$$\frac{x}{r}\,P(r)\ ,\quad \frac{y}{r}\,P(r)\ ,\quad \frac{z}{r}P(r)$$

$$\frac{5x^3 - 3xr^2}{r^3}\,F(r)\ ,\quad \frac{5y^3 - 3yr^2}{r^3}\,F(r)\ ,\quad \frac{5z^3 - 3zr^2}{r^3}\,F(r)\ .$$

Na-Cl Case

The simplest set of conditions which will give dependence on both Na and Cl functions will be obtained by ignoring the Cl-Cl conditions entirely. This leads to 12 equations of type 6.3. A natural choice of 12 functions is then

$$\mathrm{Cl}\ \left\{\begin{array}{llll} \Sigma\ , & (x^2 - y^2)/r^2\,\Delta & , & (y^2 - z^2)/r^2\,\Delta \\ x/r\,\Pi, & y/r\,\Pi & , & z/r\,\Pi \end{array}\right.$$

$$\mathrm{Na}\ \left\{\begin{array}{llll} S\ , & (x^2 - y^2)/r^2 D & , & (y^2 - z^2)/r^2 D \\ x/rP\ , & y/r\ P & , & z/r\ P \end{array}\right.$$

Double Join Cases

By choosing more than 12 functions around the Cl and the remainder of the 24 around the sodium, sets can be obtained which will satisfy both sets of boundary conditions. Possibilities of this type will be considered in Section XI.

VII.

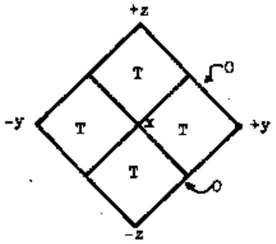
Cl-Cl CASE

As was explained in Section VI, the Cl-Cl case is equivalent to the general face-centered case discussed by Krutter. The relationship between k and $\bar{\varepsilon}$ is given by a 12^{th} order determinant which it is not practical to handle in its full generality.

The purpose of the present section is to obtain expressions from which the values of k as a function of $\bar{\varepsilon}$ can be computed for a sufficient number of planes and lines in momentum space to allow reasonable extrapolations to be made to all values of k .

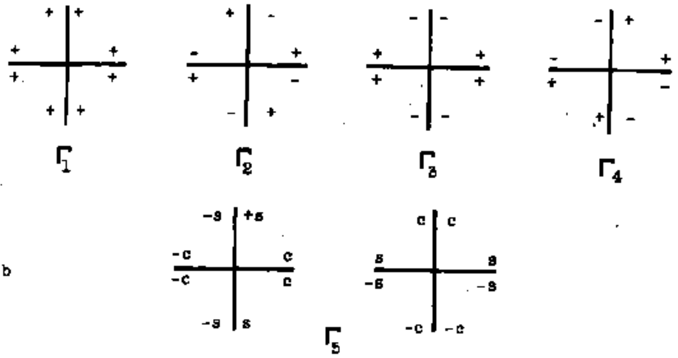
In order to obtain equations which can be used for calculation, it is necessary to restrict k to simple lines or planes in the k lattice. When this is done, it is found that the resultant symmetry of the cellular boundary conditions enables the 12 functions to be split into smaller sets, each set satisfying the conditions separately. In the language of group theory, this procedure may be described as follows: The vector k is so chosen that certain symmetry operators of the point group for the lattice leave it invariant. These operators will clearly form a sub-group of the point group, and the transformations of the spherical functions for these operators will give rise to representations of it. It is well known that in any problem having symmetry, solutions of

7a



View of duodecahedron
from 100 direction

7b



$$\begin{array}{ccc} b & a & b \\ a & & a \\ b & a & b \end{array} \qquad \begin{array}{ccc} 0 & 0 & 0 \\ 0 & & 0 \\ 0 & 0 & 0 \end{array} \qquad \begin{array}{ccc} 0 & a & 0 \\ -a & & -a \\ 0 & a & 0 \end{array} \qquad \begin{array}{ccc} b & 0 & -b \\ 0 & & 0 \\ -b & 0 & b \end{array}$$

7c

$$\begin{array}{ccc} -c & 0 & c \\ -d & & d \\ -c & 0 & c \end{array} \qquad \begin{array}{ccc} c & d & c \\ 0 & & 0 \\ -c & -d & -c \end{array}$$

different symmetry types do not mix. In our case, this means that functions transforming in different ways under the subgroup (i.e., belonging to different representations) will not mix. In order to see how we can apply these ideas and to establish the notation used in this section, let us calculate the energy bands for k in the 100 direction

1. Application of Group Theory to 100 Direction

The Figure shows the face-centered cell as seen from the 100 direction. For k in this direction, the six T (tangent) factors occurring in the equations

$$- Tg + u = 0$$

$$g' + Tu' = 0$$

of Section VI. , page 42 take on only two values:

$$0 \ , \quad \text{and} \quad T = T_{110} = \tan(\pi k_x/2) \quad .$$

Hence, the boundary conditions have symmetry of a square. There are four one-dimensional representations of this group and one two-dimensional representation. The scheme of values is shown in Figure 7b.

The value which these types give rise to on the 110, 101, 1$\bar{1}$0, and 10$\bar{1}$ faces and the 011, 0$\bar{1}$1, 01$\bar{1}$, and 0$\bar{1}\bar{1}$ faces are indicated in Figure 7c.

Let us next classify the 12 spherical functions of the face-centered lattice, in accordance with the above scheme.

In order to simplify the expressions, we shall write a surface harmonic, such as $(x^2-y^2)/r^2$ as (x^2-y^2). No error will be introduced, so long as we always use values of xyz like (110) etc., for which $x^2 + y^2 + z^2 = 2$.

The spherical functions are

$$g \qquad \Sigma \;;\; (2x^2 - y^2 - z^2)\Delta \;,\; (y^2 - z^2)\Delta \;,\; xy\Delta yz\Delta \;, zx\Delta$$

$$u \qquad x\Pi,\; y\Pi,\; z\Pi;\; x(y^2 - z^2)\Phi \;,\; y(z^2 - x^2)\Phi,\; z(x^2 - z^2)\Phi$$

When classified according to 100 symmetry, we get

Γ_1 $\quad \Sigma \;;\; (2x^2 - y^2 - z^2)\Delta \;,\; x\Pi$

Γ_2 $\quad$ none

Γ_3 $\quad (y^2 - z^2)\Delta \;,\; x(y^2 - z^2)\Phi$

Γ_4 $\quad yz\,\Delta$

Γ_5 $\quad xy\,\Delta \;,\; y\Pi \;,\; y(z^2 - x^2)\Phi$

$\quad\quad xz\,\Delta \;,\; z\Pi \;,\; z(y^2 - x^2)\Phi$.

To solve these, we make the simplifying assumption that

$$\Sigma = \Pi = \Delta = \Phi = I = 1 \qquad \text{at the cell surface;}$$

then $\Sigma' = \sigma,\ \Pi' = \pi\ ,\ \Delta' = \delta\ ,\ \Phi' = \varphi$.

Solution for Γ_1

Let $g = A\Sigma + B(2x^2 - y^2 - z^2)\Delta$

$u = C\,x\Pi$

Then, for the $T_{011} = 0$ face, we find that

$$A\sigma - 2B\delta = 0 \quad , \text{ or } \quad B = \frac{\sigma}{2\delta}A.$$

For the $T_{110} = T$ face, we find

$$-T\left[A + \frac{\sigma}{2\delta}A\right] + C = 0$$

$$A\sigma + A\frac{\sigma}{2} + TC\kappa = 0 \quad .$$

The necessary and sufficient condition for the existence of a nontrivial solution of these equations for A and C is that the determinant of the coefficients vanishes.*

$$\begin{vmatrix} -T(1 + \frac{\sigma}{2\delta}) & 1 \\ \frac{3}{2}\sigma & T\kappa \end{vmatrix} = 0 = T^2\kappa(2\delta + \sigma)/(2\delta) + \frac{3}{2}\sigma \quad .$$

This gives the condition

(100a) $$T^2 = -\frac{3\sigma\delta}{\kappa(2\delta+\sigma)} \quad .$$

Similar calculations for the other sets give the remainder of Krutter's 100 equations.

(100b) Γ_3 $\quad T^2 = -\frac{\delta}{\varphi}$

(100c) Γ_4 $\quad$ No relation between energy and momentum, merely $\delta = 0$

$\left.\begin{matrix}(100d)\\(100e)\end{matrix}\right\}$ Γ_5 $\quad T^2 = -\frac{2\delta}{\kappa+\varphi}$

The symmetry treatment shows why the zero width appears in the 100 direction. One of the symmetry types is automatically zero on all the faces whose tangent factor involves k .

---

*For a discussion of homogeneous linear algebraic equations, see, for example, Dickson "First Course in the Theory of Equations," Chapter VIII.

The possibility of such an occurrence is an indication of a weakness in the Slater conditions as applied to midpoints only. If more points on the intercell surface were used, this flaw would be removed.

2. The 001 Plane

When k_z is zero, the only symmetry operation which leaves k invariant is the change $z \rightarrow -z$. This requires the functions to be split into even and odd functions in respect to the powers of z . The odd functions are

$$O: \quad z\,x\,\Delta \;,\quad zy\,\Delta \;;\quad z\,\Pi \;;\quad z(x^2 - y^2)\,\Phi \quad .$$

The boundary conditions for this set can be solved and give

$$(001o) \quad \left[T^2_{101} + \tfrac{1}{2}\,\delta\left(\tfrac{1}{\varkappa} + \tfrac{1}{\varphi}\right)\right] \cdot \left[T^2_{011} + \tfrac{1}{2}\,\delta\left(\tfrac{1}{\varkappa} + \tfrac{1}{\varphi}\right)\right] =$$

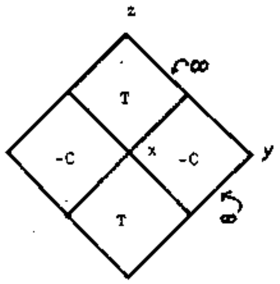
$$\left[\tfrac{1}{2}\,\delta\left(\tfrac{1}{\varkappa} - \tfrac{1}{\varphi}\right)\right]^2 \quad .$$

There are eight even functions in z . These are

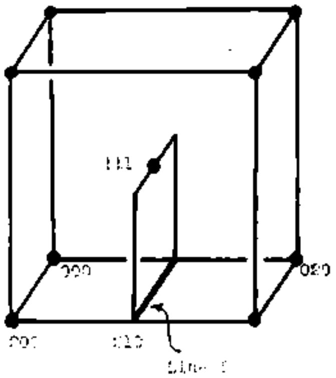
$$\Sigma \;,\; (x^2 - y^2)\Delta \;,\;\; (y^2 - z^2)\Delta \;,\;\; xy\,\Delta$$

$$E \qquad x\,\Pi \;,\;\; y\,\Pi \;,\;\; x(z^2 - y^2)\,\Phi \;,\;\; y(z^2 - x^2)\,\Phi \quad .$$

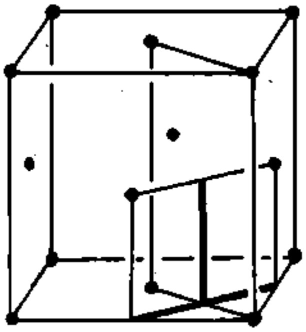
It is impossible to get a usable expression of the form (001o) from these. However, the solutions in the 100 direction are



7e



7d



7f

Special lines in face-centered k-space for body-centered lattice.

already given in Γ_1, Γ_3 and Γ_5. Solutions are also obtainable in the 110 direction. These are given by Krutter and will be tabulated later.

3. A New Line in the 001 Plane, Line I.

It is possible to effect a split of the even functions along the line $k = u(100) + (010)$ in the even functions of the 001 plane. The fundamental reason for this is that the line $k = u(100) + (010)$ is formed by the intersection of the 001 plane with an 010 plane in momentum space. This means that we should be able to split the functions into even and odd for $y \rightarrow -y$, as well as $z \rightarrow -z$ along this line.

The tangent factors are:

$$T_{110} = \tan\frac{\pi}{2}(u + 1) = - \cot \frac{\pi}{2}u = - C$$

$$T_{10\bar{1}} = \tan\frac{\pi}{2}(u - 1) = - \cot\frac{\pi}{2}u = - C$$

$$T_{101} = \tan\frac{\pi}{2}(u) = T$$

$$T_{10\bar{1}} = \tan\frac{\pi}{2}(u) = T$$

$$T_{011} = \tan\frac{\pi}{2}(1) = \infty$$

$$T_{01\bar{1}} = \tan\frac{\pi}{2} = \infty .$$

Figure 7e shows the symmetry of the tangent factors, which is the algebraic consequence of the symmetry stated above.

Digression

It is of interest to point out that similar lines exist in the face-centered k lattice for the body-centered space lattice. One of these is in a 100 and a 011 plane, another is at the intersection of a 011 and $01\bar{1}$ plane. See Figure 7f.

Splitting the functions according to the above scheme, we have:

Even in y $A\Sigma$, $B(2x^2 - y^2 - z^2)\Delta$, $D(y^2 - z^2)\Delta$

$E\,x\,\Pi$, $E\,x\,(z^2 - y^2)\,\Phi$

Odd in y $A\,xy\,\Delta$, $By\,\Pi$, $Cy(z^2 - x^2)\,\Phi$.

Even in y , solution

Since there are five functions in this set, the boundary conditions will lead to a fifth order determinant. Some of the labor involved in expanding the determinant can be avoided by eliminating one of the coefficients before setting up the determinant. The conditions on the 011 face are

$$g = u' = 0 \quad .$$

The u' is automatically fulfilled and the other gives

(011 face) $A - 2B = 0$ or $B = \frac{1}{2}A$.

Using this value of B in the other equations, we have

(101 face)

$$-T\left[A + \tfrac{1}{2}A - D\right] + \left[E + F\right] = 0$$

$$\left[A\sigma + \tfrac{1}{2}A\delta - D\delta\right] + T\left[E\kappa + F\varphi\right] = 0$$

(110 face)

$$C\left[A + \tfrac{1}{2}A + D\right] + \left[E - F\right] = 0$$

$$\left[A\sigma + \tfrac{1}{2}A\delta + D\delta\right] - C\left[E\kappa - F\varphi\right] = 0 \quad .$$

The determinant of the coefficients of A, C, E, and F is:

$$\begin{array}{c} (1) \\ (2) \\ (3) \\ (4) \end{array} \quad \left| \begin{array}{cccc} -\frac{3}{2}T & T & 1 & 1 \\ \sigma + \frac{1}{2}\delta & -\delta & T\kappa & T\varphi \\ \frac{3}{2}C & C & 1 & -1 \\ \sigma + \frac{1}{2}\delta & \delta & -C\kappa & -C\varphi \end{array} \right|$$

This determinant is most readily expanded in terms of minors of the first two columns. The main advantage of this procedure is that T and C can be factored out of the terms and that $TC = 1$. Letting w stand for $\sigma + (\delta/2)$, and indicating the rows of the minor in parentheses, we get the following terms for the expansion:

(12)
$$\begin{vmatrix} -1.5 & 1 \\ w & -\delta \end{vmatrix} \begin{vmatrix} 1 & -1 \\ -\kappa & \varphi \end{vmatrix} = (\delta - \sigma)(\varphi - \kappa)$$

(13)
$$- \begin{vmatrix} -1.5 & 1 \\ 1.5 & 1 \end{vmatrix} \begin{vmatrix} \kappa & \varphi \\ -\kappa & \varphi \end{vmatrix} = 6\kappa\varphi$$

(14)
$$+T^2 \begin{vmatrix} -1.5 & 1 \\ w & \delta \end{vmatrix} \begin{vmatrix} \kappa & \varphi \\ 1 & -1 \end{vmatrix} = T^2(\sigma + 2\delta)(\kappa + \varphi)$$

(23)
$$C^2 \begin{vmatrix} w & -\delta \\ 1.5 & 1 \end{vmatrix} \begin{vmatrix} 1 & 1 \\ -\kappa & \varphi \end{vmatrix} = C^2(\sigma + 2\delta)(\kappa + \varphi)$$

(24)
$$- \begin{vmatrix} w & -\delta \\ w & \delta \end{vmatrix} \begin{vmatrix} 1 & 1 \\ 1 & -1 \end{vmatrix} = 2(\delta + 2\sigma)$$

(34)
$$\begin{vmatrix} 1.5 & 1 \\ w & \delta \end{vmatrix} \begin{vmatrix} 1 & 1 \\ \kappa & \varphi \end{vmatrix} = (\delta - \sigma)(\varphi - \kappa)$$

Collecting terms, we obtain the expression

$$I_a \quad (T^2 + C^2)(2\sigma + \delta)(\kappa + \varphi) + 2(\delta - \sigma)(\varphi - \kappa) + \\ + 2\delta(\delta + 2\sigma) + 6\kappa\varphi = 0 \quad .$$

Since $T^2C^2 = 1$, this is a quadratic in T^2 for which the solution is

$$T^2 = -\frac{B}{2} \pm \sqrt{(B/2)^2 - 1} \qquad \text{with} \quad \frac{B}{2} = \frac{(\delta - \sigma)(\varphi - \varkappa) + (\delta + 2\sigma)\delta + 3\varkappa\varphi}{(2\delta + \sigma)(\varkappa + \varphi)}$$

Odd in y

We may eliminate C by the 011 condition, which gives $B\varkappa + C\varphi = 0$ or $C = -(\varkappa/\varphi)B$. The determinant is

$$\begin{vmatrix} C & (1 + \frac{\varkappa}{\varphi}) \\ \delta & -C(2\varkappa) \end{vmatrix} = 0 \qquad \text{or}$$

$$I_b \qquad C^2 = -\frac{\delta}{2}\left(\frac{1}{\varkappa} + \frac{1}{\varphi}\right) \quad .$$

This completes the investigation of the even functions of the 001 plane along the line $k = u(100) + (010)$. Let us now see how the odd functions behave. One solution of Equation (001o) when $T_{011} \longrightarrow \infty$ is given by

$$I_c \qquad T^2 = -\frac{\delta}{2}\left(\frac{1}{\varkappa} + \frac{1}{\varphi}\right) \quad .$$

This is obviously a companion to I_b above, and will involve the functions

$$xz\,\Delta \quad , \quad z\,\Pi \quad , \quad z(x^2 - y^2)\,\Phi \quad .$$

The function $yz\,\Delta$ has been slipped through the net; however, remembering its behavior in the 100 direction, we

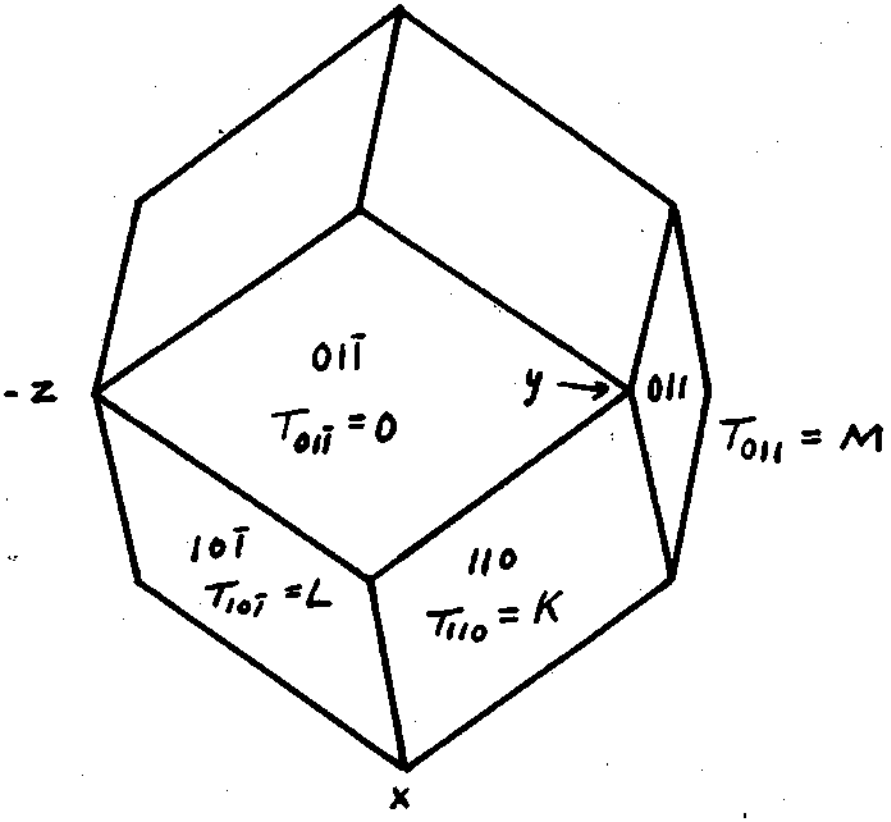


fig 7g

see that it gives a zero width band with

$$I_d \qquad \delta = \infty \quad .$$

4. The $01\bar{1}$ Plane

For the $01\bar{1}$ plane $k_y = k_z$. This means that we can split functions int odd or even with respect to the reflection $y \rightarrow z$, $z \rightarrow y$.

