

HOLE BANDS IN NaCl TYPE CRYSTALS

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The energy and state function of a NaCl type cubic crystal with a single electron removed (with a hole) are considered in the Fock many-electron approximation assuming tight binding. It is shown that three hole bands exist which are contiguous for  $K = 0$ , corresponding to a stationary (but not minimal) value of the crystal energy. The dependence of the energy  $E$  on  $K$  in the vicinity of  $K = 0$  is anisotropic and is not of a tensor nature. The band of the lightest holes is important for conduction. This band has four absolute minima for values of  $K\{\pm \pi/d; \pm \pi/d; \pm \pi/d\}$  and three relative minima for  $K\{\pm 2\pi/d; 0; 0\}$ ,  $\{0; \pm 2\pi/d; 0\}$  and  $\{0; 0; \pm 2\pi/d\}$ .

Values of the effective masses when  $K = 0$  are given for various directions of  $K$  and the effective mass tensor for the afore-mentioned extremal values is written out. Numerical results are given for KCl.

1. STATEMENT OF THE PROBLEM AND BASIC ASSUMPTIONS

WE shall consider a binary cubic ionic crystal of the NaCl type with one electron removed. We shall assume tight binding, i.e., the hole will be regarded as localized close to halogen sites. This is permissible because of the large energy required for double ionization of alkali metal atoms by comparison with halogen atoms.

As in other papers by the author<sup>1,2</sup> we shall use  $r_s^l$  to denote the equilibrium position of an  $s$ -type ion in the  $l$ -th cell ( $s = 1, 2$  for + and - ions).  $\rho_s^{\lambda}$  will denote the set of  $3N_s$  coordinates of the  $N_s$  electrons of ion  $s, l$  ( $\lambda$  is the permutation index of the electrons in the crystal), and  $\rho_{n_s}^l$  will denote the radius vector of the  $n_s$ -th electron ( $n_s = 1, 2, \dots, N_s$ ) with respect to the nucleus at  $r_s^l$ . Because of the translational symmetry of the crystal and the corresponding degeneracy the  $\Psi$  function of the crystal is taken in the form

$$\Psi_K = A \sum_{l=1}^M e^{iKr_s^l} \Psi_s^l, \tag{1}$$

where  $\Psi_s^l$  is an auxiliary many-electron function which is the antisymmetrized product of the functions of all ions  $\psi_s^l$ , including the function  $\phi_s^l$  of the ion which lacks a single electron (see Ref. 1). The wave functions  $\psi_s^l$  and  $\phi_s^l$ , of individual ions as well as of ions and the atom, will be considered

as orthogonal in the same sense as in Ref. 1.

The Hamiltonian of the system will consist of the sum of the Hamiltonians of the individual ions and of interactions between different ions. Since the hole moves only about the halogen ions (the tight binding assumption) its energy will be determined by the exchange integrals of neighboring halogen ions. In calculating these integrals we have neglected the exchange of electrons in the  $p$  valence shell with inner electrons, i.e., we have considered<sup>3</sup> only 6 (or 5) of the outermost electrons for nuclear charge  $Z = 5$ . Since the Hamiltonian is independent of spin the wave functions of atom and ion which we use are those of Fock<sup>4</sup> for many-electron atoms. We thus have

$$\Psi_s^l(\rho_s^l) = \frac{1}{\sqrt{720}} \sum_1^{20} (-1)^{\nu\alpha} \alpha(i) \alpha(j) \alpha(k) \beta(l) \beta(m) \beta(n) \times \begin{vmatrix} \psi_x(i) & \psi_y(i) & \psi_z(i) \\ \psi_x(j) & \psi_y(j) & \psi_z(j) \\ \psi_x(k) & \psi_y(k) & \psi_z(k) \end{vmatrix} \begin{vmatrix} \psi_x(l) & \psi_y(l) & \psi_z(l) \\ \psi_x(m) & \psi_y(m) & \psi_z(m) \\ \psi_x(n) & \psi_y(n) & \psi_z(n) \end{vmatrix}. \tag{2}$$

Here

$$\psi_x(n) = R(\rho_{n_s}^l) \sin \vartheta_{n_s}^l \cos \varphi_{n_s}^l, \tag{3}$$

$$\psi_y(n) = R(\rho_{n_s}^l) \sin \vartheta_{n_s}^l \sin \varphi_{n_s}^l, \quad \psi_z(n) = R(\rho_{n_s}^l) \cos \vartheta_{n_s}^l$$

are the normalized one-electron functions of the  $p$  state of the  $n_s$ -th electron of ion  $s, l$  in the coordinate system whose center is as the corresponding nucleus. As the functions in (3) are spatially asymmetrical, the directions of the axes must be specified. We shall assume hereinafter

that function (1) is given in the coordinate system where the axes of all ions are parallel to each other and to the edges of the crystal, as shown in Fig. 1.