5. The Odd Set of $01\bar{1}$

The odd functions are:

$$A(y^2 - z^2)\Delta , \quad B\,x\,(y - z)\Delta , \quad C(y - z)\Pi , \quad D\,x\,(y^2 - z^2)\Phi$$

$$E\,\left[y(z^2 - x^2) - z(y^2 - x^2)\right]\Phi \quad .$$

The tangent factors are shown in Figure 7g. It is necessary to consider only four directions for the tangent factors. The other two possible directions, $1\bar{1}0$ and 101, are equivalent to $10\bar{1}$ and 110 because of the $01\bar{1}$ reflection plane.

Before setting up the determinantal condition, we shall eliminate the coefficient E . $01\bar{1}$ gives $g' = 0$ and $u = 0$. The first is automatically fulfilled for the odd g functions. The second gives

$$+ 2C + 2E = 0 \qquad \text{or} \qquad E = - C \quad .$$

The other conditions come from $10\bar{1}$ and 110; none from 011, since all the functions vanish there.

($10\bar{1}$ face)

$$-L(-A + B) + C + C - D = 0$$

$$(-A\delta + B\delta) + L\left(C\varkappa + C\varphi - D\varphi\right) = 0$$

(110 face)

$$-K(A + B) + C + C + D = 0$$

$$(A\delta + B\delta) + K\left(C\varkappa + C\varphi + D\right) = 0 \quad .$$

If the determinant is set up and expanded, we obtain the expression

$$(01\bar{1}o) \qquad \left(T^2_{110} + \frac{\delta\,(\varkappa+3\varphi)}{2\varphi(\varkappa+\varphi)}\right)\left(T^2_{10\bar{1}} + \frac{\delta\,(\varkappa+3\varphi)}{2\varphi(\varkappa+\varphi)}\right) = \left[\frac{\delta\,(\varkappa-\varphi)}{2\varphi(\varkappa+\varphi)}\right]^2$$

6. The Even Set of $01\bar{1}$

$$\text{E} \quad \Sigma\ ,\ (2x^2 - y^2 - z^2)\Delta\ ,\ yz\Delta\ ,\ x(y + z)\Delta$$

$$x\Pi,\ (y + z)\Pi\ ,\ \left[y(x^2 - z^2) + z(x^2 - y^2)\right]\Phi \quad .$$

For the even functions we are again reduced to solutions in special directions. Krutter has given the solutions for the 100, 011, and 111 lines lying in this plane. These will be tabulated later.

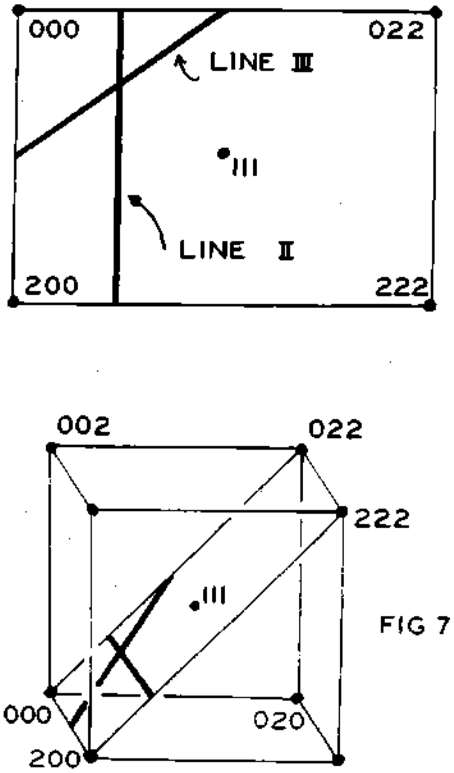


FIG 7h

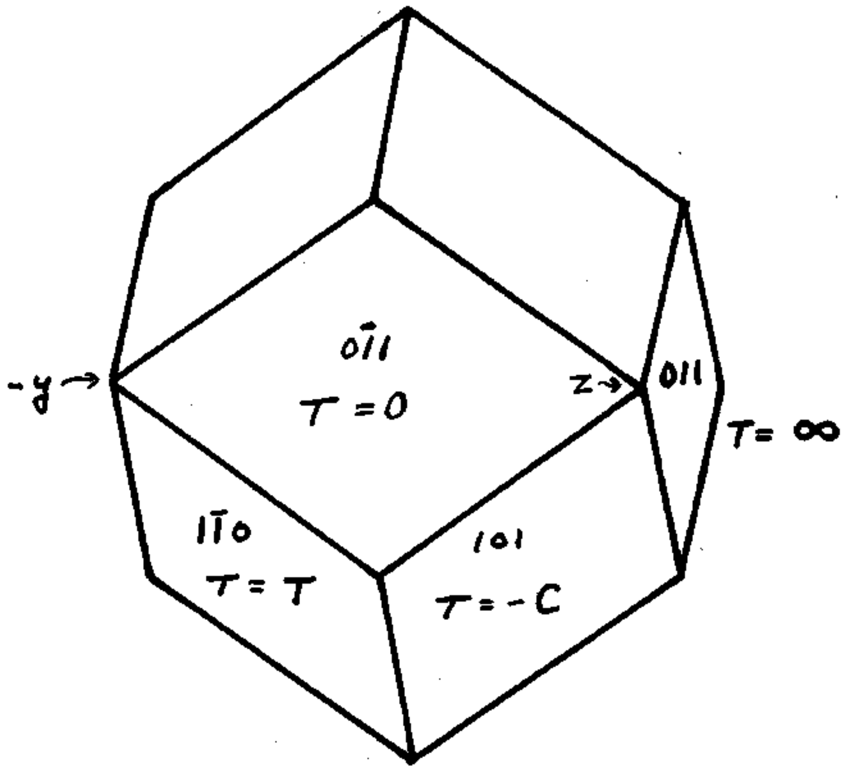


fig 7i

Two new solutions for the even function set have been obtained. They are represented by the lines

$$\text{II} \qquad k = u(100) + \tfrac{1}{2}(011)$$

$$\text{III} \qquad k = (1 - u)(100) + u(011) = u(\bar{1}11) + (100).$$

The arrangement of these lines in momentum space is shown in Figure 7h.

7. Line II.

$$k = u(100) + \tfrac{1}{2}(011)$$

The advantage of these lines is that they give rise to simple sets of tangent factors, so that it is not necessary to deal directly with more than fourth order determinants. There are four independent faces of the cell for functions of the E type, Fig. 7i. The tangent factors are

$$T_{101} = \tan\tfrac{\pi}{2}(u + \tfrac{1}{2}) = \tan\tfrac{\pi}{2}(w+1) = -\cot w = -C$$

$$T_{1\bar{1}0} = \tan\tfrac{\pi}{2}(u - \tfrac{1}{2}) = \tan\tfrac{\pi}{2}\, w = T$$

$$T_{0\bar{1}1} = 0 \qquad\qquad \text{where} \quad w = u - \tfrac{1}{2}$$

$$T_{011} = \tan\tfrac{\pi}{2}(1) = \infty$$

We shall next arrange to choose certain linear combinations of the original functions which satisfy the conditions on $0\bar{1}1$ and 011, and then use these functions to satisfy the four conditions of 101 and $1\bar{1}0$. To do this, it is best to classify the functions into type (1), even in

$$\begin{aligned} z &\rightarrow -y \\ y &\rightarrow -z \end{aligned}$$

and (2), odd for the same transformation. These are

$$g_1: \quad A\Sigma \quad B(2x^2 - y^2 - z^2)\Delta, \overset{Dyz\Delta}{\wedge}, \quad u_1: \quad E\, x\Pi$$

$$g_2: \quad F\, x(y + z)\Delta \quad , \quad u_2: \quad G(y+z)\Pi \;, H\left[y(x^2-z^2)+3(x^2-y^2\right]\phi$$

The conditions on $0\bar{1}1$ give $\dot{g}_1 = 0$,

$$A\sigma - 2B\delta - D\delta = 0 \quad .$$

The conditions on 011 give $g_1 = 0$,

$$A - 2B + D = 0 \quad .$$

Solving for B and D , we find that the linear combination of the terms of g_1 which satisfy $0\bar{1}1$ and 011 is

$$g_1\left\{\sum + \frac{1}{4}\left[\left(\frac{\sigma}{\delta} + 1\right)(2x^2 - y^2 - z^2) + \frac{1}{2}\left(\frac{\sigma}{\delta} - 1\right)yz\right]\Delta\right\}\frac{4}{\left(5 + \frac{\sigma}{\delta}\right)} \quad .$$

This function takes on the same value (arranged to be unity) on both 101 and $1\bar{1}0$ (it must, since it is of type 1). Its normal derivative on these faces is

$$(5\sigma + \delta)/(5 + \sigma/\delta) = \gamma \quad .$$

A similar process can be carried out for the u_2 type. The 011 condition then requires that

$$G\varkappa + H\varphi = 0 \qquad \text{or} \qquad H = -\frac{\varkappa}{\varphi}\,G \quad .$$

The linear combination

$$u_2 = \left\{(y + z)\Pi - \frac{\varkappa}{\varphi}\left[y(x^2 - z^2) + z(x^2 - y^2)\right]\Phi\right\}/(1 + \varkappa/\varphi)$$

has the value 1 and the derivative

$2\varkappa/(1 + \varkappa/\varphi) = \mu$ on 101, and minus these values on $1\bar{1}0$.

We can now replace the original 7 functions by the four functions

$$Ag_1 \;,\; Fx(y + z)\Delta \;,\; Ex\,\Pi \;,\; Gu_2 \quad .$$

These functions satisfy all the conditions on faces $0\bar{1}1$ and 011; the E and F terms, because they vanish there; the g_1 and u_2 terms, because we have so chosen them.

The conditions on the other faces are

(101)

$$-(-C)\left[A + F\right] + E + G = 0$$

$$A\gamma + F\delta + (-C)\left[E\varkappa + G\mu\right] = 0$$

($1\bar{1}0$)

$$-T\left[A - F\right] + E - G = 0$$

$$A\gamma - F\delta + T\left[E\varkappa - G\mu\right] = 0$$

or

$$\begin{vmatrix} C & C & 1 & 1 \\ \gamma & \delta & -C\kappa & -C\mu \\ -T & T & 1 & -1 \\ \gamma & -\delta & T\kappa & -T\mu \end{vmatrix} = 0$$

Expanding in two rowed minors of the first two columns, we easily get

$$\text{IIa} \qquad (C^2 + T^2)(\gamma + \delta)(\kappa + \mu) + 2(\delta - \gamma)(\mu - \kappa) + 4\kappa\mu + 4\gamma\delta = 0$$

Remembering that $C^2T^2 = 1$, we can solve for T^2

$$T^2 = a \pm \sqrt{a^2 - 1} \quad , \quad \text{where} \quad a = \frac{(\gamma - \delta)(\kappa - \mu) - 2(\kappa\mu + \gamma\delta)}{(\gamma + \delta)(\kappa + \mu)}$$

Another solution along line II can be obtained from $01\overline{1}o$, the odd solution in $01\overline{1}$, by replacing T^2_{110} by C^2 and $T^2_{10\overline{1}}$ by T^2. This is not particularly useful, since the odd set can be plotted for arbitrary k. It gives rise to an expression of the form

$$\text{IIb} \qquad a(C^2 + T^2) + b = 0 \quad .$$

The symmetry in C^2 and T^2 shows that an increase of $\frac{\pi}{2}$ in the phase will give another solution. Since the phase is $\frac{\pi}{2} w = \frac{\pi}{2}(u - 1/2)$, this means an increase of 1 in u. From Figure 7b, this is seen to be just the correct periodicity. A change of +u to -u is equivalent to interchanging C and T, and leaves the equation satisfied. A

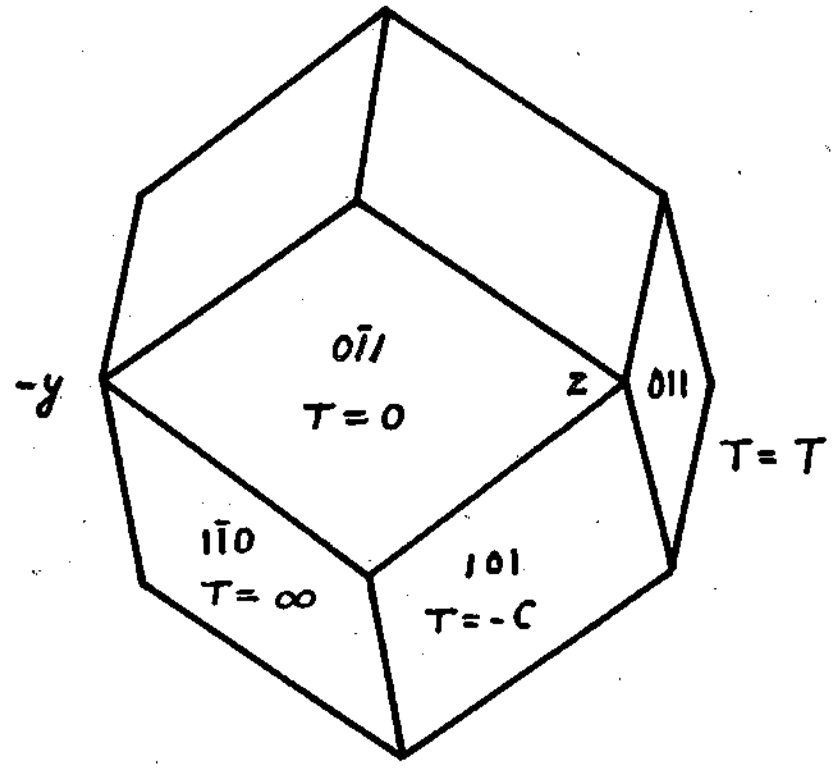


fig 7j

further check of the solution can be obtained by comparing the condition given by $u = 0$, $C^2 = T^2 = 1$ with that obtained from the solution worked out for the 011 line at the same point. The details of this check will not be given here. However, a similar check is worked out as an example on page 71.

8. The Line III. $k = (v - 1)(100) + v(011)$

This line is equivalent to

$$k = (1 - v)(100) + v(011)$$

This line, like line II, has a relatively simple set of tangent factors. They are:

$$T_{101} = \tan\frac{\pi}{2}(v - 1 + v) = -\cot\pi v = -C$$

$$T_{011} = \tan\frac{\pi}{2}(2v) = \tan\pi v \quad = \quad T$$

$$T_{1\bar{1}0} = \tan\frac{\pi}{2}(v - 1 - v) \quad = \quad \infty$$

$$T_{0\bar{1}1} = \quad 0$$

The conditions on $0\bar{1}1$ give $\dot{g} = 0$ and $u = 0$; on $01\bar{1}$ $g = 0$ and $\dot{u} = 0$. Of these, the condition $u = 0$ on $0\bar{1}1$ is automatically satisfied for even functions of the $0\bar{1}1$ plane. We shall proceed as for line II. Linear combinations of g and u functions will be found which satisfy the conditions on faces $0\bar{1}1$ and $1\bar{1}0$. These will then be used to give a fourth order determinant for the conditions on 011 and 101.

The even functions of this plane are:

$$A\Sigma\ ,\ B\left[2x^2 - y^2 - z^2 - 2yz + x(y + z)\right]\Delta\ ,\ Dyz\Delta,\ Ex(y + z)\Delta$$

$$Fx\Pi\ ,\ G\,\tfrac{1}{2}(x + y + z)\Pi\ ,\ H\left[y(z^2 - x^2) + z(y^2 - x^2)\right]\Phi \quad .$$

Here certain linear combinations of the Δ and Π functions have already been made, in order to simplify the later expressions. The condition on the g functions give

$$\begin{array}{lll} (0\bar{1}1) & A\sigma - D\delta = 0 & \text{or} \quad D = \frac{\sigma}{\delta}A \\ (1\bar{1}0) & A - E = 0 & \qquad\quad E = A \quad . \end{array}$$

Hence, eliminating D and E , we find that there are two linearly independent g functions satisfying the conditions on $0\bar{1}1$ and $1\bar{1}0$. These are the B function and

$$A\left\{\Sigma + \left[\frac{\sigma}{\delta}\,yz + x(y + z)\right]\Delta\right\} \quad .$$

The condition of $1\bar{1}0$ on the u functions gives

$$F\varkappa + H\varphi = 0 \qquad \text{or} \qquad H = -\,\varkappa/\varphi\,F \ .$$

Hence, the u functions to use are the G function and

$$F\left\{x\Pi + \frac{\varkappa}{\varphi}\left[y(x^2 - z^2) + z(x^2 - y^2)\right]\Phi\right\} \quad .$$

The conditions the other faces are then

(011)

$$-T\Big[(1+\frac{\sigma}{\delta})A - 4B\Big] - 2\,\varkappa/\varphi\, F + G = 0$$

$$2\sigma A - 4\delta B + T\big[-2\varkappa F + \varkappa G\big] = 0$$

(101)

$$C\big[2A + 2B\big] + (1+\frac{\varkappa}{\varphi})F + G = 0$$

$$(\sigma+\delta)A + 2\delta B - C\big[2\varkappa F + \varkappa G\big] = 0$$

The determinant of the coefficients of $A\ B\ F\ G$ is easily set up and, by expansion in the customary manner, gives

$$\text{IIIa} \qquad T^2\Big[\frac{3}{4}(\sigma+\delta)(\varkappa+3\varphi) + (\delta-\sigma)(\varphi-\varkappa) + \frac{1}{2}\delta(\delta+2\sigma)(\frac{\varphi}{\varkappa}+3)$$

$$+ C^2(\sigma+2\delta)(\varphi+\varkappa) = T^2 a + b + cC^2$$

This leads to the quadratic in T^2

$$a(T^2)^2 + b(T^2) + c = 0.$$

Another solution is obtained from $0\bar{1}1o$, the odds of the $01\bar{1}$ plane, by replacing T^2_{101} by C^2 and $T^2_{1\bar{1}0}$ by ∞. This necessitates the vanishing of the factor involving T^2_{101}, thus leading to

$$\text{IIIb} \qquad C^2 = -\frac{\delta(\varkappa+3\varphi)}{2\varphi(\varkappa+\varphi)} .$$

If we regard this as an algebraic equation for $\varkappa$, we see that it is linear and has one root; this corresponds to the fact that there is only one π function in the $0\bar{1}1$ odd set. In φ it is quadratic, corresponding to the two φ functions. In δ it is linear; however, there are two δ functions in the set. This suggests that there is another solution similar to Id .

Such is, in fact, the case. The function

$$\left[(y^2 - z^2) + x(z - y)\right]\Delta$$

is zero on 101, 011, and $0\bar{1}1$. The conditions on $1\bar{1}0$ give

IIIc $\Delta = 0$ or $\delta = \infty$,

a zero width band.

These two new lines, II and III, give a considerable amount of information about the contours in the $0\bar{1}1$ plane, as may be seen from the contour maps in the set of diagrams.

9. Line IV. $k = u(01\bar{1}) + 1/2(111)$

It was found that a reduction of the twelfth order determinant into two sets could be made along the line $k = u(01\bar{1}) + 1/2(111)$. It is observed that the interchange of y and z changes k to $k' = -u(01\bar{1}) + 1/2(111) = -k + (111)$. Since 111 is a lattice point of the k lattice, the interchange of y and z reverses the momentum of the lattice function from k to $-k$. This suggests classifying our g and u functions into type 1, even for interchange of y and z; and 2, odd for interchange of y and z. If this is done, the cellular function for a solution of the boundary conditions may be written as

$$\psi = (g_1 + g_2) + i(u_1 + u_2) \quad .$$

Interchange of y and z will give ψ', a function with wave vector $-k$ as explained above,

$$\psi' = (g_1 - g_2) + i(u_1 - u_2) \quad .$$

The complex conjugate $\overline{\psi}'$ will again have momentum k. From ψ and $\overline{\psi}'$, we can get two functions

$$\psi + \overline{\psi}' = 2(g_1 + iu_2)$$
$$\psi - \overline{\psi}' = 2(g_2 + iu_1) \quad .$$

Hence, we need only consider combinations (g_1, u_2) and (g_2, u_1). All other lattice functions for line IV. will be merely combinations of these types.

This same conclusion can be reached by a consideration of the tangent factors. Figure 7k shows six independent faces.

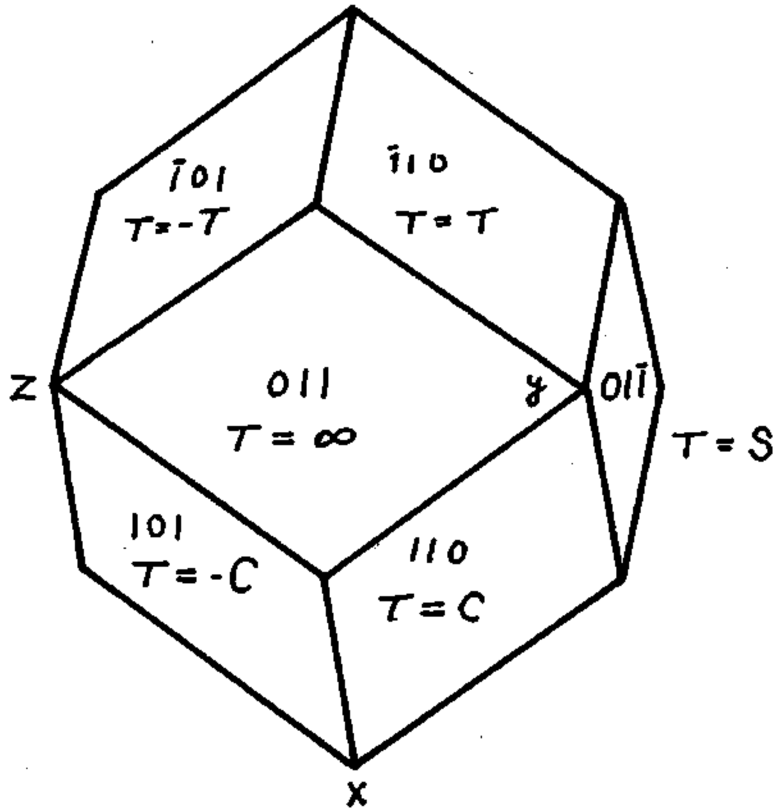


fig. 7 k

The tangent factors are:

$$T_{\bar{1}10} = \tan\tfrac{\pi}{2}(+u) \quad = +T$$

$$T_{\bar{1}01} = \tan\tfrac{\pi}{2}(-u) \quad = -T$$

$$T_{110} = \tan\tfrac{\pi}{2}(u+1) \quad = +C$$

$$T_{101} = \tan\tfrac{\pi}{2}(-u+1) = -C$$

$$T_{01\bar{1}} = \tan\tfrac{\pi}{2}(2u) \quad = \ S$$

$$T_{011} = \tan\tfrac{\pi}{2} \qquad = \ \infty$$

We next note that g_2 and u_1 must vanish u_1 must vanish on $01\bar{1}$. This follows from the conflicting symmetries of g and 2, and u and 1 on this face; thus $g_2(0\bar{1}1) = + g_2(01\bar{1})$ by g property and $= - g_2(01\bar{1})$ by 2 property; hence, $g_2(01\bar{1}) = 0$. The proof is similar for u_1. It is also evident that 2 type functions vanish on 011. Hence, there will be no mixing of (g_1,u_2) and (g_2,u_1) on 011 and $01\bar{1}$.

Suppose next that a combination of (g_1,u_2) satisfies the conditions on 110. Then on 101 the tangent factor changes sign, but so does u_2 so that the solution is good there also. A similar situation is true for $\bar{1}10$ and $\bar{1}01$. This argument can be repeated for the (g_2,u_1) set. Thus, from the tangent factors we again find that the solutions will be of the form (g_1,u_2) and (g_2,u_1).

The (g_1, u_2) set will not be worked out. It leads to a sixth order determinant which cannot be reduced further, since all of the symmetry conditions have already been used. If it were very desirable to have the solution, it could be obtained by a brute force expansion of the determinant. The functions of the set are:

$$g_1 \quad \Sigma \;, \; yz\Delta \;, \; x(y + z)\Delta \;, \quad (2x^2 - y^2 - z^2)\Delta$$

$$u_2 \quad (y - z)\Pi \;, \; x(y^2 - z^2)\Phi \;, \left[y(x^2 - z^2) - z(x^2 - y^2)\right]\Phi$$

There are 7 functions, and the number of conditions are: 2 on $01\bar{1}$, 1 on 011, 2 on 110, 2 on $\bar{1}10$; or, 7 in all. This indicates that a satisfactory solution exists.

The (g_2, u_1) functions may be handled satisfactorily. The functions are:

$$g_2 \qquad Ax(y - z)\Delta \;, \; B(y^2 - z^2)\Delta \quad ,$$

$$u_1 \quad F\,x\Pi \;, \; G(y + z)\Pi \;, \; H\left[y(x^2 - z^2) + z(x^2 - y^2)\right]\Phi \;.$$

We proceed as for lines II and III by satisfying the face not involving T, C, or S . On 011, the condition is $g = 0$ and $\dot{u} = 0$. The g condition follows, since we have g_2; the other gives

$$2\kappa G - 2\varphi H = 0 \quad , \qquad H = + \frac{\kappa}{\varphi} G \quad .$$

Hence, we shall use the two functions of g_2 , the F term,

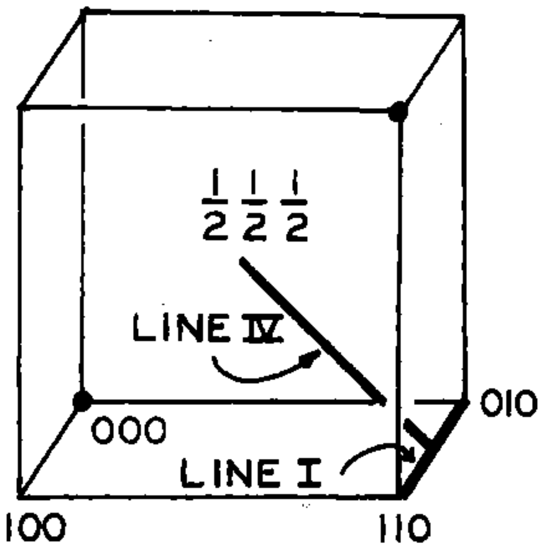


FIG. 71

and $G\left[(y + z)\Pi + \frac{\varkappa}{\varphi} \left\{ y(x^2 - z^2) + z(x^2 - y^2) \right\} \Phi \right]$

to satisfy the conditions on 110 and $1\bar{1}0$. This gives

(110)

$$-(-C)\left[A + B\right] + F + \left(1 + \frac{\varkappa}{\varphi}\right)G = 0$$

$$\delta A + \delta B - C\left[\varkappa F + 2\varkappa G\right] = 0$$

($1\bar{1}0$)

$$-T\left[- A + B\right] - F + \left(1 + \frac{\varkappa}{\varphi}\right)G = 0$$

$$\left[- \delta A + \delta B\right] + T\left[-\varkappa F + 2\varkappa G\right] = 0 \quad .$$

The determinant is set up and expanded as usual, giving

$$\text{IVa} \qquad (C^2 + T^2)\,\delta\varkappa\left(3 + \frac{\varkappa}{\varphi}\right) + 2\left[\delta^2\left(1 + \frac{\varkappa}{\varphi}\right) + 2\varkappa^2\right] = 0 \quad .$$

10. Checks on IV. and I.

This formula gives an interesting example of the type of check which can be obtained where various lines cross in k space.

Line IV intersects line I at the point $(\frac{1}{2}\ 1\ 0)$. At this point, $u = \frac{1}{2}$ for line IV and $u = \frac{1}{2}$ for line I. Hence, all C^2's and T^2's are unity for both lines at this point. This means that for a solution on line IV we must have

$$(\lambda) \quad 2(\delta\varkappa)(3 + \frac{\varkappa}{\varphi}) + 2\left[\delta^2(1 + \frac{\varkappa}{\varphi}) + 2\varkappa^2\right] = 0 \quad ,$$

and similar expressions hold for line I. If our solutions are correct, we should expect all the relationships which satisfy (λ) to satisfy certain of the four solutions of line I. By inspection of the functions of lines I and II, we see that the functions of line IV are contained among the sets of line I as follows:

Functions	Line I
$(y^2 - z^2)\Delta$, $x\Pi$	Ia
$x(y-z)\Delta$, $(y+z)\Pi$, $[y(x^2-z^2)+(x^2-y^2)z]\Phi$	combinations of Ib and Ic

Hence, we should expect (λ) to give two roots for δ , one of which satisfies Ia , and one of which satisfies Ib and Ic. Ib and Ic are degenerate at this point. The same statement should hold true for the $\varkappa$ roots. The one root for φ should satisfy Ib and Ic .

The roots of (λ) for δ , $\varkappa$ and φ, are:

$$\delta = -\varkappa \quad , \quad -2\varkappa/(1 + \frac{\varkappa}{\varphi})$$

$$\varkappa = -\delta \quad , \quad -\delta/(2 + \frac{\delta}{\varphi})$$

$$\varphi = -\frac{\varkappa\,\delta}{(2\varkappa + \delta)} \quad .$$

The conditions required by I are:

$$\text{Ia} \quad (2\delta + \sigma)(\varkappa + \varphi) + (\delta - \sigma)(\varphi - \varkappa) + \delta(\delta + 2\sigma) + 3\varkappa\varphi = 0$$

$$\text{Ib} \quad 1 + \frac{\delta}{2}(\frac{1}{\varkappa} + \frac{1}{\varphi}) = 0 \quad .$$

The first roots, $\varkappa = -\delta$, satisfy Ia . The second roots and the φ root -- all three are algebraically equivalent -- satisfy Ib . Thus, the check is satisfactory.

This type of check is very convincing, since all of the terms in equations Ia, Ib, and IVa are involved. The same situation does not occur with the line III, for example. Where line III crosses 100 and 111, some of the tangent factors become infinite leading to conditions of the form $\varkappa = 0$ or $\varkappa = \infty$. These usually involve only one or two terms of the expressions at one time, and an algebraic error of a numerical factor would not be detected. Such an error could not escape detection for the check given above.

VIII.

THE METHOD OF $k \rightarrow 0$

Although we must abandon hope of getting usable expressions for the twelfth order determinant for general points in k space, it is still possible to carry out calculations for a wide range of k directions, if k is small enough. This is true because it is possible to expand the determinantal equation in powers of k for small k.

In order to see how this is done, let us represent schematically the twelfth order determinant. There are 6 g functions and 6 u functions in all. The conditions on ψ for 6 independent faces of the duodechahedron give equations of the form

$$(8.1) \qquad -Tg + u = 0$$

and the ψ' conditions are

$$(8.2) \qquad g' + Tu' = 0 \quad .$$

We will denote the 6 even functions by A_1g_1, $A_2g_2 \cdots A_6g_6$, where the A's are the variable coefficients, and the six u's by $B_1u_1, \cdots, B_6u_6$.

It is also necessary to use an index for the face on which the g's and u's are evaluated. Thus, the ψ equation for the third face would be

$$(8.3)\quad -T_3(A_1g_{13} + A_2g_{23} + \cdots + A_6g_{63}) + B_1u_{13} + \cdots + B_6u_{63} = 0.$$

The twelfth order determinant would then be

$$(8.4)\quad \begin{vmatrix} -T_1g_{11} & -T_1g_{21} & \cdots & -T_1g_{61} & u_{11} & u_{21} & \cdots & u_{61} \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ -T_6g_{16} & -T_6g_{26} & \cdots & -T_6g_{66} & u_{16} & u_{26} & \cdots & u_{66} \\ g'_{11} & g'_{21} & \cdots & g'_{61} & T_1u'_{11} & T_1u'_{21} & \cdots & T_1u'_{61} \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ g'_{16} & g'_{26} & \cdots & g'_{66} & T_6u'_{16} & T_6u'_{26} & \cdots & T_6u'_{66} \end{vmatrix} = 0$$

If this is expanded in terms of six-rowed minors of the first six columns, there will be first of all a term independent of the T factors equal to the product of the u and g' minors. Then, if we omit one row of the g' minor and replace it by a Tg row, we will get a term of the form

$$T^2g^5u^5\,gu' \quad .$$

By omitting still more rows of g', we get terms of the form

$$T^4(g'u)^4(gu')^2 \quad , \quad T^6(g'u)^3(gu')^3 \cdots$$

$$T^{12}(gu')^6 \quad .$$

Thus, schematically we have

$$(8.5) \quad (g'u)^6 + T^2(g'u)^5(gu') + T^{4}{}'g'u)^4(gu')^2 + \cdots = 0 \quad .$$

It is seen now that if either the g' or u determinant vanishes, we have a solution for $T = 0$ or $k = 0$. The easiest way for g' to vanish it for one of the radial functions in the spherical functions g_i to have zero derivative. Then an entire column of the g' determinant will vanish.

Suppose that the radial function does not have zero slope but a very small slope, q say. Then we can consider powers of q in 8.5. The first term will be of the first power in q and all the others of q^0. This follows from the fact that if we replace a row of the g' determinant by a $-Tg$ row, the terms involving $-Tg$ in the first column will not have any first column g' as a factor.

Thus, T^2 will be of the same order as q and (8.5) can be represented by

$$(8.6) \qquad aq + bT^2 = 0$$

where higher orders of q are omitted. For small k, any T^2 is of the form $\frac{\kappa^2}{4}(k_x \pm k_y)^2$. Hence, (8.5) will be quadratic in the components of k. Since our problem has cubic symmetry, the only possible form is

$$(8.7) \qquad q+(b/a)(k_x^2 + k_y^2 + k_z^2) = 0 \quad .$$

For small values of q , q should be a linear function of the energy. Hence, the equal energy surfaces will be spheres and the energy a linear function of k^2 .

Now the process as outlined above is impractical, due to the great difficulty in obtaining the terms of (8.5). However, in order to evaluate the coefficient in (8.7), it is necessary to know the relationship of k and q for one pair of values only. This can be done from the solutions in any of the three directions 100, 111, or 011. If the energy curve is known in any one of these directions, the spherical surfaces can be drawn in momentum space.

So far in the discussion we have supposed that only one of the g' columns was small. This means that we have been dealing with s bands for $\sigma \cong 0$. For the d bands, the case is different, for 5 of the g' columns would vanish at once.

It is apparent from the form of the determinant that the arguments presented for the case of a $g' \cong 0$ can be repeated for the case of a $u \cong 0$. The u band in which we are interested arises from $\kappa = 0$ or $\kappa = \infty$. This causes three columns of the u determinant to vanish. Suppose now that $\pi = q$, a very small quantity. Then the u determinant is of the order q^3. The $T^2(g'u)^5gu'$ term involves q^2, since one of the rows in u' is replaced by a Tu row for these terms. Such a minor will give terms of the second and third order in q and only the lowest order need be considered. Similarly, the T^4 term will be of the first order in q and all the others will be of the zeroeth order. For this case, then, 8.5 is of the form

$$(8.8) \quad aq^3 + bq^2T^2 + cqT^4 + dT^6 + eT^8 + \cdots = 0 \quad .$$

This shows that T^2 is of the order of q and only the first four terms should be kept. To see what this implies, let us fix the direction of k and allow its magnitude, ℓ, alone to vary. (8.8) will then be of the form

$$(8.9) \quad aq^3 + bq^2(\ell^2) + cq(\ell^2)^2 + d(\ell^2)^3 = 0 \quad .$$

This is a cubic in (ℓ^2). Hence, for a given value of q there will, in general, be three distinct roots of ℓ^2 each linear in q . What this means in the case of the p bands is that there will be three surfaces in momentum space for each value of q . That is, the three p functions give rise to three bands.

From the two cases considered above we can conclude that whenever a g function has zero derivative in its radial function, or a u function zero value, we will get a set of solutions for $k = 0$. For energies slightly different from these, k will not be zero and we will get as many surfaces in k space as there are spherical functions for the given radial function.

Thus for the s band we get one surface for energies near to the energy for $\sigma \cong 0$. For the p functions we get 3 bands for $\pi \cong \infty$; for the d's, 5 for $\delta \cong 0$; for the f's, 3 for $\varphi \cong \infty$. Since only three of the seven possible f' functions are used, we should not place much reliance on these bands. As a matter of fact, even the 5 d's are not right. This is a consequence of the fact that a field of cubic symmetry, such as we have, will split the d functions into 2 sets; 3 of the form xy , and 2 of the form x^2-y^2 . *
The occurrence of five-fold degeneracy in our case for $k = 0$ is an indication of weakness in the boundary conditions.

The method of small k can be used quite conveniently for the even functions of the 001 and $01\bar{1}$ planes. It is not necessary to expand the determinant. The form of the polynomial is largely determined by symmetry conditions and the unknown coefficients can be evaluated from the known solutions

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*H. Bethe gives a discussion of "Term Separation in Crystals" in the Ann. d. Phys. 3.2, 133 (1929). His discussion is not for lattice functions but for perturbed atomic levels. However, for $\varkappa = 0$ his conclusions in regard to symmetry and degeneracy are valid for lattice functions.

in particular directions. To see how this is done, consider p bands in the 001 plane. Let $\frac{1}{\varkappa} = q$. If the energy be expressed as $\bar{\varepsilon} = \bar{\varepsilon}_0 + \Delta\bar{\varepsilon}$ where $\varkappa = \infty$ for $\bar{\varepsilon} = \bar{\varepsilon}_0$, then, for small $\Delta\bar{\varepsilon}$, q will be a linear function of the energy of the form $q = \alpha\Delta\bar{\varepsilon}$. Since there are two p functions in the even set, we expect to get a second order expression in q and fourth order in k_x and k_y. However, a large number of the possible terms in k_x and k_y are excluded by the symmetry. In the first place, the problem is symmetrical for $k_x \longrightarrow -k_x$, and hence no odd terms in k_x are present. Also, the expression must be symmetrical in k_x and k_y. The most general expression satisfying these requirements is

$$q^2 - a(k_x^2 + k_y^2)q + b(k_x^4 + k_y^4) + ck_x^2k_y^2 = 0 \quad .$$

For brevity, we introduce the notation $k_x^2 = x$, $k_y^2 = y$ and get

$$q^2 - A(x + y)q + B(x^2 + y^2) + Cxy = 0 \quad .$$

From solutions 100a and 100d, we see that

$$T_{110}^2 = -\frac{3\delta\sigma}{\varkappa(2\delta + \sigma)} \quad \text{or} \quad -\frac{2\delta}{\varkappa + \varphi} \quad .$$

For small k and q these give

$$\frac{\varkappa^2}{4}k_x^2 = \frac{\varkappa^2}{4}x = -\frac{3\delta\sigma}{(2\delta + \sigma)}q \quad \text{or} \quad -2\delta q \quad .$$

Since the quantity $\frac{4}{\kappa^2} q$ occurs continually in these expressions, we will denote it by t .

$$t = \frac{4}{\kappa^2} q = \frac{4}{\kappa^2} \alpha \Delta \bar{\varepsilon} \quad .$$

Hence, for k in the 100 direction,

$$(8.10) \qquad t = -\frac{2\delta + \sigma}{3\delta\sigma} x \qquad \text{or} \qquad -\frac{1}{2\delta} x \quad .$$

If we use the t notation, we have

$$(8.11) \qquad t^2 + a(x + y)t + b(x^2 + y^2) + cxy = 0$$

For the 100 direction $y = 0$ and

$$t^2 + axt + bx^2 = 0 \quad .$$

Since this must lead to the two roots above,

$$t^2 + atx + bx^2 = \left(t + \frac{2\delta + \sigma}{3\delta\sigma} x\right)\left(t + \frac{1}{2\delta} x\right)$$

$$= t^2 + \frac{1}{6\delta\sigma}(4\delta + 5\sigma)xt + \frac{2\delta + \sigma}{6\delta^2\sigma} x^2 = 0$$

or

$$(8.12) \qquad a = \frac{1}{6\delta\sigma}(4\delta + 5\sigma) \quad , \qquad b = \frac{2\delta + \sigma}{6\delta^2\sigma} \quad .$$

To evaluate the coefficient c we use the 110 solutions. These are 110a and 110b and they give

$$(8.13) \qquad t = -\frac{8\delta + 7\sigma}{6\delta\sigma} x \qquad \text{or} \qquad t = -\frac{1}{2\delta} x \quad .$$

For this direction (8.11) reduces to

$$t^2 + 2axt + (2b + c)x^2 = 0 \quad .$$

Equating this to the equation derived from (8.13) we have

$$(t + \frac{8\delta + 7\sigma}{6} x)(t + \frac{1}{2\delta} x)$$

$$= t^2 + \frac{1}{6\delta\sigma}(8\delta + 10\sigma)xt + \frac{8\delta + 7\sigma}{12\delta^2\sigma} x^2 = 0$$

or

$$a = \frac{1}{6\delta\sigma}(4\delta + 5\sigma) \quad , \qquad 2b + c = \frac{8\delta + 7\sigma}{12\delta^2\sigma} \quad .$$

The fact that the value of "a" comes out the same for both directions is a check on the correctness of our procedure. Solving for c, we get

$$c = \frac{4\delta + 3\sigma}{12\delta^2\sigma} \quad .$$

When the values of a, b, and c are known numerically, it is a straightforward problem to compute a series of values of x and y for a given energy and make a plot of the corresponding $k_x\, k_y$ contours. For $\bar{\varepsilon} = 0.30$, $\varkappa = \infty$ and $\alpha = 0.470$. The other numerical values needed are

σ	δ	a	b	c
0.151	0.274	7.46	10.3	3.33

From these, the contours for $\Delta\,\bar{\varepsilon} = -\,0.025$ are shown. (Plate 1.)