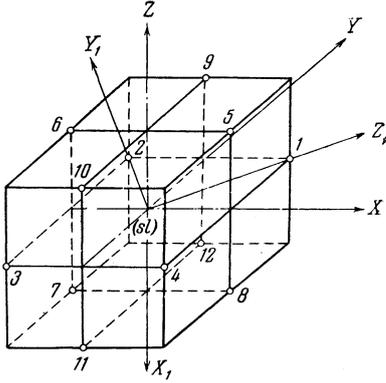


FIG. 1

The form of the radial part  $R(r)$  of (3) depends on the crystal and in first approximation on the halogen. For KCl,  $R(r)$  in the region that is important for exchange between ions is taken to agree with Hartree's results<sup>5</sup> for the 3p shell of Cl. For lack of other information we assume that the radial function is identical for the atom and ions in the crystal and for chlorides is given by

$$R(r) = (3\alpha^3/\pi) e^{-\alpha r} \quad \text{with} \quad (4)$$

$$\alpha d/2 = 4.835;$$

where  $d/2 = 3.145 \times 10^{-8}$  cm is the lattice constant of KCl. For fluorides Eq. (4) can also be used, with  $\alpha = 1.481 \times 10^8$  cm<sup>-1</sup>, but with less accuracy; in this case it is better to use

$$H_{\kappa} = \frac{2e^2}{d} \left[ B - \sum_{\nu=1}^{12} I^{\nu\nu} \exp \{i\kappa(r_s^l - r_s^{\nu})\} \right]. \quad (5)$$

In (2)  $\alpha(n)$  and  $\beta(n)$  denote the usual one-electron spin eigenfunctions of the corresponding electrons<sup>6</sup> (of different orientations). The number of these functions corresponds to the total zero (saturated) spin of a halogen ion. The summation in (2) is performed over all permutations of six electrons  $i, j, \dots$  with two spins  $\alpha, \beta$ , of which 20 are possible. The factor  $(-1)^{\nu}$  is +1 or -1 depending upon whether the given term is obtained by an even or odd number of electron permutations from some initial order such as 1, 2, ..., 6.

In the atom one electron of the p shell is absent, so that its electron functions are triply degenerate and their linear combination must be used. The total spin of the crystal is unchanged (and is assumed to be negative). Then for the atom, using the previous notation,

$$\psi_{am} \equiv \varphi_s^l(\rho_s^l) = \frac{1}{\sqrt{120}} \sum_1^{10} (-1)^{\nu} \alpha(j) \alpha(k) \beta(l) \beta(m) \beta(n)$$

$$\times \begin{vmatrix} b & c & a \\ \psi_x(j) & \psi_y(j) & \psi_z(j) \\ \psi_x(k) & \psi_y(k) & \psi_z(k) \end{vmatrix} \begin{vmatrix} \psi_x(l) & \psi_y(l) & \psi_z(l) \\ \psi_x(m) & \psi_y(m) & \psi_z(m) \\ \psi_x(n) & \psi_y(n) & \psi_z(n) \end{vmatrix}; \quad (6)$$

here  $b, c, a$  are coefficients, so far unknown, of the linear combination of mutually-orthogonal functions (minors of the determinant) which satisfy the normalization condition

$$|a|^2 + |b|^2 + |c|^2 = 1. \quad (7)$$

They will be determined subsequently by minimizing the total energy of the system.

A check of the orthogonality of (4) and (6) for KCl shows that  $I_{\text{orth}} = 5.2 \times 10^{-4}$  for two ions and  $\leq 5 \times 10^{-3}$  for an atom and an ion.

## 2. TOTAL ENERGY AND EXCHANGE INTEGRALS

The average energy, using the function (1), is

$$\bar{H}_{\kappa} = \sum_{\alpha_1} \dots \sum_{\alpha_N} \int \Psi_{\kappa}^* \hat{H} \Psi_{\kappa} d\tau$$

$$= \frac{1}{M} \sum_i \sum_{i'} \exp \{i\kappa(r_s^i - r_s^{i'})\} \bar{H}_{ss}^{ii'}. \quad (8)$$

The diagonal term is

$$\bar{H}_{ss}^{ii} = \int \Psi_s^{i*} \hat{H} \Psi_s^i d\tau = \frac{2e^2}{d} B = 2 \frac{\alpha e^2}{d} + V_{\text{Cl}}^- + U_+, \quad (9)$$

where  $\alpha = 1.747$  is the Madlung constant,  $V_{\text{Cl}}^- = 3.72$  eV is the electron affinity of Cl (Ref. 7), and  $U_+$  is the eigenvalue of the energy of a hole in the field of the ions which it has polarized. As shown in Ref. 2,  $U_+ = -1.352$  eV for KCl. Hence we obtain for (9) 10.4 eV.

The offdiagonal terms  $\bar{H}_{ss}^{ll'}$  differ from zero only when  $sl$  and  $sl'$  are nearest neighbors. We denote

$$\bar{H}_{ss}^{ll'} = \int \Psi_s^{l'*} \hat{H} \Psi_s^l d\tau = -\frac{2e^2}{d} I^{ll'} \delta_{l, l' \pm 1}, \quad (10)$$

where  $\delta_{l, l' \pm 1} \neq 0$  only for the 12  $l'$  of the nearest like neighbors of the site  $sl$ . Then

$$\bar{H}_{\kappa} = \frac{2e^2}{d} \left[ B - \sum_{\nu=1}^{12} I^{\nu\nu} \exp \{i\kappa(r_s^l - r_s^{\nu})\} \right]. \quad (11)$$

Substituting (1) into (10) and taking into account the orthogonality of the  $\psi$  functions,<sup>1</sup> we obtain

$$I^{ll'} = -\frac{d^2}{2} \sum_{\alpha_1} \dots \sum_{\alpha_{11}} \int \Psi_s^{l'*} \varphi_s^l \left\{ -\frac{\hbar^2}{2me^2} \Delta_{\rho} \right.$$

$$\left. - \sum_{s'', l''} V_{s''} (\rho - r_{s''}^{l''}) - Z_s / |\rho - r_s^l| - Z_s / |\rho - r_s^{l'}| \right.$$

$$\left. + \sum_{n_s=1}^5 1/|\rho - \rho_{n_s}^l| + \sum_{n_s=1}^5 1/|\rho - \rho_{n_s}^{l'}| \right\} \varphi_s^l \varphi_s^{l'} d\tau. \quad (12)$$

In (12) the electron whose radius vector is denoted by  $\rho$  passes from site  $sl$  to site  $sl'$ . The first term in the braces is its kinetic energy operator, the second term is the potential of all ions of the crystal except  $sl$  and  $sl'$  at  $\rho$ , and the last

four terms describe the interaction of the indicated electron with nuclei and with the other five electrons at sites  $sl$  and  $sl'$ . Here  $Z_S = 5$  is the effective charge of the halogen nucleus, since part of the charge is screened by inner electrons, the interaction with which we are neglecting in the exchange integral.

We shall add a second term to the Madelung potential in the brace of Eq. (12). For this purpose we must add inside the braces terms which are the average quantum mechanical potentials at the point  $\rho$  of ordinary halogen ions at the sites  $sl$  and  $sl'$ . The exchange integral of the Madelung potential is zero, by virtue of the latter's constancy within the important region of integration between ions and from the orthogonality condition. Since the ionic functions  $\psi_S^l$  have been antisymmetrized, all ions are equivalent and all components of their average quantum mechanical potentials are respectively equal. On the other hand, the integrals of the exact electron potentials depend on whether the spins at  $\rho$  and  $\rho_{n_S}^l$  (or  $\rho_{n_S}^{l'}$ ) are equal or different.

There are two of the first kind in each ion and three of the second kind. Therefore

$$I^{ll'} = \frac{d}{2} \sum_{\sigma_1} \dots \sum_{\sigma_{11}} \int \psi_s^{l'*} \varphi_s^{l'*} \left\{ \frac{\hbar^2}{2me^2} \Delta_\rho + 12 \int \frac{|\psi_s^l|^2}{|\rho - \rho_{n_S}^l|} d\tau - \frac{4}{|\rho - \rho_{n_S}^l|} \right\} \left. \begin{array}{l} \text{same} \\ \text{spin} \end{array} \right\} \psi_s^l \varphi_s^{l'} d\tau \equiv T^{ll'} \quad (13)$$

$$- \frac{6}{|\rho - \rho_{n_S}^l|} \left. \begin{array}{l} \text{different} \\ \text{spin} \end{array} \right\} \psi_s^l \varphi_s^{l'} d\tau \equiv T^{ll'}$$

$$+ 12V_s^{ll'} - 4E_s^{ll'} - 6E_2^{ll'}.$$

To obtain the energy we must substitute into (11) the 12 exchange integrals of (12), and for this purpose (13) must be calculated.