$0 1 \bar{1}$ Plane

As for the 100 plane, there are two p functions in the even set for this plane. We expect then to get a quadratic in t . In this plane $k = k_x(100) + u(011)$ and the symmetry requires that the quadratic be unchanged by $k_x \rightarrow -k_x$ and $u \rightarrow -u$. If we denote $k_x{}^2$ by x and u^2 by v , the allowed quadratic is

$$(8.14) \qquad t^2 + (ax + bv)t + (\alpha x^2 + \beta v^2 + \gamma xv) = 0 \quad .$$

For the 100 direction, v = 0 , the roots for t are found from 100a and 100d (as for the same line in the 001 plane). These give

$$t = -\frac{2\delta + \sigma}{3\delta\sigma}\, x \qquad \text{and} \quad -\frac{1}{2\delta}\, x$$

or

$$t = -r_1\, x \qquad \text{and} \quad -s_1 x \quad \text{for brevity.}$$

For the 011 line, x = 0 , we find

$$t = -\left(\frac{8\delta + 7\sigma}{6\delta\sigma}\right)v = -r_2 v \qquad \text{and} \quad -\frac{1}{\delta}v = -s_2 v \quad .$$

For the 111 direction, v = x, we find

$$t = -\frac{2(\sigma + \delta)}{\sigma\delta}\, x = -r_3 x \qquad \text{and} \quad -\frac{1}{\delta}\, x = -s_3 x \; .$$

We can determine the five constants of (8.14) from the six expressions given above. We find

$$100 \qquad a = r_1 + s_1 \quad , \qquad \alpha = r_1 s_1$$

$$011 \qquad b = r_2 + s_2 \quad , \qquad \beta = r_2 s_2$$

$$111 \qquad a + b = r_3 + s_3 \quad , \qquad \alpha + \beta + \gamma = r_3 s_3$$

Hence $\gamma = r_3 s_3 - r_1 s_1 - r_2 s_2$. The results can be checked from the a and b equations. We should have

$$r_3 + s_3 = r_1 + s_1 + r_2 + s_2 \quad .$$

This equation is readily found to be fulfilled. The numerical values necessary to compute the constants of (8.14) were given for the 001 plane.

The contour for $\Delta \bar{\varepsilon} = -0.025$ are shown in Plate 1.

The Odd Functions in 001 and 01$\bar{1}$

For the odd functions of the two planes considered above, we have exact solutions. We can readily get the approximation for $k \rightarrow 0$ by making approximations in the expressions. The expression 001o is

$$\left[T^2_{101} + \frac{1}{2}\delta\left(\frac{1}{\varkappa} + \frac{1}{\varphi}\right)\right] \cdot \left[T^2_{011} + \frac{1}{2}\delta\left(\frac{1}{\varkappa} + \frac{1}{\varphi}\right)\right] = \left[\frac{1}{2}\delta\left(\frac{1}{\varkappa} - \frac{1}{\varphi}\right)\right]^2 \quad .$$

For $k \rightarrow 0$ we have $T_{101}^2 = \frac{\pi^2}{4} k_x^2$, $T_{011}^2 = \frac{\pi^2}{4} k_y^2$, $\frac{1}{\pi} = q$ a small quantity. Making these substitutions we find (neglecting powers of higher than the first)

$$\frac{\pi^2}{4}(k_x^2 + k_y^2)(\frac{1}{2}\delta\frac{1}{\varphi}) + \frac{1}{4}\delta^2\frac{1}{\varphi^2} + \frac{1}{2}\delta^2\frac{1}{\varphi}q = \frac{1}{4}\delta^2\frac{1}{\varphi^2} - \frac{1}{2}\delta^2\frac{1}{\varphi}q$$

or

$$(8.15) \qquad \frac{4}{\pi^2} q + \frac{1}{2\delta}(k_x^2 + k_y^2) = t + \frac{1}{2\delta}(k_x^2 + k_y^2) = 0 \quad .$$

Hence, the contours are circles. These touch the even function contours at the 100 direction where $k_y^2 = 0$.

As a matter of fact, we could have drawn the contours without using 001o at all. Since we know that there is only one p function in the 001 plane, the expression for t must be linear in t and quadratic in k . From the symmetry it must be a circle. From the solutions along the 100 line we know that there is degeneracy in the p band between the odd and even functions for 100d. This would lead to the contour obtained above without calculation.

Applying the methods used above to the odds of the $01\bar{1}$ plane, we get

$$(8.16) \qquad t + \frac{1}{2\delta}(k_x^2 + u^2) = 0 \quad .$$

This is an ellipse, cutting the even function contours at

100 and 111, as is required by the degeneracy in the p bands.

The Contours

Plate 1 shows the contours drawn for the two planes. An extrapolation from them to arbitrary directions of k space are also shown. For a given energy, the allowed values of k fall on a surface having three sheets. One is nearly spherical, I. Another, II, has the same traces as a sphere in the coordinate planes, but is plucked out into a conical cusp which, with the cusp of III, forms a cone with the 111 line as axis.

The contour lines represent the intersection with the surface of 111 planes and a set of six planes passing through the 111 line and set 30° apart.

A Remark concerning Arbitrary Directions

It should be possible to calculate the contours for arbitrary directions of small k by extending the above process. For arbitrary directions, the expression will be cubic in t and sixth order in k . The expression will be of the form

$$(8.17) \qquad t^2 + At^2 + Bt + C = 0 \quad .$$

A, B, and C are polynomials of the second, fourth, an sixth degrees in k . Due to the cubic symmetry, these must be of a particular form. The most general forms are easily seen to be

$$A = a(k_x^2 + k_y^2 + k_z^2)$$

$$B = b(k_x^4+k_y^4+k_z^4) + \beta\,(k_x^2k_y^2 + k_y^2k_z^2 + k_z^2k_x^2)$$

$$C = c(k_x^6+k_y^6+k_z^6) + \gamma\Big[k_x^4(k_x^2+k_y^2) + k_y^4(k_z^2+k_x^2) + k_z^4(k_x^2+k_y^2)\Big] + d(k_x^2k_y^2k_z^2) \quad .$$

There are just six constants here and there are nine known solutions for the three directions 100, 011, and 111. From these, it should be possible to determine the values of the constants and have three extra conditions available for a check. The solutions for k would be carried out by choosing the direction of k and solving equation (8.17) which would then be a cubic in $|k|^2$.

IX.

METHODS OF CONSTRUCTING CONTOURS FOR THE FACE-CENTERED LATTICE

So far we have discussed lines and planes in momentum space. What we ultimately desire is the relationship of energy to momentum for all values of momentum. Due to the cubic symmetry in momentum space, all representative momenta are contained in a segment being one forty-eighth of the first Brillouin zone. There seems at present no method of obtaining solutions at interior points of the segment. However, we can extrapolate with some confidence to interior points from our information on the surface.

The Plate 7 shows a portion of the body-centered k lattice and the fundamental segment. The latter is outlined with the heavy solid and dotted lines. It is bounded by 100 and 110 planes and a plane bisecting the line between nearest lattice points. Our first problem will then be to calculate the conditions on the boundary surfaces.

001 Plane

Odd Set

The Slater conditions give the expression

$$\left[T_{101}^2 + \tfrac{1}{2}\delta\left(\tfrac{1}{\varkappa} + \tfrac{1}{\varphi}\right)\right] \cdot \left[T_{011}^2 + \tfrac{1}{2}\delta\left(\tfrac{1}{\varkappa} + \tfrac{1}{\psi}\right)\right] = \left[\tfrac{1}{2}\delta\left(\tfrac{1}{\varkappa} - \tfrac{1}{\varphi}\right)\right]^2$$

for the odd functions in the 001 plane. For a given value of the energy, the coefficients involving , $\varkappa$, and φ are fixed. It is then possible to compute the allowed values of T_{101} and T_{011} and the corresponding values of k_x and k_y, thus getting a curve in the k_xk_y plane. Values of σ, $\varkappa$, δ, and φ used for these calculations are given in Table III. The corresponding contours in k space are shown in Plate 4.

Even Set

For these we have the solutions for small k and the lines 100, 110, and I. The results of the calculations for these are shown in Plates 1, 2 and 3.

Correlations

As we have seen from general considerations, there are three p bands. That is, for a given energy there will in general be three surfaces in k space for which solutions of the Slater conditions can be obtained. From the information at small k we can give these surfaces numbers as shown in Plate 1. For certain energies, one of these surfaces gives the traces in the 001 plane shown in Plate 5 odd set. We do not know the traces of the other two but only their intercepts along the lines of Plates 2 and 3. However, we know from symmetry conditions that the traces must be perpendicular to these lines in the 001 plane. We also know how these traces behave for small k . Using this information for a start, we can follow the intercepts along in the plane and sketch in the curves shown in Plate 5, even set.

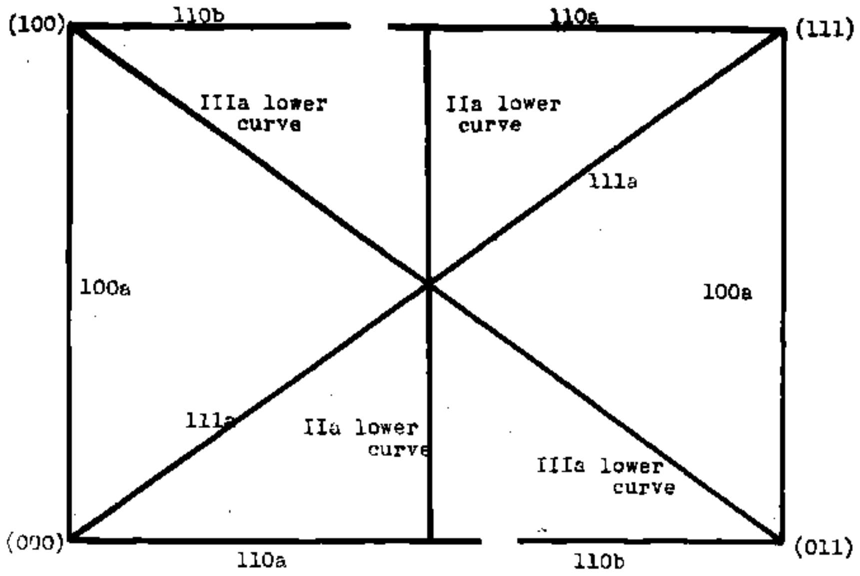
It is to be noted that along the dotted lines in Plate 5 the energies are the same. This fact is important in the later work.

$01\bar{1}$ Plane

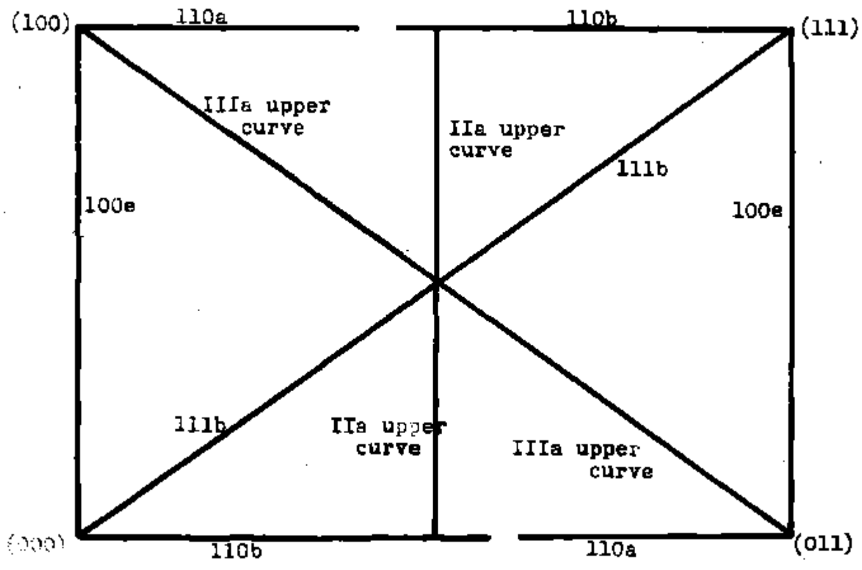
The odd functions can again be handled separately and give the contours shown in Plate 6 for the $01\bar{1}$ plane.

For the even functions, the situation is somewhat more complicated than in 001. The intercepts for the even functions are known for the solutions 110a, 110b, Plate 2; 111a, 111b, Plate 3; IIa and IIIa, Plate 4.

We note that among all the even solutions there is only one crossover of the energy contours. This is at the point where 110a and 110b cross. In order to have the contours move continuously with changes in energy, it is necessary to use a mixture of 110a and 110b. This can



(100)
110b
110a
(111)
IIIa lower curve
IIa lower curve
111a
100a
100a
111a
IIa lower curve
IIIa lower curve
(000)
110a
110b
(011)



(100)
110a
110b
(111)
IIIa upper curve
IIa upper curve
111b
100e
100e
111b
IIa upper curve
IIIa upper curve
(000)
110b
110a
(011)

be done in only one way, as shown in the adjacent figure. The contours drawn from these values are shown on Plate 6.

The 111 Plane

The 111 line normal to this plane at $\frac{1}{2}(111)$ is a 30° rotation reflection axis. (Plate 7.) That is, rotation through 30° about the 111 line and reflection in the plane brings the lattice back to coincidence with itself. Since the reflection does not alter the contours in the plane, these contours must have sixfold symmetry. The further symmetry introduced by the reflection planes 110 and 100 of the lattice show that the contours must have the symmetry of a regular hexagon. The elementary region of this hexagon is a 60 - 30 triangle of which the hypotenuse is the line IV. The other two sides lie in $01\bar{1}$ and 001 planes and the connection between energy and momentum along them can be interpolated from contours in those planes. The symmetry of the regular hexagon requires that the contours be perpendicular to the hypotenuse and the longer side of the 60 - 30 triangle. These conditions should be sufficient to enable fairly accurate contours to be drawn on this face.

The calculations outlined above have not been carried out in this work. The line IV was developed after the space contours were already drawn and it did not appear worth while to try to make them more accurate. The above discussion is given in the interests of completeness in regard to solutions for the face-centered lattice.

Space Correlations

From the definitions for small k , we see that surface I is the innermost surface in k space for a given energy. This can be restated by saying that for a given k , surface I has the lowest energy. Surfaces II and III have the next lowest and highest energies respectively. (It is noticeable in Plates 2, 3 and 4 that the trend is for $\bar{\varepsilon}$ to decrease as $|k|$ increases) Utilizing this definition, we see that the traces of I and II are mixed between odd and even sets of Plate 5, the traces of surface I being obtained from the lower energy regions of the two sets, II from the higher energy regions.

A similar situation is true for surfaces II and III in the $01\bar{1}$ plane. It is difficult to estimate the lines of degeneracy on these, but the location is indicated approximately and the choice of which contour belongs to each set is shown.

When the contours are known in the boundary planes of the fundamental segment, Plate 7 , the surface in k space can be drawn. Since the 100 and 110 planes are reflection planes of the lattice the equal energy surfaces must be normal to them. This puts fairly stringent conditions on the behavior of the surface near the edges of the cell.

On Plate 7 is another view of the k space. The fundamental segment is indicated in heavy lines. Solid lines are those for which solutions are known. The other figures of Plates 7 and 8 show the surfaces as drawn for the same view. To aid visualization, they have been continued by repetition of the fundamental segment twenty four times.

X.

Na-Cl CUBE-CUBE JOINING

As was discussed in Section IV, the simplest way of setting up boundary conditions which involve both Na and Cl functions is to disregard the Cl-Cl midpoints and retain only the Na-Cl midpoints. If the wave function around the Cl is $g + iu$ and $g_1 + iu_1$ around the Na, then the boundary conditions for the 100 midpoint are

$$g + iu = e^{i\mathcal{K}\cdot R_{100}}\left[g_1 - iu_1\right]$$
$$g' + iu' = e^{i\mathcal{K}\cdot R_{100}}\left[-g_1' + iu_1'\right] \quad .$$

$$\mathcal{K}\cdot R_{100} = (2\pi/a)k_x(a/2) = \pi k_x \quad .$$

The wave functions which we shall use are

Cl $\quad \Sigma\ ,\ (x^2 - y^2)\Delta\ ,\ (y^2 - z^2)\Delta\ ,\ x\Pi\ ,\ y\Pi\ ,\ z\Pi$

Na $\quad S,\ (x^2 - y^2)D\ ,\ (y^2 - z^2)D\ ,\ xP\ ,\ yP\ ,\ zP\ .$

Since the surface harmonics are evaluated at the same radius in every case, we are justified in leaving out the factor $r^{-\ell}$. We shall assume that $\Sigma = \Pi = \Delta = S = P = D = 1$ at the midpoints, and that the derivatives are σ, π, δ, s, p, and d respectively. (It must be noted that the values of σ, π, δ used in this section are evaluated at the Na-Cl radius, rather than at the Cl-Cl radius.)

The methods employed in obtaining solutions for these boundary conditions are the same as for the Cl-Cl type. We choose such values for k that the functions can be split into smaller sets in accordance with their symmetry types.

001 Plane

For this plane we can split our functions into even and odd for $z \longrightarrow -z$.

Odd Set of 001 Plane

There is only one odd function from each atom, the entire odd set being

$$C\,z\,\pi \quad , \qquad N\,z\,P \quad .$$

These functions vanish for the 100 and 010 directions and, hence, the boundary conditions on those faces are satisfied trivially. For the 001 face, $\boldsymbol{\kappa} \cdot R_{001} = 0$ and we have

$$i\,C = -\,i\,N$$

$$i\,C\pi = i\,Np$$

and the determinantal equation is

$$\pi + p = 0 \quad .$$

When the energy is correct to satisfy this equation, there will be a solution for all values of k in the 001 plane. This is a rather aggravated form of zero width band and indicates that the boundary conditions are none too satisfactory.

It is worth while showing, however, that this condition gives roughly the correct energy for the case of large separation where the band is very narrow anyway. At large radii, the eigenfunctions for any given atomic level are exponentially decaying functions of the radius. For these, it is clear that $d\psi(r)/dr$ (= κ for our Cl functions) will be negative. If the energy is shifted slightly from the eigenwert, then the function becomes a mixture of positive and negative exponentials, and, since the positive will usually dominate, κ will be positive. In the immediate neighborhood of the eigenwert, however, κ will run through all negative values from 0 to $-\infty$. The range of energy values for which κ is negative form a "p band." For large separation, then, these bands are very narrow, and, since $\kappa + p = 0$ can be satisfied only for $\kappa = -p$, the energy must be in either the Cl or the Na p band.

It was a line of reasoning similar to this which led us to conclude that even for the Cl-Cl joining conditions the zero width Na bands would be approximately correct for large separation or X-ray levels. (Section IV.)

Even Set of 001 Plane

The remaining ten of the twelve functions are even in the 001 plane. It is obviously not worth while to attempt to get a general solution for the plane. Consequently, we shall consider only special directions.

100 Direction

For $k = (k, 0, 0)$ we can classify our functions according to their evenness or oddness in y. This gives two sets:

Odd in y: Cl, $y\Pi$; Na, yP

Even in y: the remaining eight functions.

The odd in y set is formally identical with the odd in z set. It gives $\varkappa + \varphi = 0$ as the condition for a zero width band in the 100 direction.

The even function set satisfies eight conditions: four on the 010 face (equivalent to 001 for this symmetry) which do not involve k, and four on the 100 face with do. It is possible to eliminate four of the coefficients by using the 010 face and set up and expand the resulting fourth order determinant for the 100 face. The resulting expression is very involved and complicated. In view of the unsatisfactory behavior of the zero width bands, the effort necessary in order to calculate the eighth order band did not seem worth while.

110 Direction

The odd in z set has already been worked out for all directions in the 001 plane. The even functions may be split into two sets, according to their symmetry for interchange of x and y .

The odd set for interchange of x and y is

$$\begin{array}{lll} \mathrm{Cl} & \alpha(x^2 - y^2)\Delta & , \quad \beta(x - y)\Pi \\ \mathrm{Na} & A(x^2 - y^2)D & , \quad B(x - y)P \quad . \end{array}$$

These functions vanish on the 001 face and satisfy the boundary conditions there trivially. Due to the symmetry, we need consider only one of the 100 or 010 faces. For the 100 face,

$$e^{i\kappa \cdot R_{100}} = \cos \pi k_x + i \sin \pi k_x = c + i s \quad .$$

The boundary conditions then give

$$\alpha + i\beta = (c + is)(A - iB)$$

$$\alpha\delta + i\beta\pi = (c + is)(-Ad + iBp)$$

or

$$\alpha = cA + sB$$

$$\beta = sA - cB$$

$$\alpha\delta = -cdA - \quad B$$

$$\beta\varkappa = -sdA + cpB \quad .$$

The resultant determinant is

$$\begin{vmatrix} 1 & 0 & -c & -s \\ 0 & 1 & -s & c \\ \delta & 0 & cd & sp \\ 0 & \varkappa & sd & -cp \end{vmatrix}$$

When this is expanded, we get

$$s^2(\varkappa p + \delta d) + c^2(d\varkappa = p\delta) + dp + \varkappa\delta = 0 \ .$$

This expression can be written in other forms by making use of the relation $s^2 + c^2 = 1$. The one used for calculation was

$$\sin^2\varkappa k_x = -\frac{(p + \varkappa)(d + \delta)}{(p - d)(\varkappa - \delta)} \quad .$$

It was found upon calculation that the right-hand side was practically a linear function of the energy when its value lay between 0 and +1 . Hence, the energy was a cosine function of k_x .