The functions  $\psi$  and  $\varphi$  under the integral sign in (13) are the 3rd order determinants (2) and (6), whose elements (3) in each row are three "projections" of certain "vectors" on the coordinate axes. These "vectors" are of equal "length"  $R(r)$  with the exception of the "vector"  $a\{b; c; a\}$ , which is of "length" 1. The determinants are then analogous to "volumes." When the coordinate system is rotated the lengths of the vectors and magnitudes of the volumes are unchanged, and the projections of the vectors change in magnitude but not in form. Therefore in integrating (13) we can rotate the coordinate axes at will without changing the form of the integrands nor the magnitudes of the integrals. However,  $b, c, a$  then are transformed into  $b', c', a'$ , which are linear combinations of the original

quantities depending on the angles of rotation. We now rotate the coordinate axes in (13) so that the polar axis  $Z^{ll'}$  passes through the sites  $sl$  and  $sl'$  (Fig. 1). The new coefficients, which differ for different sites, are denoted by  $b^{ll'}, c^{ll'}, a^{ll'}$ . The  $I^{ll'}$  will be identical quadratic forms of their coefficients.

Simple calculations show that the terms  $V_S^{ll'}$  and  $E_2^{ll'}$  in (13) are identical (exchange with electrons of different spin is forbidden). The remaining term  $6V_S^{ll'}$  is also reduced by the Coulomb part  $4E^{ll'}$ . The general result<sup>3</sup> is

$$I^{ll'} = T^{ll'} + (6V_s^{ll'} - 4E_1^{ll'}) = D (|b^{ll'}|^2 + |c^{ll'}|^2) - E |a^{ll'}|^2 = D - (D + E) |a^{ll'}|^2, \quad (14)$$

where  $D$  and  $E$  are exchange integrals, i.e., constants of the crystal. In the case of crystals for which the radial part can be given in the form of (4), such as all chlorides, we have

$$E = -\frac{d}{6} \int \{Q(r_s^{l'}) + P(r_s^{l'})\} \psi_3^*(r_s^l) \psi_3(r_s^{l'}) d\tau, \quad (15)$$

$$D = \frac{d}{6} \int \{Q(r_s^{l'}) + P(r_s^{l'})\} \psi_1^*(r_s^l) \psi_1(r_s^{l'}) d\tau;$$

where

$$\psi_{1,2}(r) = \frac{R(r)}{V^{1/2}} \sin \vartheta e^{\pm i\varphi}; \quad \psi_3(r) = \psi_z(r); \quad (16)$$

$$Q(r) + P(r) = \frac{\hbar^2}{2me^2} \left( \alpha - \frac{2\alpha}{r} - \frac{2}{r^2} \right) + \frac{2\alpha}{5} \left[ \frac{5}{\rho} + \frac{6}{\rho^3} - e^{-2\rho} \left( 4\rho + 13 + \frac{17}{\rho} + \frac{12}{\rho^2} + \frac{6}{\rho^3} \right) - 8\rho^2 \text{Ei}(-2\rho) \right]. \quad (17)$$

Here  $\rho = \alpha r$  and  $\text{Ei}(-x)$  is the familiar tabulated function.<sup>8</sup>

For KCl with the already indicated values of  $\alpha$  and  $d$  we obtain

$$D = 0.9 \cdot 10^{-2}; \quad E = 4.6 \cdot 10^{-2}; \quad (18)$$

$$2e^2 D / d = 0.041 \text{ eV}; \quad 2e^2 E / d = 0.211 \text{ eV}.$$

For the other crystals which contain Cl the numerical difference from (18) should not be very large since their lattice constants are approximately the same.

Substituting (14) in (11), we obtain

$$\frac{d}{2e^2} \bar{H}_K = B - D \sum_{l'=1}^{12} \exp \{i\mathbf{k} \cdot (\mathbf{r}_s^l - \mathbf{r}_s^{l'})\} + (E + D) \sum_{l'=1}^{12} |a^{ll'}|^2 \exp \{i\mathbf{k} \cdot (\mathbf{r}_s^l - \mathbf{r}_s^{l'})\}. \quad (19)$$

For the determination of  $\bar{H}_K$  it is necessary to replace  $a^{ll'}$  by  $\{b; c; a\}$  for all sites. (The lat-

TABLE I. Coefficients of  $a\{b, c, a\}$

No. of site	Coordinates of site $l'$ , in units $d/2$			$\sqrt{2} \cdot b^{l'}$	$\sqrt{2} \cdot c^{l'}$	$\sqrt{2} \cdot a^{l'}$	No. of site	Coordinates of site $l'$ , in units $d/2$			$\sqrt{2} \cdot b^{l'}$	$\sqrt{2} \cdot c^{l'}$	$\sqrt{2} \cdot a^{l'}$
	$x$	$y$	$z$					$x$	$y$	$z$			
1	1	1	0	$-a$	$(-b+c)$	$(b+c)$	7	-1	0	-1	$(-b+a)$	$c$	$(-b+a)$
2	-1	1	0	$-a$	$-(b+c)$	$(-b+c)$	8	1	0	-1	$(b+a)$	$c$	$(-b+a)$
3	-1	-1	0	$-a$	$(b-c)$	$-(b+c)$	9	0	1	1	$(c-a)$	$-b$	$(c+a)$
4	1	-1	0	$-a$	$(b+c)$	$(b-c)$	10	0	-1	1	$-(c+a)$	$b$	$(-c+a)$
5	1	0	1	$(b-a)$	$c$	$(b+a)$	11	0	-1	-1	$-(c+a)$	$-b$	$(c-a)$
6	-1	0	1	$-(b+a)$	$c$	$(b-a)$	12	0	1	-1	$(c-a)$	$b$	$(-c+a)$

ter are determined from Fig. 1 and are listed in Table I.) When this has been done, using  $\mathbf{k} = \mathbf{K}d/2$ , we obtain, in the original coordinate system,

$$\frac{d}{2e^2} \bar{H}_{\mathbf{k}} = B - 4D \sum_{x \neq y} \cos k_x \cos k_y + 2(E + D) \left\{ \sum_{x \neq y} b^2 \cos k_x (\cos k_y + \cos k_z) - 2 \sum_{x \neq y} bc \sin k_x \sin k_y \right\} \quad (20)$$

3. DETERMINATION OF THE COEFFICIENTS  $b, c, a$  AND OF THE ENERGY AS A FUNCTION OF  $\mathbf{K}$

From the minimum of (20), taking into account the normalization of  $\mathbf{a}$  (7), we obtain for  $\mathbf{a}$  three linear homogeneous equations which can be solved if their determinant is zero:

$$\Delta_{\mathbf{k}} = \begin{vmatrix} 2 \cos k_x (\cos k_x + \cos k_z) - \lambda & -2 \sin k_x \sin k_y & -2 \sin k_x \sin k_z \\ -2 \sin k_x \sin k_y & 2 \cos k_y (\cos k_x + \cos k_z) - \lambda & -2 \sin k_y \sin k_z \\ -2 \sin k_x \sin k_z & -2 \sin k_y \sin k_z & 2 \cos k_z (\cos k_x + \cos k_y) - \lambda \end{vmatrix} = 0 \quad (21)$$

There are three real roots  $\lambda_{1,2,3}$  of (21), giving three hole bands that do not generally coincide. The roots  $\lambda$  and the coefficients  $b, c, a$  depend essentially on  $\mathbf{K}$  and are independent of the crystal parameters  $D$  and  $E$ ; they are identical for all cubically symmetrical crystals with  $p$  electrons.\*

In the general case the energy can be expressed in terms of the exchange integrals  $D$  and  $E$  [Eqs. (14) and (15)]. The values of  $E$  and  $D$  vary with the crystal but are always positive with  $E > D$ , because  $E$  (15) is derived from  $\psi_3 = \psi_2$ , which contains  $\cos \vartheta$ , while  $D$  is derived from  $\psi_1$  and  $\psi_2$ , which contain  $\sin \vartheta$  and therefore overlap much less. In KCl, for example,  $E/D = 5$ . Therefore for alkali-halide cubic crystals it is possible to establish the general approximate character of the dependence of the energy on the wave vector  $\mathbf{K}$  in hole bands by assuming  $D \approx 0$ . Such "reduced" curves for one direction of the wave vector  $\mathbf{K}$  in units of  $10E$  are plotted with discontinuous lines in Fig. 2.  $\mathbf{K}$  is taken along the diagonal of the coordinate cube. The same figure shows corresponding curves of the energy for KCl, in eV by continu-

\*Nothing is changed when the integer vectors of the reciprocal lattice are added to  $\mathbf{K}$ . When the sign of a component of  $\mathbf{K}$  is reversed, the sign of the corresponding component of  $\mathbf{a}$  is reversed.  $\lambda$  and  $\bar{H}_{\mathbf{K}}$  remain unchanged.