The even functions for the x-y interchange must satisfy six conditions. As for the even functions of the

100 line, the labor necessary to obtain a solution did not appear to be justified by the accuracy of the cube-cube approximation.

$01\bar{1}$ Plane

For this plane, the separation into odd and even function for y and z interchange can be made. The odd set is

$$\begin{array}{lll} \text{Cl} & \alpha(y^2 - z^2)\Delta \quad , & \beta(y - z)\Pi \\ \text{Na} & A(y^2 - z^2)D \quad , & B(y - z)P \quad . \end{array}$$

These functions take on zero value on the 100 face. The 010 and 001 faces are equivalent, and for either we will plainly get the same conditions as we found for the 110 line in the 001 plane. If we express k as (k_x, u, u), we will get the condition

$$\sin^2 \varkappa u = - \frac{(p + \varkappa)(d + \delta)}{(p - d)(\varkappa - \delta)}$$

for the existence of a solution for the odd set. We see that there is no relation between energy and momentum in the 100 direction.

The Even Functions of the $01\bar{1}$ Plane

It is too difficult to attempt a general solution for these. Of the three simple lines in the $01\bar{1}$ plane, the 100 and 011 types have already been treated. Only the 111 line remains.

111 Line

The 111 line $k = u\ u\ u$ is a three-fold axis in k space, and has a symmetry group isomorphic with the permutation group for three objects. This group has two one-dimensional representations and one two-dimensional representation. For the trivial one-dimensional representation, the function will be

Cl $\quad \alpha\Sigma, \beta(x + y + z)\Pi$

Na $\quad AS, B(x + y + z)P$.

The odd functions of the $01\bar{1}$ plane clearly do not form a one-dimensional representation (rotation through 120° certainly gives a linearly independent set of functions). Hence, the remaining four functions

Cl $\quad (2x^2 - y^2 - z^2)\Delta, \quad (2x - y - z)\Pi$

Na $\quad (2x^2 - y^2 - z^2)D, \quad (2x - y - z)P$

must also belong to the two-dimensional representation, and the condition along this line must be given by

$$\sin^2 \varkappa u = - \frac{(p + \varkappa)(d + \delta)}{(p - d)(\varkappa - \delta)}$$

We can get the condition for the one-dimensional representation without calculation from the above expression. Since only one interface need be considered for the 111 direction, the only difference between the conditions arising from the two- and one-dimensional representations will be that the d functions are replaced by s functions. Hence, the result will be

$$\sin^2 \varkappa u = - \frac{(p + \varkappa)(s + \sigma)}{(p - s)(\varkappa - \sigma)} .$$

Concerning the Energy Parameters

In making calculations with the above formuli, it is necessary to use the same energy for the wave functions of both atoms. The wave functions themselves are solutions of the wave equation in the field of a Cl neutral atom (ion less a hole of one electron) and a Na^+ ion. Let the positive energy parameters of these solutions be $\overline{\varepsilon_c}$ (denoted by $\overline{\varepsilon}$ in the work with Cl-Cl) and $\overline{\varepsilon_n}$, respectively. If the Madelung potential is 0.66, then the energy in the lattice will be

$$\overline{\varepsilon_\ell} = \overline{\varepsilon_c} - 0.66 = \overline{\varepsilon_n} + 0.66 .$$

Due, however, to the hole on the Cl, which should follow the electron around even when it goes onto the Na, there should be a lowering of the Na potential. If we suppose that this hole distributes itself so as to leave, on the average, a defect of one-sixth electron on each of the six surrounding Cl's, then the decrease in Na potential will be $2/5.30 = 0.38$. This gives the relation $\overline{\varepsilon}_{\ell} = \overline{\varepsilon}_n + 0.28$. The theory of this type of hole is not well-founded, and it is interesting to see what effect will be produced by a change in assumptions regarding it. The calculations were such that the relationship $\overline{\varepsilon}_{\ell} = \overline{\varepsilon}_n + 0.58$, corresponding to a hole potential of only 0.08, could easily be investigated. For the Cl^- 3p band, this change did not make much difference; the band shifted by only about +0.06 for this shift of +0.30 in the Na potential. The reason for this smaller shift is that Cl atomic bands are not widened as much as the Na bands of approximately the same eigenwert. Also, the energies in question actually lie within the Cl band and outside of the Na bands. Both of these circumstances tend to make $\varkappa$ a much more sensitive function of $\overline{\varepsilon}_{\ell}$ than s, p or d . Hence, a fairly large shift in the Na potential can be compensated by a much smaller one in $\overline{\varepsilon}_{\ell}$.

Summary

The cube-cube joining conditions are, on the whole, unsatisfactory. They give rise to absurdly simple conditions, or else rather complicated ones. So far as giving sensible results for the Cl^- 3p band, they are considerably inferior to the Cl-Cl joining, when compared with the double joining conditions discussed in the next section. The results of calculations for the cube-cube formuli are shown on Plate 9. They will be discussed in comparison with the other methods in Section XII.

XI.

Cl-Cl-Na JOINING

The two types of joining conditions discussed in the preceding sections are not satisfactory on the basis of their own merits. The Cl-Cl case does not make sufficient allowance for the Na functions and the Na-Cl is too prolific of zero width bands. A better method is to use both sets of boundary conditions simultaneously. This leads to twenty-four boundary conditions and, consequently, it is not feasible to get solutions over as wide a range in k space as for either of the two cases. In spite of this, however, we can get enough solutions for this case to allow a comparison to be made between it and the other two.

k = 0

For $\varkappa = 0$ the lattice function is periodic. Since the factor $e^{i\varkappa \cdot R} = 1$, a worthy function will consist entirely of even or odd parts. Since we are dealing with p functions, we are interested in the odd type. There are three equivalent Cl p functions:

$$(x/r)\,\Pi \;,\quad (y/r)\,\Pi \;,\quad (z/r)\,\Pi \;.$$

These belong to a certain symmetry type as regards cubic crystals (they form a basis for the representation $_{4}$

of the octahedral group). The next functions of the same type are

$$(x^3 - \tfrac{3}{5}xr^2)/r^3\,\Phi\ , \quad (y^3 - \tfrac{3}{5}yr^2)/r^3\,\Phi\ , \quad (z^3 - \tfrac{3}{5}zr^2)/r^3\,\Phi\ .$$

If we consider the x type of function, we see that it takes the same value on the 110, 101, $1\bar{1}0$, and $10\bar{1}$ faces and vanishes on the 011 and $01\bar{1}$ Cl-Cl interfaces and on the 010 and 001 Na-Cl interfaces. Hence, we shall use functions around the Na which vanish on 010 and 001. This leads to the same type of symmetry around both Na and Cl atoms. (This result can be proved more generally by group thoery.)

For this type of symmetry, there are only three boundary conditions: two across the Na-Cl 100 face and one across the 110 type of Cl-Cl face. The condition on ψ' is automatically satisfied on the latter, since

$$g' + Tu' = 0 + 0\,u' = 0 \qquad .$$

There are four ways of choosing the functions: 3 around Cl, 0 around Na; 2 - 1; 1 - 2; 0 - 3. Of these, 3 - 0 and 0 - 3 can be disregarded. 1 - 2 is analogous to the Cl-Cl case, the energy is fixed by the Cl-Cl boundary condition alone and the Na functions are merely buffers. 2 - 1 contains the properties which we seek, and makes the solution depend on both atoms.

In carrying out the calculations, we shall assume that the Cl radial functions are unity at the Cl-Cl midpoint and have derivative $\varkappa$ and φ. At the Na-Cl midpoint, their values will be $\varkappa_c$ and φ_c and their derivatives $\dot{\varkappa}_c$ and $\dot{\varphi}_c$. The Na functions will be unity at the Na-Cl midpoint and have derivatives s, p, d, f, etc.

In carrying out the solutions, it is most convenient to satisfy the Cl-Cl conditions, thus eliminating one constant, and then use the resultant function to satisfy the Na-Cl conditions. Let the functions be

Cl $\quad A\sqrt{2}\,(\frac{x}{r})\,\Pi\ ,\quad B\,5\,\sqrt{8}\,(x^3 - \frac{3}{5}\,x\,r^2)/r^3\ \Phi$

Na $\quad C(\frac{x}{r})\,P$

110 gives

$$A - B = 0 \qquad \text{or} \qquad B = A \quad .$$

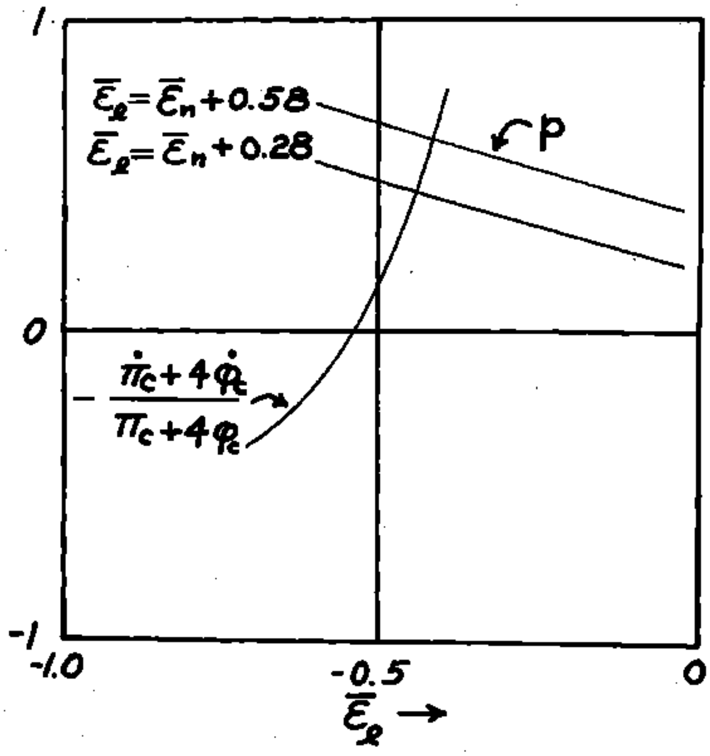
100 then gives for the conditions

$$g + iu = 1(g_1 - iu_1) \quad \text{and} \quad g' + iu' = 1(-g_1' + iu_1')$$

the equations

$$A\sqrt{2}\,\varkappa_c + A4\sqrt{2}\,\varphi_c = -\,C$$

$$A\sqrt{2}\,\dot{\varkappa}_c + A4\sqrt{2}\,\dot{\varphi}_c = Cp \quad .$$


1
$\bar{\varepsilon}_\ell = \bar{\varepsilon}_n + 0.58$
$\bar{\varepsilon}_\ell = \bar{\varepsilon}_n + 0.28$
P
0
$-\frac{\dot{\pi}_c + 4\dot{\varphi}_c}{\pi_c + 4\varphi_c}$
-1
-1.0
-0.5
0
$\bar{\varepsilon}_\ell \rightarrow$

This gives the condition

$$p = - \frac{\dot{\kappa}_c + 4\dot{\varphi}_c}{\kappa_c + 4\varphi_c} \quad .$$

When the right and left sides of this equation are plotted as functions of $\overline{\varepsilon_\ell}$ (see end of last section for a discussion of $\overline{\varepsilon_\ell}$ in relation to the $\overline{\varepsilon}$'s of the atoms), it is found that the right side is very much more sensitive as a function of $\overline{\varepsilon_\ell}$ than the left. This means that a variation in the assumption about the potential of the electron on the Na atom is even less important here than for the Na-Cl join.

$k = 100$

This point corresponds to half periodicity, that is the factor $e^{ik \cdot R} = \pm 1$, rather than just $+1$. Since this factor is real, we again use odd functions in both cells. If we use functions of the (x/r) symmetry type, the number of boundary conditions and the symmetry is just the same as for $k = 000$. The 110 face now gives no condition on ψ, but one on ψ' instead ($T_{110} = \tan\frac{\pi}{2}(k_x + k_y) = \infty$); hence,

$$A\kappa - B\varphi = 0 \quad , \qquad B = (\kappa/\varphi)A \quad .$$

The conditions on 100 are the same except for a factor -1.

$$A\sqrt{2}\,\pi_c + A4\sqrt{2}\,(\pi/\varphi)\varphi_c = +C$$

$$A\sqrt{2}\,\dot{\pi}_c + A4\sqrt{2}\,(\pi/\varphi)\dot{\varphi}_c = -Cp \quad .$$

And

$$p = -\frac{\dot{\pi}_c + 4(\pi/\varphi)\dot{\varphi}_c}{\pi_c + 4(\pi/\varphi)\varphi_c} \quad .$$

$\underline{k = k_x00}$

In the last paragraph, we considered the (x/r) type function. For the (z/r) type we can get a solution for all values of k in the 100 direction. The (z/r) function satisfies the same conditions for k = 0 as the (x/r) and was not considered separately there.

The (z/r) type has a nodal plane through the points 100, 010, 110, etc. Hence, there will be conditions on it for the 001, 011 and 101 faces only. This gives five conditions

011 one condition $u = 0$

101 two conditions involving $T_{101} = \tan\frac{\pi}{2} k_x = T$

001 two conditions not involving T.

We must use at least three Cl functions to satisfy the Cl conditions; this gives only the possibilities 3 - 2 and 4 - 1. 3 - 2 is essentially the Cl-Cl case again, so we are reduced to 4 - 2.

The functions chosen to satisfy the conditions are

$$\begin{aligned}\mathrm{C1} \qquad & i\Big\{A\sqrt{2}(z/r)\Pi + B\,5\sqrt{8}(z^3 - \tfrac{3}{5}zr^2)/r^3\Phi \\ & \quad + C\sqrt{8}\,z(x^2 - y^2)/r^3\Phi\Big] + E\,2xy/r^2\Delta \quad = \\ & \quad i(AK\Pi + BL\Phi + CM\Phi) + EN\Delta\end{aligned}$$

$$\mathrm{Na} \qquad G(z/r)P \qquad .$$

The values of the surface harmonics on the various faces are

	K	L	M	N	Tan
011	1	-1	-1	0	0
101	1	-1	1	1	T
001	$\sqrt{2}$	$4\sqrt{2}$	0	0	$e^0 = 1$

We eliminate A from the 011 condition, which is

$$A - B - C = 0 \qquad \text{or} \qquad A = B + C \quad .$$

The conditions on 101 are then

$$\begin{aligned} -T(E) + A - B + C &= \\ -TE + 2C &= 0 \end{aligned}$$

and

$$E\,\delta + T\big[B(\varkappa - \varphi) + C(\varkappa + \varphi)\big] = 0 \quad .$$

On 001 we find

$$\sqrt{2}\left[B(\pi_c + 4\varphi_c) + C\pi_c\right] = +1\left[-G\right]$$

$$\sqrt{2}\left[B(\dot{\pi}_c + 4\dot{\varphi}_c) + C\dot{\pi}_c\right] = +1\left[Gp\right] \quad .$$

When the determinant of the coefficients of B, C, E and G is set up and expanded, we obtain

$$\tan^2 \frac{\pi}{2} k_x = - \frac{\delta\left[p(\pi_c+4\varphi_c) + (\dot{\pi}_c+4\dot{\varphi}_c)\right]}{\varphi\left[p(\pi_c+2(\frac{\pi}{\varphi}+1)\varphi_c)+\dot{\pi}_c+2(\frac{\pi}{\varphi}+1)\dot{\varphi}_c\right]} \quad .$$

This formula can be checked against $k = 0$ when $T = 0$. It has also been checked by working out independently the solution for $k = 100$ or $T = \infty$.

Since the z/r and y/r types are equivalent for propagation in the 100 direction, the (y/r) type will give another band with the same solution.

Values plotted from this formula are shown in Plate 9 for the two assumptions in regard to the Na potential.

$k = \frac{1}{2}(111)$

For this value of k , $T_{110} = T_{011} = T_{101} = \infty$ and $T_{1\bar{1}0} = T_{01\bar{1}} = T_{10\bar{1}} = 0$. The factor $e^{i \ \cdot R} = i$ for the 100, 010 and 001 Na-Cl conditions. This shows that we can use odd functions around the Cl and even functions around the Na. We already know what functions to use around the Cl for $k = 0$. We must, however, choose the right linear combinations for propagation in the 111 direction. These prove to be terms of three types

$$\Gamma_1 \qquad (x + y + z)$$

$$\begin{array}{llll} \Gamma_3 & a & (y - z) \quad \text{or} & (y^2 - z^2) \\ & b & (2x - y - z) & (2x^2 - y^2 - z^2) \end{array} \quad .$$

The numbers correspond to the representations of the symmetry group of the 111 axis to which they belong.

The type Γ_1 takes on the same value on all three of the faces about a Na, and suggests using an s there. The Γ_1 type vanishes on all the $01\bar{1}$ type faces, and is subject only to the condition $u' = 0$ on the 110 faces. It satisfies two conditions on the 100 faces. Hence, a satisfactory set of functions is

$$\text{Cl} \quad A\sqrt{2}\,\frac{x+y+z}{r}\,\Pi , \quad B\,5\sqrt{8}\,\left(\frac{x^3+y^3+z^3 - 3/5(x+y+z)r^2}{r^3}\right)\,\Phi$$

$$\text{Na} \quad C\,S \qquad .$$

The 110 face requires

$$2A\pi - 4B\varphi = 0 \qquad \text{or} \qquad B = \frac{1}{2}\,\frac{\pi}{\varphi} \qquad .$$

The 100 face requires

$$\sqrt{2}A \quad \varkappa_c + 4\frac{\varkappa}{\varphi}\varphi_c \quad = C$$

$$\sqrt{2}A \quad \dot{\varkappa}_c + 4\frac{\varkappa}{\varphi}\dot{\varphi}_c \quad = -Cs$$

or

$$s = -\frac{\dot{\varkappa}_c + 4(\varkappa/\varphi)\dot{\varphi}_c}{\varkappa_c + 4(\varkappa/\varphi)\varphi_c} \quad .$$

The functions of Γ_2 type give one more condition, since they do not vanish on the $01\bar{1}$ type faces. This requires the use of one more function. For the "a" set, which are odd for interchange of y and z, we use the functions

$$\text{Cl} \qquad A\sqrt{2}\,\frac{(y-z)}{r}\Pi + B\;5\;\sqrt{8}\;\frac{z^3-y^3-3/5(z-y)r^2}{r^3}\,\Phi \; +$$

$$C\sqrt{8}\;\frac{2x(z^2-y^2) + z(x^2-y^2) - y(x^2-z^2)}{r^3}$$

$$= AK\Pi + BL\,\Phi + CM\,\Phi$$

$$\text{Na} \qquad E\frac{(y^2-z^2)}{r^2}\,D = END \quad .$$

The choice of the surface harmonics was such that they all transform in the same way from one equivalent face to another in regard to propagation in the 111 direction. This may be seen from the table of values.

	K	L	M	N
011	0	0	0	
101	-1	-1	3	
011	1	1	-3	
$01\bar{1}$	2	2	2	
$10\bar{1}$	1	1	1	
$1\bar{1}0$	-1	-1	-1	
100	0	0	0	0
010	$\sqrt{2}$	$-4\sqrt{2}$	0	1
001	$-\sqrt{2}$	$4\sqrt{2}$	0	-1

It is seen that fitting at 011, $10\bar{1}$ and 010 will cause all the other faces to fit also.

The condition on $10\bar{1}$ is $u = 0$.

$$A + B + C = 0 \quad .$$

On 011, it is $u' = 0$

$$A\varkappa + B\varphi - 3C\varphi = 0 \quad .$$

Therefore

$$B = -\frac{A}{4}\left(\frac{\varkappa}{\varphi} + 3\right) \quad , \quad C = \frac{A}{4}\left(\frac{\varkappa}{\varphi} - 1\right) \quad .$$

This gives for the condition on 010

$$\sqrt{2}A(\varkappa_c + (\frac{\varkappa}{\varphi} + 3)\varphi_c) = E$$

$$\sqrt{2}A(\dot{\varkappa}_c + (\frac{\varkappa}{\varphi} + 3)\dot{\varphi}_c) = - Ed \quad .$$

And, finally

$$d = - \frac{\dot{\varkappa}_c + (\frac{\varkappa}{\varphi} + 3)\dot{\varphi}_c}{\varkappa_c + (\frac{\varkappa}{\varphi} + 3)\varphi_c} \quad .$$

The values obtained for $k = \frac{1}{2}(111)$ are shown on Plate 9.

XII.

SUMMARY OF THE WORK ON THE Cl^- 3p BAND

REMARKS ABOUT TOTAL ENERGY

Calculations have been carried out for the Cl^- 3p band on the basis of three different sets of boundary conditions: Cl-Cl, Na-Cl, and Cl-Cl-Na. The energy versus k curves for these are shown on Plate 9. We see from these that the Cl-Cl is a much better approximation to the Cl-Cl-Na than is the Na-Cl. However, the Na-Cl energy values cover roughly the same range as the other two.