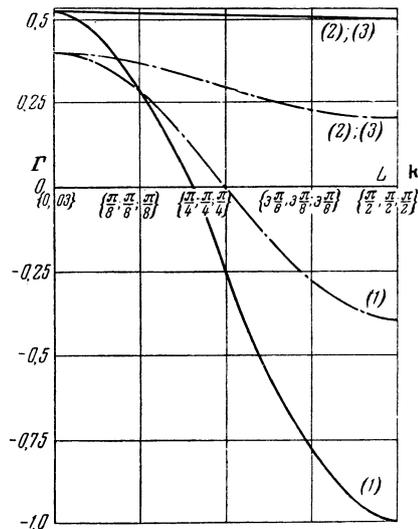


FIG. 2

ous lines. The usual notation<sup>9</sup> is used to indicate points on the boundary of the first Brillouin zone, namely the points  $\Gamma(0, 0, 0)$  and  $L(\pi/d, \pi/d, \pi/d)$ .

Table II contains analytic expressions for the branches of  $\bar{H}(\mathbf{K})$ . It can be seen that the curves in the figure essentially provide a qualitative description of the energy variation for all three branches. It can be regarded as established that

TABLE II. The energy  $\bar{H}_K$  as a function of the modulus of  $\mathbf{k}$ , for the directions of  $\mathbf{k}$  (0; 0; 1), (0; 1; 1), and (1; 1; 1)

Vector $\mathbf{k}$			No. of branches	$\lambda$	Vector $\mathbf{a}$			Energy $\frac{d}{2e^2} \bar{H}_K - B$	$\mu$ in the given wave vector direction			
$k_x$	$k_y$	$k_z$			$b$	$c$	$a$		At (0; 0; 0)		For $\alpha = \pi$	
									General form	For KCl	General form	For KCl
0	0	$k \equiv \alpha$	1 2;3	$4 \cos k$ $2(1 + \cos k)$	0 $b^2 + c^2 = 1$	0 0	1 0	$4[E \cos k - D(1 + \cos k)]$ $2[E(1 + \cos k) - D(1 + 3\cos k)]$	$-C(E - D)^{-1} \cdot 0.5$ $-C(E - 3D)^{-1}$	-1.14 -4.45	$0.5C(E - D)^{-1}$ $C(E - 3D)^{-1}$	1.14 4.45
0	$\frac{k}{\sqrt{2}} \equiv \alpha$	$\frac{k}{\sqrt{2}} \equiv \alpha$	1 2 3	$4 \cos \alpha$ $2[\cos \alpha + 1]$ $2[\cos \alpha + \cos 2\alpha]$	1 0	0 $\frac{1}{\sqrt{2}}$ $\frac{1}{\sqrt{2}}$	0 $-\frac{1}{\sqrt{2}}$ $\frac{1}{\sqrt{2}}$	$4 \cos \alpha [E - D(1 + \cos \alpha)]$ $2[E(1 + \cos \alpha) - D(2 \cos^2 \alpha - 1 + 3 \cos \alpha)]$ $2[E(\cos \alpha + \cos 2\alpha) - D(1 + 3 \cos \alpha)]$	$-C(E - 3D)^{-1}$ $2C(7D - E)^{-1}$ $-2C(5E - 3D)^{-1}$	-4.45 10.0 -0.84	$C(E + D)^{-1}$ $2C(E + D)^{-1}$ $-\frac{2}{3}C(E + D)^{-1}$	1.55 3.1 -1.0
$\frac{k}{\sqrt{3}} \equiv \alpha$	$\frac{k}{\sqrt{3}} \equiv \alpha$	$\frac{k}{\sqrt{3}} \equiv \alpha$	1 2;3	$4 \cos^2 2\alpha$ $2(1 + \cos^2 \alpha)$	$\frac{1}{\sqrt{3}}$ $\frac{1}{\sqrt{3}}$ $\frac{1}{\sqrt{3}}$	0 $a + b + c = 0$	0 $ac + ab + ac = -\frac{1}{2}$	$4[E \cos 2\alpha - D(1 + \cos^2 \alpha)]$ $2[E(1 + \cos^2 \alpha) - D(4 \cos^2 \alpha - \sin^2 \alpha)]$	$-\frac{3}{4}C(2E - D)^{-1}$ $-\frac{3}{2}C(E - 5D)^{-1}$	-0.77 -128	for $\alpha = \pi/2$ $\frac{3}{4}C(2E - D)^{-1}$ $\frac{3}{2}C(E - 5D)^{-1}$ for $\alpha = \pi/2$	0.77 128

in the crystals under consideration\* the energy minimum corresponds to  $\mathbf{k} \{ \pi/2, \pi/2, \pi/2 \}$  rather than to  $\mathbf{K} = 0$ . In the vicinity of  $\mathbf{k} \{ \pi/2, \pi/2, \pi/2 \}$  branch 1, which is important in all processes, lies  $6(E + D)$  (corresponding to 1.5 eV for KCl) below the other two branches. Therefore in crystal calculations involving holes, for which the present theory is employed, it is not essential to take the spin-orbit interaction into account, because the degeneracy at the unimportant minima of the 2nd and 3rd branches is thus removed while the main branch is only slightly shifted. The absolute minimum of the energy  $\bar{H}_K$  is that required for transferring an electron from the valence band to the vacuum. In our case this is  $\bar{H}_{K\min} = 10.4 - 1 = 9.4$  eV. This is in fair agreement with data on the fundamental absorption bands of alkali halides,<sup>10</sup> which for KCl give  $\lambda = 1320 \text{ \AA}$  or 10.4 eV.