This result is not as trivial as might appear at first glance. For the Na-Cl joining, the Cl functions are evaluated at the Na-Cl radius rather than the Cl-Cl radius. At this radius the Cl^- 3p band (defined as the energy values for which $\dot{\varkappa}_c/\varkappa_c < 0$) is about three times as wide as for the Cl-Cl radius. We can see, roughly, that the Na-Cl band edges, which come at $-\dot{\varkappa}_c/\varkappa_c = s$, p, and d of the Na functions, will lie in the central part of the range. This is a consequence of the fact that the s, p, and d values are of the order of +1. The values of $\dot{\varkappa}_c/\varkappa_c$ range from 0 to ∞ with +1 near the middle of the range. However, it is gratifying and, on the whole, somewhat surprising that the Na-Cl band actually lies within the Cl-Cl-Na band.

So far as the detailed structure is concerned, there is no great resemblance between the Na-Cl and the other two.

For this reason, it appears doubtful if a great amount of faith can be placed in the structure of any of the bands. On the other hand, the marked similarity between the Cl-Cl and Cl-Cl-Na bands indicates that they may be fairly good. It would not be wire, however, to assert a definite opinion on this point.

The overlapping of the energy ranges on the three schemes does have a definite interpretation. We should certainly expect that an exact solution of the one electron Schrödinger equation in the field used would give an energy band in very nearly the same place.

One thing we should expect to depend upon the Cl^- 3p band is the binding energy of the lattice. In the case of a monovalent metal, the heat of formation and the compressibility are dependent upon the behavior of the band for the valence electron. As the lattice is squeezed together, the band widens. At first it spreads equally to both sides of the free atom energy level. Since the band is only half filled, the electrons go into the lower half and the total energy decreases. When the spacing is made too close, even the bottom of the band starts to rise and the energy increases. The minimum in the energy versus lattice constant curve gives the equilibrium spacing and the binding energy. The curvature at the minimum gives the compressibility.

The situation is quite different for the valence electrons of the Cl^- ion. These form a filled band, and for large lattice spacing, the spreading of the band does not affect their mean energy. Thus, to begin with the entire change in energy is due to the Madelung energy. This causes the total energy to decrease as $-1/\delta$. When the lattice is squeezed very close together, the band begins to widen more at the top than at the bottom and repulsive forces set in and hold the ions apart. A rough idea of the total energy can be obtained by taking the average of the top and bottom of the band as the average energy of the band. If this is multiplied by six, for the six electrons, and added to the Madelung energy, the resultant total energy per molecule has a shallow minimum within 2% of the observed lattice spacing. However, the corresponding binding energy is <u>negative</u>. That is, our calculations indicate that the lattice is unstable.

It is not difficult to find the reason for this absurd result. In section IV, the calculation of the potential for the Cl ions was discussed. It seemed reasonable to renormalize Hartree's potentials so as to include all the electrons in a certain amount of space about a Cl nucleus. This change in normalization sufficiently affected the field as to cause an appreciable difference between Hartree's energy parameters and ours. In fact, the center of our band is about 0.15 At.U. higher than Hartree's level. Since the Madelung energy per molecule is only 0.66 At.U., the excess energy at the minimum is 6 x 0.15 - 0.66 = 0.24. In regard to this difficulty, NaCl is very different from the alkali metals. For them the potential on an electron is nearly independent of the lattice spacing and calculation of wave functions for one field is all that is necessary. For the Cl ions this is far from true. As the lattice is squeezed together, the change in the charge distribution affects the field of the valence electrons quite appreciably. Hence, for various radii it is necessary to carry out self-consistent field calculations for the wave functions.* If the total energy is then plotted as a function of δ, the minimum should indicate the lattice spacing and binding energy.

Even if the above process is carried out, we cannot expect as good results as for the alkali metals. For the outer electrons of the Cl^- ion, the Hartree approximation is not nearly as good as for the outer electrons of sodium. (For sodium, a field can be chosen which gives good agreement with the spectral terms.) Hence, there will be a considerable error in calculating the zero of energy for infinitely separated ions. If this zero error varies as the lattice is s squeezed together, it may well so mask the repulsive effect of the band widening as to obfuscate the results.

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* Self-consistent field calculations for LiF have been carried out by Ewing and Seitz. Abstract in Phys. Rev. 49, 639 (1936). An article by them is expected in the near future.

XIII.

CONCERNING EXCITATION

Since Section II, we have been entirely concerned with the mechanics of calculating one electron wave functions. The next question is what to do with them when we get them. Since the bands in NaCl are filled, we cannot use them for the calculation of a non-existent conductivity.

However, they can be used to calculate the energy of electronic excitation in the lattice, and this should be very closely related to phenomena connected with dispersion and absorption of light.

For a free atom we consider the light as producing a probability of finding the atom in an excited state. This probability and, hence, the interaction of the light and the atom depends on the frequency of the light, a situation which results in the Kramers Heisenberg formula for the phenomenon of dispersion.* When the frequency of the light is very nearly one of the natural frequencies of the atom, this probability of excitation becomes very large. There is then a large amount of light scattered by the atom and considerable probability of transfer of energy to colliding atoms in the case of a gas or to lattice vibrations for a solid.

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*J. C. Slater and N. H. Frank "Introduction to Theoretical Physics," page 549.
G. Wentzel, Handbuch der Physik XXIV, 779.

By analogy with the case of the free atoms, we are led to investigate the probability of excitation of the crystal by light waves. The interaction between a light wave whose vector potential is $A(x)$ and an electron is

$$H_1 = \frac{e}{mc}\; p\cdot A + \frac{e^2}{2mc^2} A^2 \qquad *$$

For a plane wave, A is of the form $f\, e^{is\cdot r}$, where f is a polarization vector. The perturbation H_1 is capable of causing transitions of the electron from one lattice function to another. There is a selection rule for these transitions. If the lattice functions are

$$\psi = \sum_{\alpha} e^{i\varkappa\cdot R_\alpha}\, \psi_\alpha \qquad \text{and}$$

$$\psi' = \sum_{\alpha} e^{i\varkappa'\cdot R_\alpha}\, \psi'_\alpha \qquad , \quad \text{then}$$

$$\varkappa - \varkappa' = \pm s$$

For visible and ultraviolet light, k will be much smaller than $\varkappa$. $\varkappa$ is of the order of $1/S$, the reciprocal vector for the lattice, while k is of the order of $1/\lambda$, the wavelength of the light. Hence, this selection rule is practically equivalent to

$$\varkappa = \varkappa'$$

and the latter will be used for calculating energy differences

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*For a thorough discussion of the interaction of electrons and radiation, see G. Breit, Rev. Mod. Phys. 4, 504 (1932). See also, E. Fermi, Rev. Mod. Phys. 4, 87 (1932).

between the lattice functions.

The interaction of the light with the crystal can then be thought of as the sum of the interactions with each of the electrons. We suppose that in the lowest state there is one electron in each of the lattice functions for the filled bands. Under the influence of the light a given electron has a probability of jumping to vacant states in higher bands. Due to this probability, there will be a current in the lattice. The value of this current and its influence on the light can be calculated and interpreted in terms of an index of refraction. This method has been carried out by Wilson.* There is an important objection to his method. He does not specifically consider the interaction between the electrons. In considering any one electron, he replaces all the other electrons and the ions by a periodic potential field. This field is taken to be the same for all the electrons and his one electron wave functions are solutions of Schrödinger's equation for this potential. The energy required to excite an electron is taken to be the difference in energy values for the solutions of Schrödinger's equation.

This method of treatment is obviously rather crude. In Section II, we saw that the potential in which an electron moves is not independent of the energy of the electron. This change is due to the difference in interaction between

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*A. H. Wilson, Proc. Roy. Soc. A151, 274 (1935).

the electrons, and we must take into account its effect on the total energy in determining the excitation energy of a single electron.

If we treat the crystal by the Fock method, using lattice functions, we must consider what is meant by an excited state.

The most natural interpretation of excitation will consist of replacing one of the lowest one electron lattice functions by the wave function for an excited state. We have shown in the last part of Section II that the energy difference between the two determinantal functions is just the difference in the energy parameters of the Fock equations for the two lattice functions. In dealing with the Fock equations, we have replaced them by Schrödinger equations, and in this the treatment is similar to Wilson's. However, we have found it logical to use a different potential function in the Schrödinger equation, depending on the energy of the lattice function in question. This difference is just such as to make the energy parameters include the effect of the varying exchange energy of different energy lattice functions. The writer, independently of Wilson's work, developed a theory of dispersion, using determinants, rather than treating the electrons individually and taking the energy differences as those given by the Fock scheme.* The formula

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*W. Shockley, Phys. Rev. A49, 639 (1936).

for index of refraction was the same as that obtained by Wilson, save that the wave functions and values of ε have a different interpretation.

On both Wilson's theory and the writer's, absorption of light by the crystal would be expected when the frequency of the light corresponds to that of a transition from an occupied to an unoccupied band. The difference in interpretation of the transition energy has been discussed above.

In order to calculate the dispersion properties, it is necessary to know the wave functions for the excited states. It is impractical to carry out calculations, such as those for the Cl^- 3p band, for enough higher bands to evaluate the expressions for index of refraction. However, the ultraviolet absorption should depend upon the energy difference between the highest occupied and lowest unoccupied bands.

It is therefore worth while to attempt to calculate the first excited band.

Cl-Cl Joining

The Cl-Cl joining approximation is evidently cruder for the excited electrons than for the filled levels. The excited functions will certainly be less restricted to the Cl's and the Na's will play a correspondingly more important role. Nevertheless, there are several points of interest in this method.

In the first place, we are interested in states in the two bands having the same value of the quantity $\varkappa$ (= $2\pi k/a$ as defined in section 6). On the Cl-Cl approximation, the highest value in the Cl^- 3p band comes at $\pi = \infty$ and $k = 0$. The next highest solution is for $\delta = 0$ and $k = 0$. The difference between the energies should then give us the ultraviolet absorption frequency. The ultraviolet absorption edge is at 1720Å.* This corresponds to an energy difference of 0.54 At.U. If we use the same potential field for the p and d functions, we find the energy difference between bands to be 0.30 At.U. If we use a potential which does not have the hole, the value is about 1.3 At.U. By assuming a proper fraction of the 3p hole to be left after the electron has jumped to a higher band, it would be possible to obtain any band separation between about one-half and twice the ultraviolet absorption edge.

Na-Cl Joining

On this approximation, we can allow the sodium atoms to play an important part, and this permits us to use some physical reasoning in connection with what should be the first excited band.

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* Landolt-Börnstein, HWII, 913.
Handbuch d. Exp. Phys. XIX, 183.

We may consider the ionic lattice as being formed in the following way out of ions, Arrange the ions in the NaCl lattice, but at infinite lattice constant, and then shrink the lattice together. At infinite separation the ions are not affected by each other, and individual ion wave functions may be used. The first excited state for these conditions will be formed by removing an electron from one of the Cl^- ions and putting it on one of the Na^+ ions. As the lattice is squeezed together, the electrons on the Cl^- ions find themselves more closely surrounded by the positive ions and, hence, their energy band drops lower on the energy scale, the amount being obtained from the lattice potentials. Finally, when the atoms get very close together, the band widens and its average energy begins to increase. This introduces a repulsive force and holds the lattice apart at the equilibrium spacing. On the other hand, the electron in excited level finds itself more closely surrounded by negative ions and its potential rises. Due to the greater spatial extension of the wave functions, the excited level begins to widen at a larger spacing than the filled levels, and its lower edge tends to drop.[*] Our problem is to see if there is an analogue to this behavior in the Na-Cl joining case.

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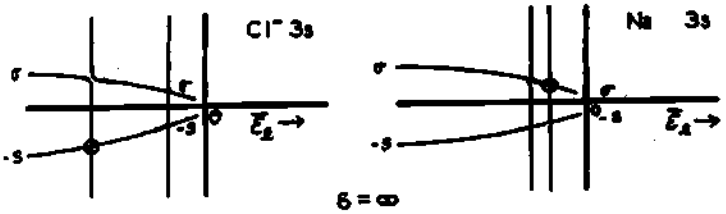
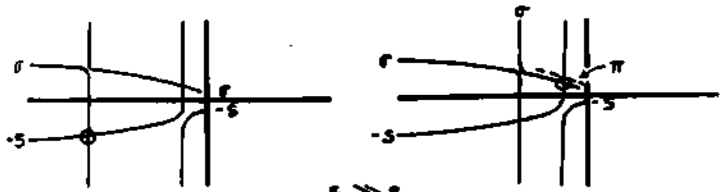
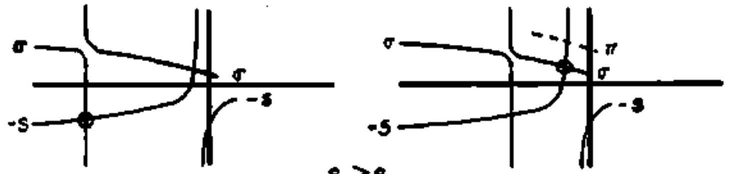
[*] The above picture of the band situation is due to J. C. Slater, and any flaws in its presentation here are the writer's. Dr. Slater carries the treatment much farther and works out a theory of the U.V. absorption edge from it.



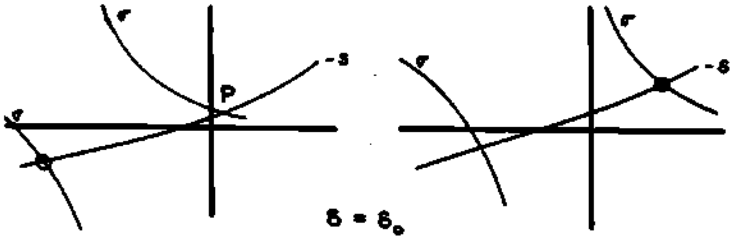
$\delta = \infty$



$\delta \gg \delta_0$



$\delta > \delta_0$



$\delta = \delta_0$

As was pointed out in Section X, page 96, the Na-Cl joining treatment gives the correct bands when the atoms are far apart. It will thus give the correct band for the excited state at infinite separation. The $k = 0$ condition for this band will be given by $-s = \sigma$ (the notation is that of Section X), and the limits in the 111 direction by $-s = \kappa$. For very large separation, s, σ and κ are continuous functions of the energy and approximately equal to $+\sqrt{-\overline{\varepsilon_\ell}}$ where this is real, except when $\overline{\varepsilon_\ell}$ is near an eigenvalue and there they are discontinuous.

For the filled band σ is computed with a hole on the Cl^- ion, whereas for the unfilled band it is computed without a hole. This causes the σ discontinuity to occur at higher $\overline{\varepsilon_\ell}$ for the unfilled band. This situation is indicated in the adjacent figure. As the lattice spacing is decreased, the only effect at first is that of the Madelung potential. As the actual lattice spacing is approached, the bands begin to widen and finally become very wide at the actual spacing. The energy difference between the filled levels and the unfilled one is then about 1.5 At.U. or, roughly, three times the observed value. If we use the σ for the filled band (point P of the figure), however, the difference is about 0.75 At.U., which is the closest to observed value of 0.54 of any of the trials thus far.

The $s = -\kappa$ edges appear to come generally somewhat higher.

Cl-Cl-Na Joining

We shall work out only the $k = 0$ case for this. For this the lattice function should be even about both atoms and, since it is s-like around the Na, it should consist only of spherical harmonics of full cubic symmetry. Then the 110 type face gives one condition, $g' = 0$. The 100 face gives two conditions. By reasoning similar to that of Section XI, we conclude that we should use two Cl functions and one Na. The condition of symmetry requires these to be

$$\text{Cl} \qquad A\Sigma \;, \quad B(x^4+y^4+z^4-\tfrac{3}{5}r^4)/r^4\,\Gamma$$

$$\text{Na} \qquad CS$$

The 110 condition is

$$A\sigma - \tfrac{1}{10}B\gamma = 0 \qquad \text{or} \qquad B = 10(\sigma/\gamma)A\,.$$

The 100 conditions are then

$$\begin{aligned} A\left(\sigma_c + 4\tfrac{\sigma}{\gamma}\gamma_c\right) &= C \\ A\left(\dot{\sigma}_c + 4\tfrac{\sigma}{\gamma}\dot{\gamma}_c\right) &= -Cs \end{aligned} \qquad \text{or} \qquad s = -\frac{\dot{\sigma}_c + 4\frac{\sigma}{\gamma}\dot{\gamma}_c}{\sigma_c + 4\frac{\sigma}{\gamma}\gamma_c}\,.$$

The g functions which are needed for evaluating γ have not been computed. However, for a large part of the integration the value of $\ell(\ell+1)/r^2 = 20/r^2$ is the dominant term. Hence, a fair approximation to the g functions can be obtained from the solution of the wave equation in free space,* $j_4(\sqrt{-\epsilon_g}\ r)$, where $j_4(x) = \sqrt{2\pi/x}\ J_{\frac{9}{2}}(x)$. A usable approximation for the energy range involved can be obtained from just the first term of the expansion, r^4.

The value of the energy gap between bands, based on the Bessel functions and σ values for a potential without a hole, is about 1.1 At.U. Calculations were not made with the potential with the hole, but the value can be estimated as about 0.0 to 0.1 At.U. (The shift in wave functions due to the hole is about 1.1 At.U.) Thus, we are again at a situation where the desired value can be obtained by a suitable estimate of the effective hole.

Concluding Remarks

There are two questions which are raised by the above work: how genuine is the variation of the hole which we find from the Fock approximation, and how good are any of our joining conditions? Certainly, from the point of view of the Fock approximation, the hole must behave in much the way outlined in Section II. Physically, also, we should expect a decrease in the hole for an excited electron. The excited electron will be moving more rapidly through the lattice and the other electrons will not have a chance to move

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*P. M. Morse, "Methods of Theoretical Physics," M.I.T., first edition, pages 187 and 188.

out of its way as much as for a slower electron. On the other hand, perhaps the picture of lattice functions is not as good as the older picture of atomic excitation. On the basis of that picture, individual atoms are considered as the units and excitation corresponds to a change in the energy level of the atom. The other atoms perturb the levels and afford a means of transforming excitation energy into lattice vibrations. For this case, there will be a hole, as there always is in the case of definite number of electrons around an atom, regardless of the state of excitation of the atom. There does not seem to be any satisfactory answer to the first question at present.

Regarding the second question, which concerns the boundary conditions, it is possible to obtain some further information by the considerations of the next section.

XIV.

TEST OF THE SLATER CONDITIONS FOR FACE-CENTERED AND BODY-CENTERED LATTICES

There is one case where it should be legitimate to use the Slater boundary conditions for which the exact lattice functions are known. This is the trivial case of constant potential. For this case, Schrödinger's equation reduces to the wave equation in free space

$$H\psi = -\nabla^2\psi = \varepsilon\psi \quad .$$

The lattice function solutions of this equation are

$$\psi = e^{iv\cdot r}$$

where the wave vector v satisfies

$$v^2 = \varepsilon \quad .$$

If spherical coordinates are used, the solutions are

$$\psi = S_{nm}(\theta,\varphi)j_n(\omega r) \quad .^*$$

Here

$$j_n(z) = \sqrt{\pi/2z}\, J_{n+1/2}(z) \quad ,$$

$$\omega^2 = \varepsilon$$

and S_{nm} is an n^{th} order surface harmonic.

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*P. M. Morse, "Methods of Theoretical Physics," M.I.T., first edition, pages 187 and 188.

Hence, for our potential, $V = 0$, we know both the correct lattice functions and the spherical functions. We should then put in a fictitious lattice, of unit lattice spacing, and solve the Slater boundary conditions. The results will then be compared with the correct plane waves.

Face-Centered Lattice

Let the unit vectors for the lattice be

$$a_1 = 0\,\tfrac{1}{2}\,\tfrac{1}{2}\ , \quad a_2 = \tfrac{1}{2}\,0\,\tfrac{1}{2}\ , \quad a_3 = \tfrac{1}{2}\,\tfrac{1}{2}\,0 \qquad .$$

The reciprocal vectors are

$$b_1 = \bar{1}\;1\;1\ , \quad b_2 = 1\;\bar{1}\;1\ , \quad b_3 = 1\;1\;\bar{1} \qquad .$$

In terms of k, the wave vector v will be

$$v = 2\pi k \quad .$$

Then, if k is a point in the reciprocal lattice, the wave function is periodic. The radius R_{110}, at which the functions should be evaluated and which occurs in $\tan v \cdot R_{110}$, is

$$R_{110} = \tfrac{1}{4}\,\tfrac{1}{4}\,0 \ , \quad \left| R_{110} \right| = \frac{\sqrt{2}}{4} = d$$

and

$$T_{110} = \tan R_{110} \cdot v = \tan \frac{\pi}{2}(k_x + k_y) \ .$$

For energy $\varepsilon = \omega^2$, the values of σ, π, etc. are

$$\sigma = \frac{\frac{d}{dr}\, j_1(\omega r)}{j_o(\omega r)} = \omega\, \frac{j_o'(\omega d)}{j_o(\omega d)} \quad .$$

Since the expressions we obtain are always of zero dimensions in the quantities σ , $\varkappa$, etc., the common factor ω will cancel out. Hence, in all calculations σ/ω, $\varkappa/\omega$, etc. are used in place of σ , $\varkappa$, etc.