Since the minimum energy corresponds to the edge of the Brillouin zone it is not unlikely that for localized hole states (such as hole F center) with  $\psi$  functions which, according to Ref. 1, can be written as linear combinations  $\Psi_S = \sum_l b_S^l \Psi_S^l$ , the minimum energy state will be similar to a p state, with coefficients  $b_S^l$  of opposite signs on the two sides of the defect. Indeed, this state will possess a minimum number of nodal surfaces.

\*The energy of the hole in all cases means the energy of the crystal. We have not used the concept of an "almost filled" valence band.

#### 4. EFFECTIVE MASS IN A HOLE BAND

We shall now expand the energy (21) in powers of  $\Delta \mathbf{k} = \mathbf{k} - \mathbf{k}_0$  in the vicinity of the stationary point  $\mathbf{k} = 0$  and the minima  $\mathbf{k}_0 \{ \pi/2; 0; 0 \}$  and  $\mathbf{k}_0 \{ \pi/2; \pi/2; \pi/2 \}$ , where  $\mathbf{k}$  is the dimensionless wave vector  $\mathbf{k} = d\mathbf{K}/2$ . As E. I. Rashba has noted, the existence of the stationary condition for  $\mathbf{K} = 0$  and of the extremals at  $\mathbf{k}_0 \{ \pi; 0; 0 \}$  and  $\mathbf{k}_0 \{ \pi/2; \pi/2; \pi/2 \}$  can be derived through group theory from considerations of symmetry.

1. About the point  $\mathbf{k}_0 \{ 0; 0; 0 \}$  (for small  $\mathbf{K}$ ),  $\lambda$  is given by

$$\varepsilon^3 + 4\varepsilon^2 + (5-3u)\varepsilon + (2-3u+5v) = 0, \quad (22)$$

where

$$\lambda = \lambda_0 + \varepsilon = 4 + \varepsilon;$$

$$u = \sum_{x+y} \xi^2 \eta^2, \quad v = \xi^2 \eta^2 \zeta^2; \quad \xi = \Delta k_x / |\Delta \mathbf{k}|.$$

Since (22) is a cubic equation, the energy cannot be expressed as an analytic function of  $\mathbf{K}$ . This results from the fact that for  $\mathbf{K} = 0$  all three bands are contiguous, i.e., this is a case of degeneracy. But here also we can introduce the effective hole mass  $m_+$  and the dimensionless mass  $\mu = m_+/m$  (which is not a tensor) depending on the direction of  $\mathbf{K}$  through the equation  $\hbar^2/m_+ = \partial^2 |E(\mathbf{K})| / \partial |\mathbf{K}|^2$ . The values of  $\mu$  for a number of directions of  $\mathbf{k}$  in KCl are given at the end of Table III.

2. Near the point  $\mathbf{k}_0 \{ \pi; 0; 0 \}$  in the branches of light holes, for which  $\bar{H}_{\mathbf{k}_0} - (2e^2/d)B = -4E$ ,

**TABLE III.** Variation of the energy in the vicinity of extremals inside of the Brillouin zone

Direction of $\mathbf{K}$			No. of branches	Energy $\frac{d}{2e^2} \bar{H}_{\mathbf{K}} - B$ in the vicinity of the extremal	$\mu$ for KCl	Kind of extremal
$k_x$	$k_y$	$k_z$				
0	$\alpha$	$\alpha$	2	$2[E(1+C_2) - D(2C_2^2 - 1 + 3C_2)]$	-6.3	max
			3	$2[E(C_3 + \cos 2\alpha_3) - D(3C_3 + 1)]$	0.16	min
0	$\alpha - k$	$\alpha + k$	2	$\bar{H}_0 - k^2 [3.5E + 1.5D(1 - C_2)]$	-6.08	max
			3	$\bar{H}_0 + k^2 [4D(1 + C_3) + (E + D)(3 - C_3^2)]$	10.12	min
$\delta \neq 0$	$\alpha$	$\alpha$	2	$\bar{H}_0 - \delta^2 C_2 (E - 3D)$	-193	max
			3	$\bar{H}_0 - \delta^2 \left[ -4C_3 D + \frac{B}{A} (E + D) \right]$	-7.6	max