All that was needed to make calculations from the Slater conditions were tables of $j_n'(\mu)/j_n(\mu)$ for $n = 0$ to 3.* The value of the energy is then

$$\varepsilon = \omega^2 = (\mu/d)^2 = 8\mu^2 \quad .$$

Face-Centered 111

There are five bands for the face-centered 111 direction. (See list of Solutions.) For this direction $k = u, u, u,$ and the energy of the correct lattice functions is $\varepsilon = v^2 = 4\varkappa^2 3u^2 = 12\varkappa^2 u^2$. There is only one type of tangent factor, $T_{110} = M = \tan \varkappa u$.

For a given value of μ , the values of the 111 line formulae were worked out and the values of k found. From these, the curves shown on Plate 10 were constructed. Calculations were carried out in detail for energies below 100 At.U. For higher energies, several roots for $k = 0$

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*The writer is greatly indebted to Professor P. M. Morse, who kindly furnished him with tables of $j_n(\mu)$ and $j_n'(\mu)$.

are shown.

The $k = 0$ roots are very interesting for comparison with the exact solution. For the exact solution, the lowest energy periodic lattice function (i.e., one which takes the same value in every cell) is obtained by letting $v = 0$. The function is then a constant. The next highest energy for which we get periodic functions is given by $v = 2\pi b$. There are eight functions for this energy. They are obtained from the eight possible values of k_o of the form

$$k_o = \pm 1 \pm 1 \pm 1 \quad .$$

The energy is

$$v^2 = 4\pi^2 k_o^2 = 12\pi^2 = 118 \text{ At.U.}$$

For slightly different momenta, the degeneracy of these 8 periodic functions is removed. If we consider them as functions of k, which are periodic in space for $k = 0$, then for values of k in the 111 direction they will be given by

$$\psi = e^{2\pi i(\pm 1+u,\ \pm 1+u,\ \pm 1+u)\cdot r} \quad .$$

These functions split into 4 sets for $u \neq 0$. They can be classified according to the values of v^2 which determine their energies.

$$v^2 = 4\kappa^2 \; 3(1 + u)^2 \qquad \text{1 function}$$

$$v^2 = 4\kappa^2 \left[2(1 + u)^2 + (-1 + u)^2 \right] \qquad \text{3 functions}$$

$$v^2 = 4\kappa^2 \left[(1 + u)^2 + 2(-1 + u)^2 \right] \qquad \text{3 functions}$$

$$v^2 = 4\kappa^2 \; 3(-1 + u)^2 \qquad \text{1 function}$$

For points in the first zone of k space, u runs from $-1/2$ to $+1/2$. The energy contours computed from the above values are also shown in Plate 10. (Dotted lines.) The last type is omitted, since it is merely a duplication of the values already shown between $u = 1/2$ and 1.

We see that for $k=0$, the eightfold degeneracy at $\varepsilon = 118$ is represented by a fivefold degeneracy at 89 with $\delta = 0$, and a threefold degeneracy at 163 for $\kappa = \infty$. Thus the average error in the Slater method for the first excited set of periodic functions is about 25%. So far as detailed correlation is concerned, there is almost none. It is possible to decide to some extent which functions of one set should go with those of the other on the basis of symmetry properties, but nothing is gained by this.

When we consider the simplicity of the approximation, it is not surprising that the agreement is as bad as it is. The first excited set of periodic functions in the exact solution is eightfold degenerate. In the method of mid-point fitting, only 12 functions were used in all. This is an average of 1.5 spherical harmonics for each of the eight plane waves. It is evident that we should not expect our approximation to work too well.

For $k < 0.4$ in the lowest band, the agreement is really remarkably good, the difference between the two curves being less than 1% for both the 100 and 111 lines in the face-centered lattice.

It may also be noted that the spurious energy gaps at the edge of the central zone $(u = 0.5)$ are roughly the same as those found by Slater for metallic sodium* when the difference in lattice constant is allowed for. The implication of this is that the energy gap at the edge of the zone is narrower than he supposed, and that the laws of Bragg reflection for diffracted electrons should be more exactly fulfilled.

Comparison with the Na-Cl Problem

It is interesting to see roughly what part of the graphs of Plate 10 correspond to the Cl^- 3p band. We might expect that on the scale of these drawings the 3p band would be so narrow as to be considered more Bloch-like than plane wave-like. As a matter of fact, however, the 3p band takes almost precisely the same energy range as the central zone.

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*J. C. Slater, Phys. Rev. 45, 800 (1934).

The lattice spacing of NaCl is 10.6 At.U. The lattice spacing for this section was 1 unit and the energy range of the lowest zone was 30 units. If we enlarge the lattice spacing to 10 units, this difference will decrease to 0.3 units. (The energy of the plane waves is proportional to the square of the reciprocal vector.) The Cl 3p band has a width of 0.35 units.

Having seen how poor the correspondence is outside the first zone, we cannot expect to get a check of much better than about 25% for the band to band transition in NaCl.

Face-Centered 100

On Plate 10, the results of similar computations for the 100 line of the face-centered lattice are shown. These are not given in as much detail as those of the 111 line. The method of calculation and the results are generally similar to those of 111.

Body-Centered Lattice

Similar calculations have been carried out for the body-centered lattice. Using the same notation as for the face-centered lattice, the various quantities were

$$a_1 = \frac{\bar{1}}{2}\,\frac{1}{2}\,\frac{1}{2} \quad , \quad a_2 = \frac{1}{2}\,\frac{\bar{1}}{2}\,\frac{1}{2} \quad , \quad a_3 = \frac{1}{2}\,\frac{1}{2}\,\frac{\bar{1}}{2}$$

$$b_1 = 0\ 1\ 1 \quad , \quad b_2 = 1\ 0\ 1 \quad , \quad b_3 = 1\ 1\ 0$$

$$v = 2\pi k$$

The k lattice has the b's for unit vectors.

$$|R_{111}| = \left|\left(\frac{1}{4}\,\frac{1}{4}\,\frac{1}{4}\right)\right| = \frac{\sqrt{3}}{4} = d$$

$$T_{111} = \tan \pi/2(k_x + k_y + k_z)$$

$$= \omega \frac{j_o(\omega d)}{j_o(\omega d)} = \omega \frac{j_o'(\mu)}{j_o(\mu)} .$$

The energy for a given value of is

$$\varepsilon = \omega^2 = \frac{16}{3}\,\mu^2 .$$

Using this notation, the lines 110 and 100 were worked out for the body-centered lattice. The equations for the lines were taken from Slater's paper.* The curves are shown on Plate 11.

Concluding Remarks

It is found that the method of fitting midpoints between nearest neighbors gives a good approximation to the

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* J. C. Slater, Phys. Rev. 45, 798 and 799 (1934).

exact plane wave solution inside the central zone. Outside of this, it is very unreliable. For X-ray levels and very narrow bands in general, it will give solutions qualitatively similar to the Bloch scheme. For higher energies, where the metallic correspondence is reached, its validity may be little better than it is for plane waves. For these cases, it would be desirable to have an approximation in which we could place more faith. There are two ways of improving the approximation. Either more points can be fitted -- this is feasable for the body-centered lattice, but not convenient for the face-centered lattice -- or tangential derivatives at the midpoints of the faces can be made continuous. It would be interesting to test such improvements by the method of this section, and the writer has been prevented from doing so only by the discrepancy between the Earth's rate of motion about the sun and the writer's rate of doing work.

LIST OF SOLUTIONS FOR THE FACE-CENTERED LATTICE

	Name of solution and page reference or formula	Even or odd in planes 001	Even or odd in planes $01\bar{1}$	Sheets of 3p band connected with this solution
001o	page 52	0	-	I and II
$01\bar{1}$o	page 59	-	0	II and III
	100 line, k = u00			
100a	$\tan^2(\frac{\pi}{2}u) = -\frac{3\sigma\delta}{\pi(2\delta+\sigma)}$	E	E	I
100b	$\tan^2(\frac{\pi}{2}u) = -\frac{\delta}{\varphi}$	0	0	
100c	$\delta = 0$	0	E	
100d	$\tan^2(\frac{\pi}{2}u) = -\frac{2\delta}{\pi+\varphi}$	E	0	II and III
100e		0	E	
	110 line, k = uu0			
	Let $K = \tan\pi u$, $M = \tan(\pi u/2)$			
110a	$K^2M^2\pi\varphi(5\delta+\sigma) + K^2\delta(\pi+\varphi)(\delta+5\sigma)$ $+ 4KM\,\delta(\varphi-\pi)(\sigma-\delta)$ $+ 2M^2\delta(\pi+\varphi)(2\delta+\sigma) + 12\delta^2\sigma = 0$	E	E	I and II
110b	$M^2 = -\frac{\delta}{\pi}$	0	E	I and II
110c	$M^2 = - - \frac{2\delta}{\pi+\varphi}$	E	0	III

110d	$M^2 = -\frac{\delta}{\varphi}$	0	E	

111 line, k = uuu

111a	$\tan^2(\varkappa u) = -\frac{2\sigma\delta}{\varkappa(\sigma+\delta)}$	-	E	I
111b	$\tan^2(\varkappa u) = -\frac{4\delta}{\varkappa+3\varphi}$	-	E	II and III
111c			0	
111d	$\delta \doteq 0$	-	E	
111e			0	
111f	$\varphi = \infty$	-	0	

Line I, k = u(100)+(010)

Ia	page 56	E	-	III
Ib	page 57	E	-	I and II
Ic	page 57	0	-	
Id	page 58 , $\delta = \infty$	0	-	

Line II, k = u(100) + $\frac{1}{2}$(011)

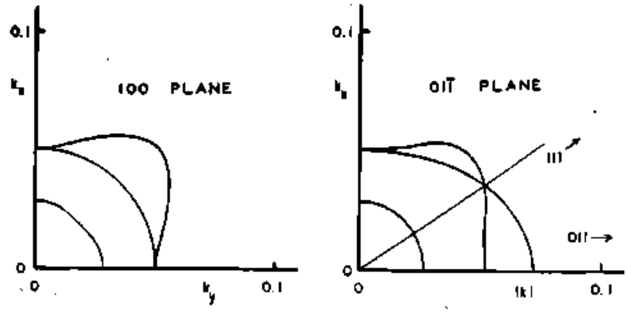
IIa	page 63	-	E	I and II
IIb	page 63	-	0	III

Line III, $k = (v=1)(100) + v(011)$

IIIa	page 66		-	E	I and II
IIIb	page 66		-	0	III
IIIc	page 67	$\delta = \infty$	-	0	

Line IV, $k = u(01\bar{1}) + \frac{1}{2}(111)$

IVa	page 71		-	-
IVb	page 67	(discussion of IVb)	-	-



CONTOURS FOR $k \to 0$ $\bar{E} = -0.025$

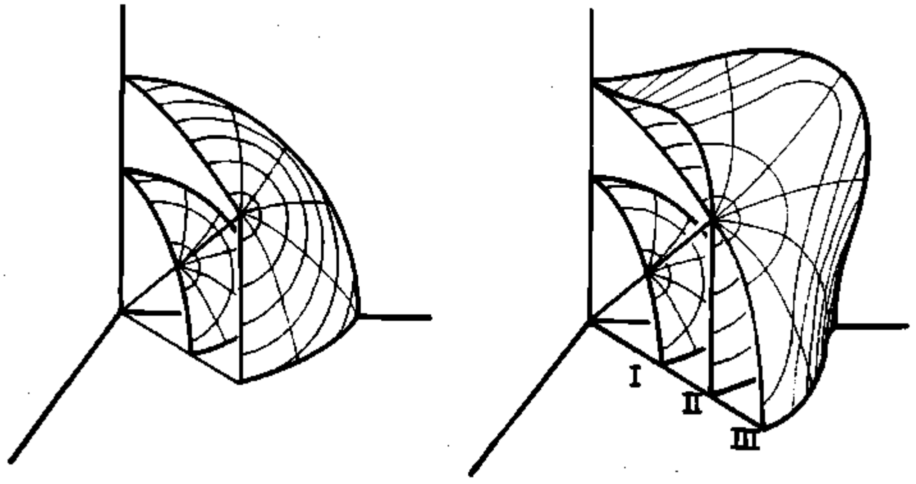


PLATE I.

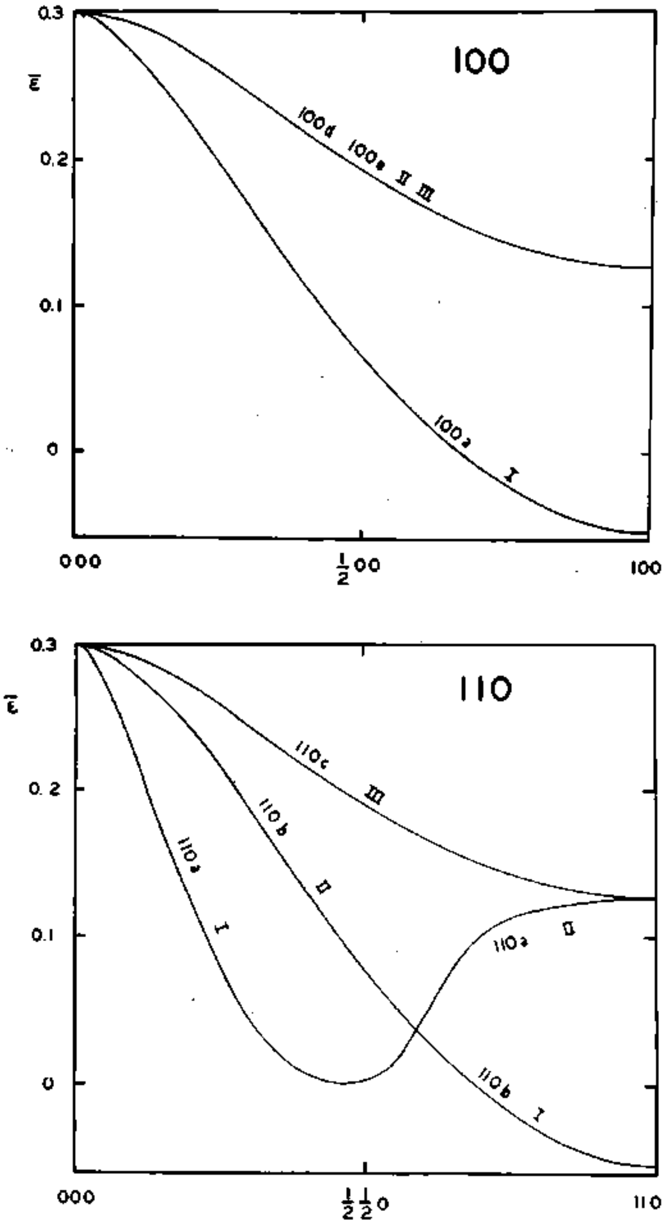

100
ε̄
0.3
0.2
0.1
0
100d 100e II III
100a I
000
½00
100
110
ε̄
0.3
0.2
0.1
0
110c III
110b II
110a I
110a II
110b I
000
½½0
110

PLATE II.

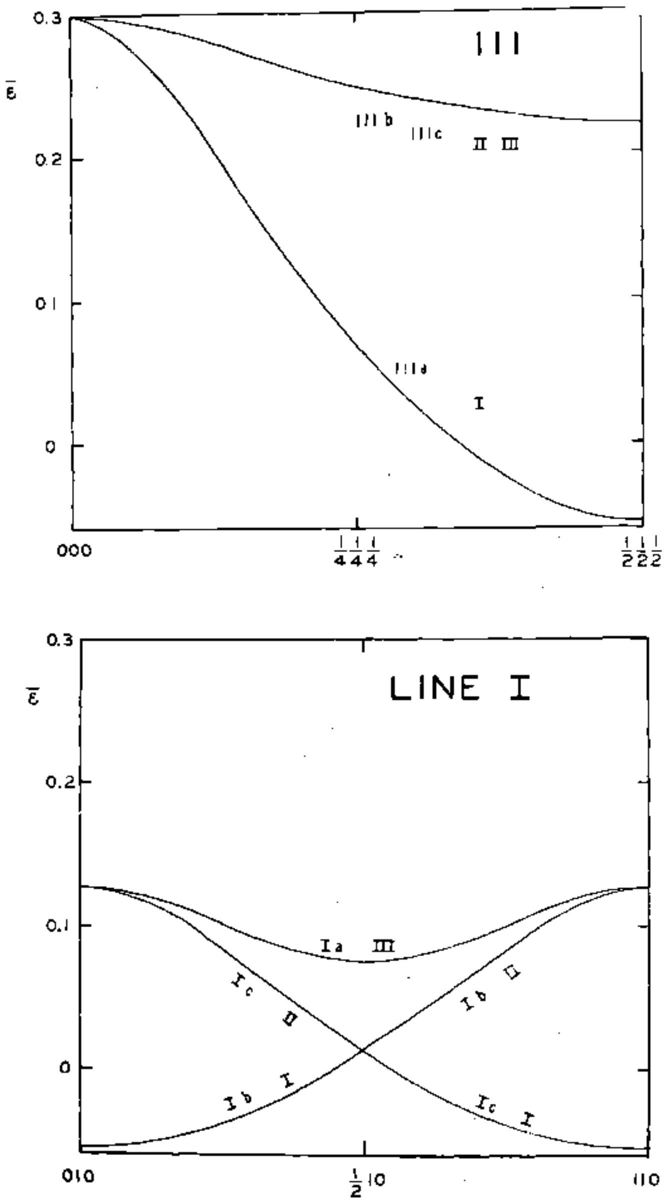

0.3
ε̄
111
111b
111c
II III
0.2
0.1
111a
I
0
000
¼¼¼
½½½
0.3
ε̄
LINE I
0.2
0.1
Ia III
Ic II
Ib II
0
Ib I
Ic I
010
½10
110

PLATE III.

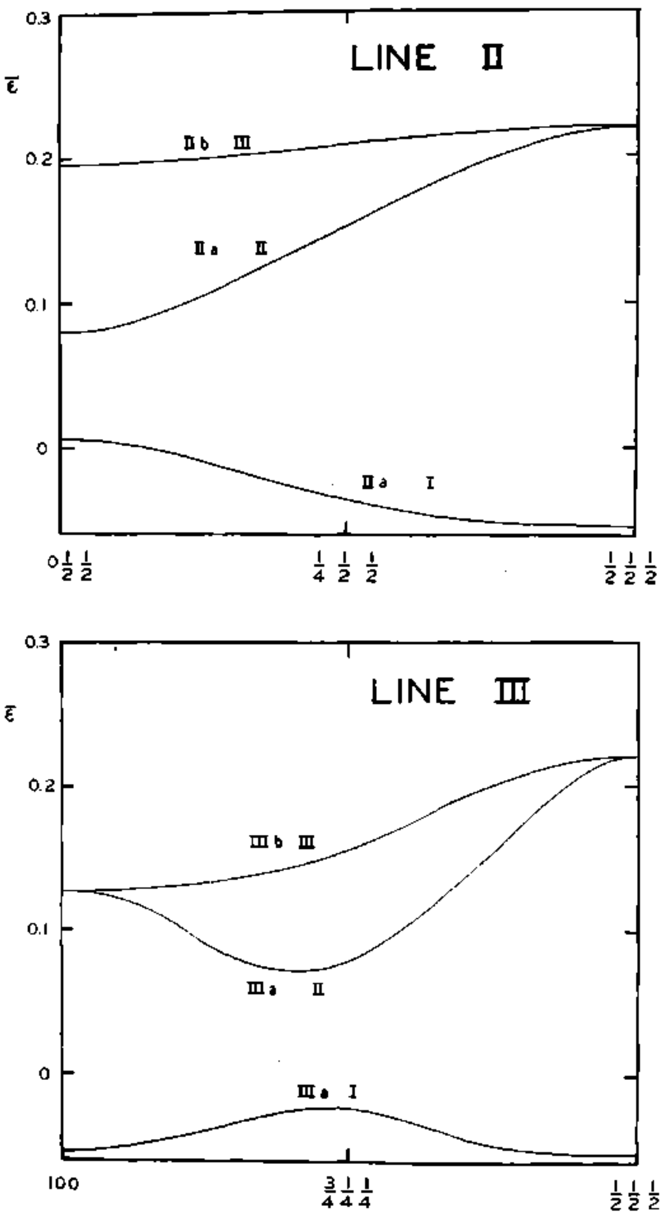
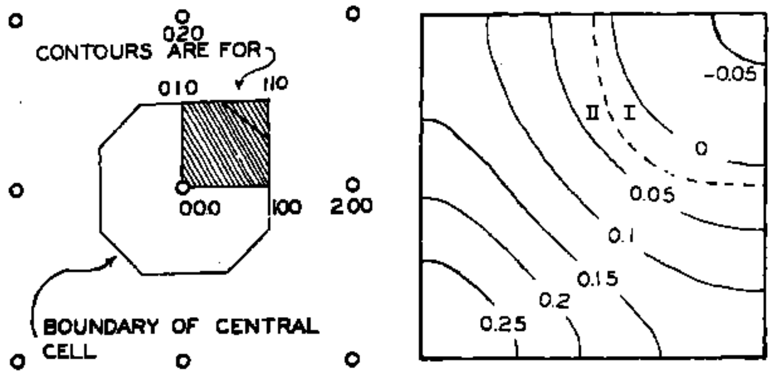
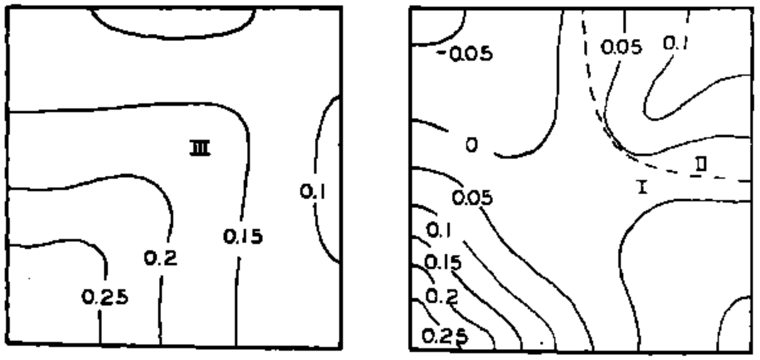

0.3
$\bar{\varepsilon}$
LINE II
IIb III
0.2
IIa II
0.1
0
IIa I
0 ½ ½
¼ ½ ½
½ ½ ½
0.3
$\bar{\varepsilon}$
LINE III
0.2
IIIb III
0.1
IIIa II
0
IIIa I
100
¾ ¼ ¼
½ ½ ½

PLATE IV.



k LATTICE

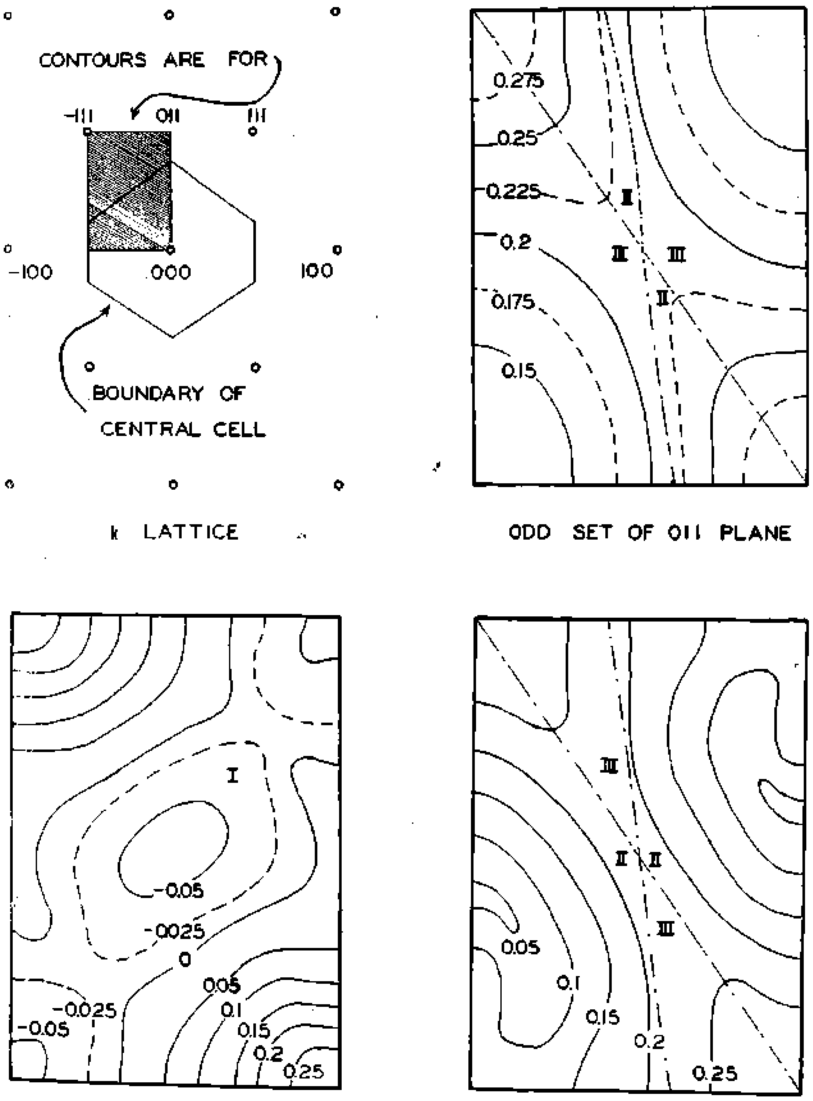
ODD SET OF 001 PLANE



EVEN SET

001 Plane

PLATE V.



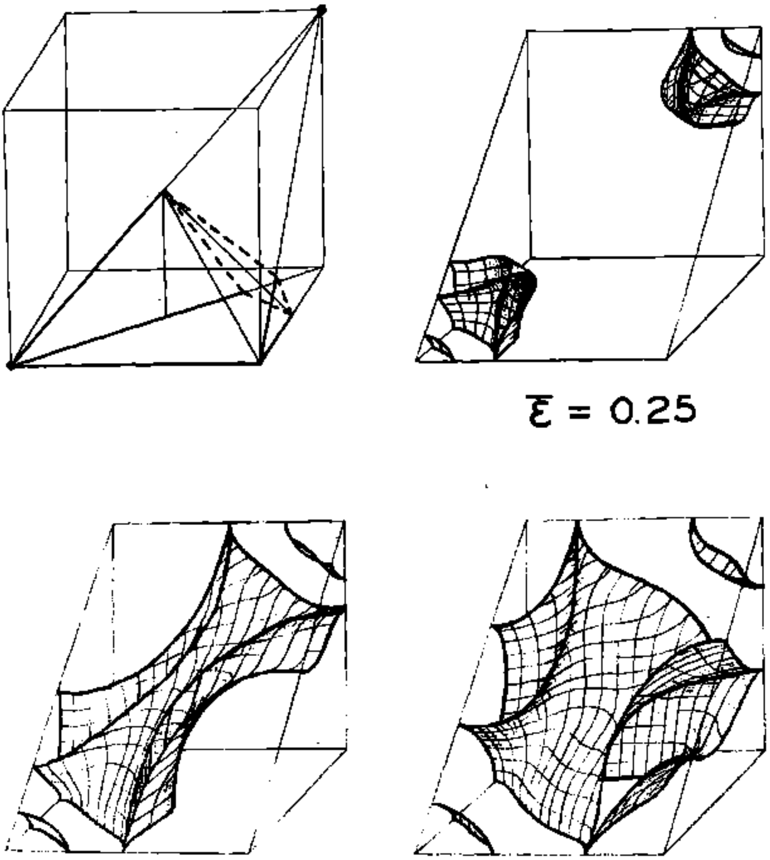
k LATTICE

ODD SET OF 011 PLANE

EVEN SET

$01\bar{1}$ Plane

PLATE VI.

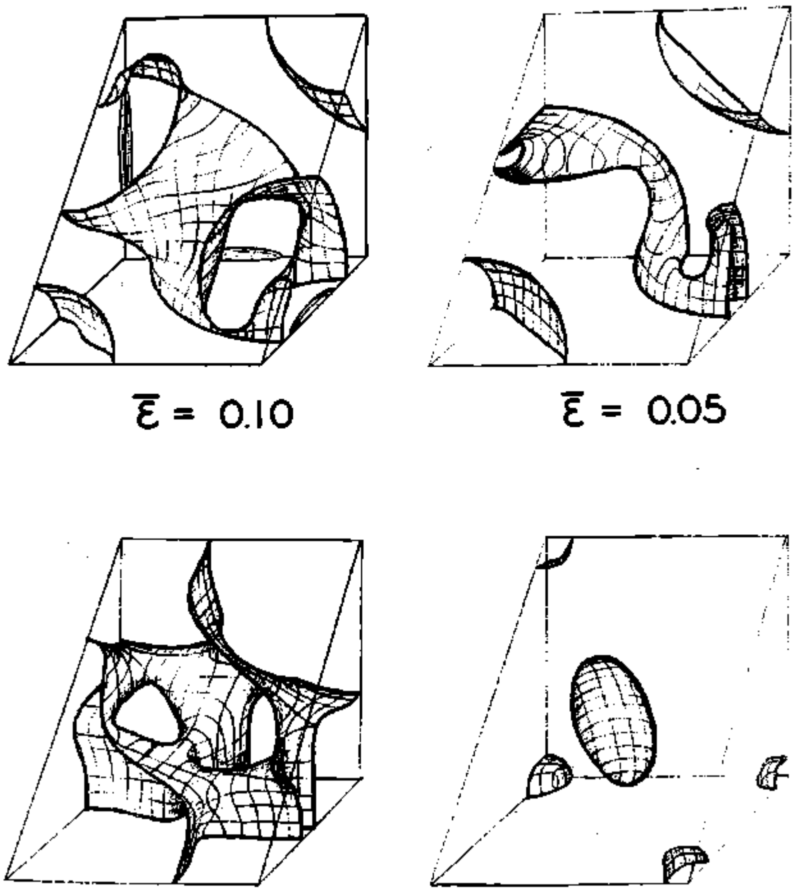


$\bar{\varepsilon} = 0.25$

$\bar{\varepsilon} = 0.20$

$\bar{\varepsilon} = 0.15$

PLATE VII.



$\bar{\varepsilon} = 0.10$

$\bar{\varepsilon} = 0.05$

$\bar{\varepsilon} = 0.00$

$\bar{\varepsilon} = -0.05$

PLATE VIII.

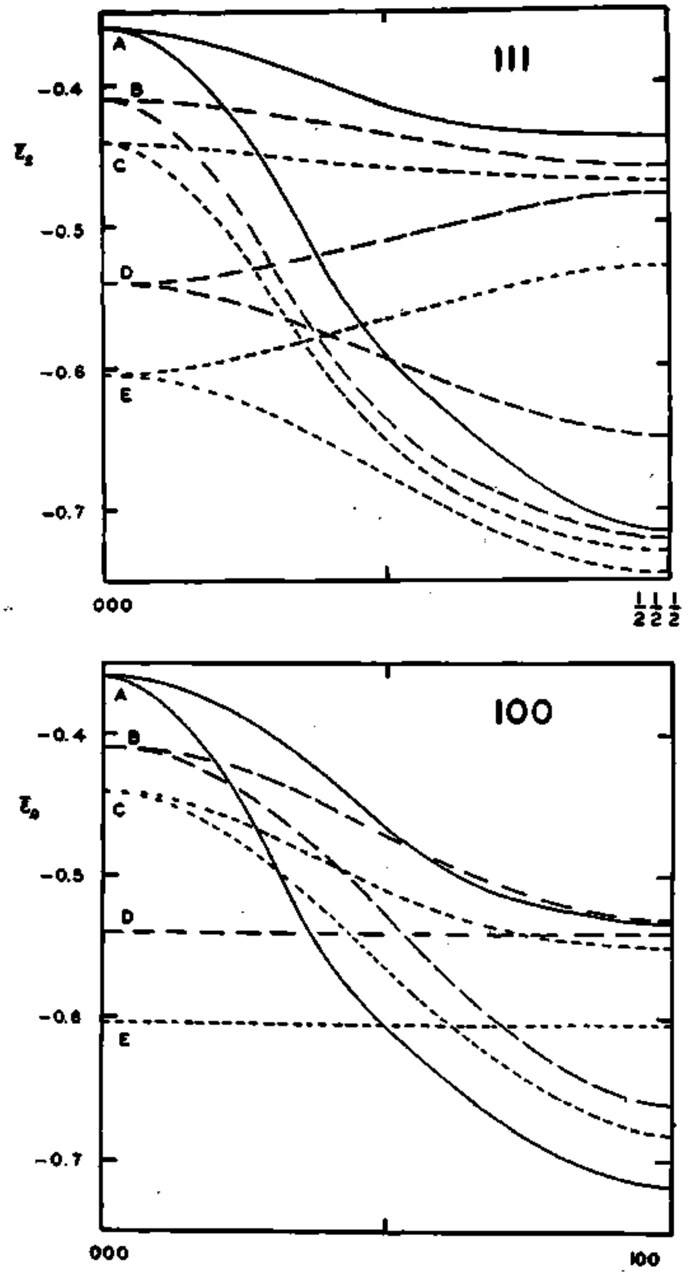

111
A
B
C
D
E
-0.4
-0.5
-0.6
-0.7
$\bar{E}_s$
000
$\frac{1}{2}\frac{1}{2}\frac{1}{2}$
100
A
B
C
D
E
-0.4
-0.5
-0.6
-0.7
$\bar{E}_0$
000
100

PLATE IX.

EXPLANATION OF PLATE 9

A Cl-Cl join

B Cl-Cl-Na join

$\bar{\varepsilon}_{\ell} = \bar{\varepsilon}_n + 0.58$

C Cl-Cl-Na join

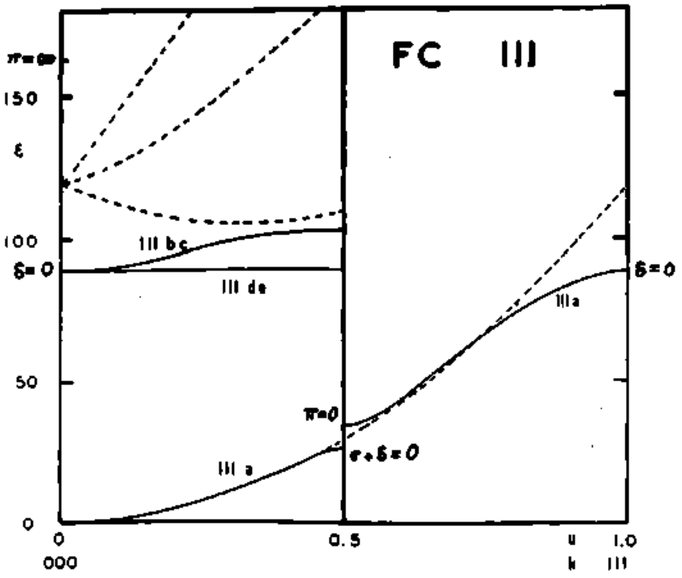
$\bar{\varepsilon}_{\ell} = \varepsilon_n + 0.28$

D Na-Cl join

$\bar{\varepsilon}_{\ell} = \bar{\varepsilon}_n + 0.58$

E Na-Cl join

$\bar{\varepsilon}_{\ell} = \bar{\varepsilon}_n + 0.28$


FC 111
π=∞
150
ε
100
δ=0
50
0
111 bc
111 de
π=0
111 a
σ+δ=0
δ=0
111a
0
0.5
u
k
1.0
000
111

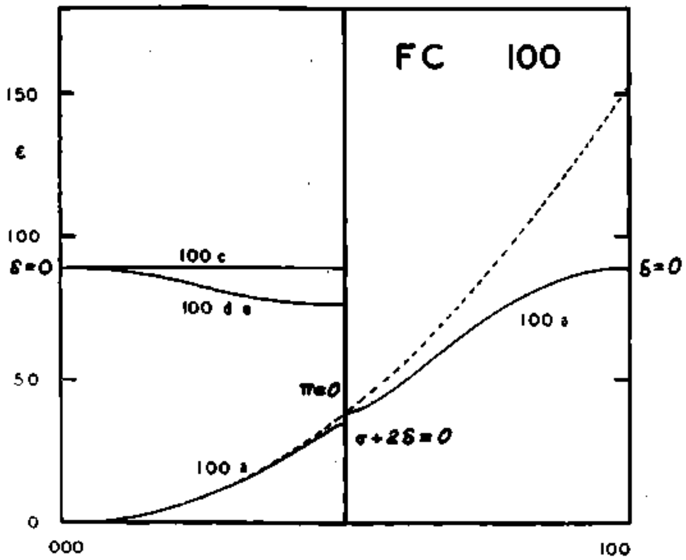
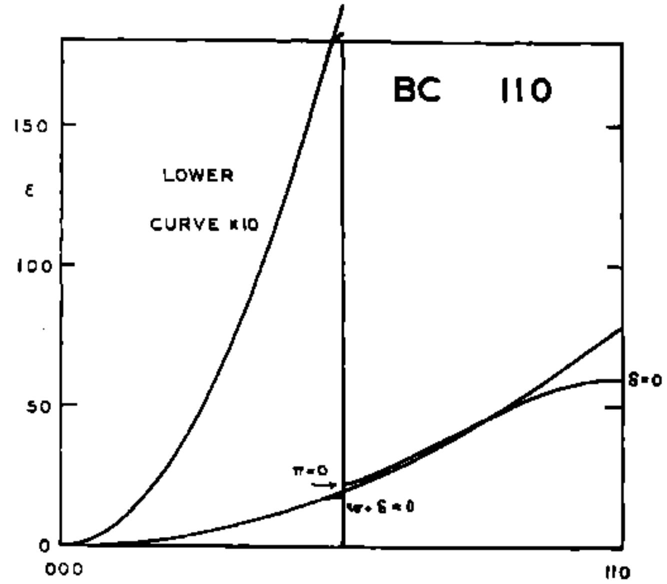

FC 100
150
ε
100
δ=0
50
0
100 c
100 d e
π=0
100 a
σ+2δ=0
δ=0
100 a
000
100

PLATE X.


BC 110
150
ε
100
50
0
000
110
LOWER
CURVE ×10
π = 0
π + δ = 0
δ = 0

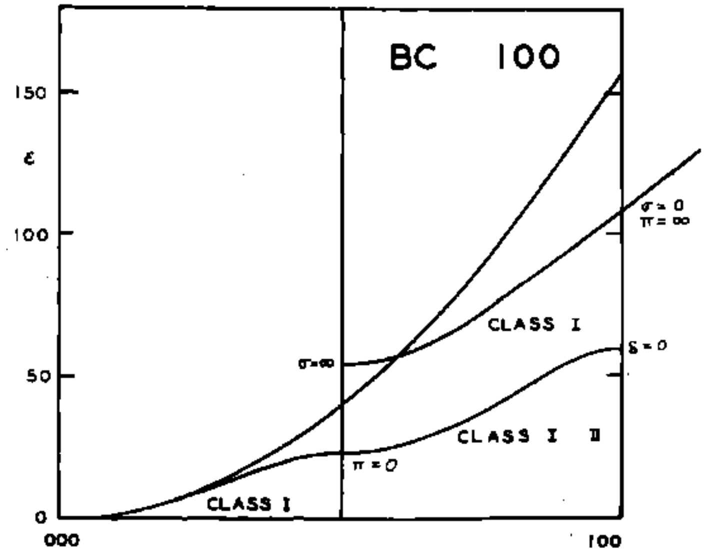

BC 100
150
ε
100
50
0
000
100
σ = 0
π = ∞
CLASS I
σ = ∞
δ = 0
CLASS I II
π = 0
CLASS I

PLATE XI.

Biographical Note

Born February 13, 1910.

B.Sc., California Institute of Technology, 1932.

Teaching Fellow at Massachusetts Institute of Technology, 1932-1936.

Publications:

"An Electron Microscope for Filaments: Emission and Adsorption by Tungsten Single Crystals." (With R. P. Johnson.) Phys. Rev. 49, 436 (1936).

"Application of An Electrical Timing Device to Certain Mechanics Experiments." Am. Physics Teacher 4, 76 (1936).

Member of Tau Beta Pi, Sigma Xi, and the American Physical Society.

Wm Shockley,

ABSTRACT

The purpose of this thesis has been to extend the methods of calculation of wave functions in solids and to investigate the applications of these wave functions. The point of view has been that of the modified Hartree-Fock scheme of calculating wave functions developed by Wigner and Seitz,[*] together with the Slater[**] method of calculating excited states.

In particular, detailed computations have been made for the highest filled band in crystalline sodium chloride (rock salt), which originates from the completed 3p shell of the Cl^- ion. In the process of this work, new methods were required in order to treat the type of boundary conditions arising for the case of two different kinds of atoms. Three different approximations, which may be characterized by the joining conditions, have been investigated. The most exact of these involves satisfying the Slater boundary conditions (continuity of ψ, and the component of $\nabla\psi$ along the interatomic line) at the midpoint of both the 110 type inter-chlorine line and the 100 type chlorine-sodium line. The approximation obtained by using the Cl-Na points alone differs markedly from this in its energy contours and is unsatisfactory for various

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

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

other reasons. Another approximation is obtained by neglecting the Na-Cl points and using the Cl-Cl points alone. Although this formulation would obviously be inadequate for the bands arising from Na levels, its results are quite close to those of the most complete method where that method has been worked out. It also has the advantage of leading to the face-centered lattice conditions which have already been investigated by Krutter.*

In the course of investigating the face-centered lattice, several new methods of increasing the information concerning the energy contours have been developed. It has been found possible to make calculations for small values of the wave vector, k, for cases in which it is impractical to carry out the details of the Slater method for larger values of k . Several new reductions of the general Slater determinant have been found which allow the energy contours to be drawn throughout space with a good deal more confidence than before.

It is possible to test the adequacy of the Slater method by applying it to the one case for which the correct solution is actually known: that of the case of zero potential which gives rise to plane waves. This test has been carried out for the important directions in body and face-centered lattices. For momenta within the first Brillouin zone, the agreement is excellent. For the outer zones, it is quite unsatisfactory and indicates definitely that some other

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*H. M. Krutter, Phys. Rev. 48, 664 (1935).

method must be employed there to obtain accurate results.