Here  $\alpha_2 = \arccos \frac{1}{4} \left( -3 + \frac{E}{D} \right)$ ;  $\alpha_3 = \arccos -\frac{1}{4} \left( 1 - 3 \frac{D}{E} \right)$ ;  $C = \cos \alpha$ ;  $A = 1 + C - 2C^2$ ,  $B = (AC + 4 - 4C^2)$

$$\bar{H}_{\mathbf{k}} - H_{\mathbf{k}_0} = (\Delta \mathbf{k})^2 \{ E + D + (E - 3D) \xi^2 \}. \quad (23)$$

Thus the constant energy surface is an ellipsoid of revolution which is oblate along the  $x$  axis of rotation. The effective mass is a tensor; for KCl

$$\begin{aligned} \mu_{xx} &= C / (2E - D) = 1.15; & \mu_{yy} \\ &= \mu_{zz} = C / (E + D) = 1.55; & C = 8.51 \cdot 10^{-2}. \end{aligned} \quad (24)$$

An analogous expansion with respect to  $\Delta \mathbf{k}$  at the same point for the other two (degenerate) branches gives, in virtue of the non-analyticity,

$$\begin{aligned} \Delta H_{\mathbf{k}} &= (\Delta \mathbf{k})^2 \{ -4D\xi^2 + (E + D) \\ &\times \{ (\xi^2 - \zeta^2) c_0^2 + (\xi^2 - \eta^2) a_0^2 - 4a_0 c_0 \xi \eta \} \}, \end{aligned} \quad (25)$$

where

$$\begin{aligned} a_0^2 &= \left[ 1 + \frac{\xi^2 - \eta^2 - \varepsilon}{\xi^2 - \zeta^2 - \varepsilon} \right]^{-1}; & c_0^2 &= \left[ 1 + \frac{\xi^2 - \zeta^2 - \varepsilon}{\xi^2 - \eta^2 - \varepsilon} \right]^{-1}; \\ 2\varepsilon &= 2\xi^2 - \zeta^2 - \eta^2 \pm \sqrt{\zeta^4 + \eta^4 + 14\eta^2 \zeta^2}. \end{aligned}$$

The numerical values of  $\Delta \bar{H}_{\mathbf{k}}$  and  $\mu$  for these branches can be obtained only for specific values of  $\Delta \mathbf{k}$ , i.e., when  $\xi, \eta$  and  $\zeta$  are given. For example, with  $\Delta \mathbf{k} \{ 0; \Delta k; 0 \}$ , i.e.,  $\xi = \zeta = 0$ ,  $\Delta \bar{H}_{\mathbf{k}}$  has the two values 0 and  $-(E + D) (\Delta \mathbf{k})^2$ , which in KCl correspond to the effective masses  $\mu_1 = \infty$ ;  $\mu_2 = -1.55$ . In the direction  $(1; 0; 0)$

$$\mu_1 = \mu_2 = C / (E - 3D) = 4.45.$$

**3. In the vicinity of the most important point  $\mathbf{k}_0 \{ \pi/2; \pi/2; \pi/2 \}$  for which  $\bar{H}_{\mathbf{K}_0} - (2e^2/d) B =$**

$-4(E + D)$ , similar calculations lead to

$$\bar{H}_{\mathbf{k}} - \bar{H}_{\mathbf{k}_0} = (\Delta \mathbf{k})^2 \frac{4}{3} \{ D + E + (E + 4D) \sum_{x+y} \xi \eta \}. \quad (26)$$

The constant energy surface is again an ellipsoid of revolution, which is more oblate than the preceding one and has its axis along the diagonal of the coordinate cube;  $\mu$  is again a tensor. Along the diagonal of the coordinate cube, with  $\xi = \eta = \zeta$ ,

$$\mu = \mu_{\min} = \frac{6.38 \cdot 10^{-2}}{(2E + 5D)} = 0.47,$$

while perpendicular to the diagonal, with  $\xi + \eta + \zeta = 0$ ,  $\mu = 4.56$ .

Thus in the principal hole band there exists strong anisotropy of the hole effective masses, which are positive. The principal role in conduction and in other effects is played by light holes.

In addition to these three points extremals were also found at two points on the less important branches of Table III. The locations and character of these extremals depend on  $E$  and  $D$ , but they were not investigated in detail. In Table IV, which gives the band widths, these extremals provide the top of band 2 and the bottom of band 3.

A simplified calculation of the hole bands was also carried through in which  $I^{\text{ell}}$  was calculated<sup>10</sup> not by means of the functions (2), (3), and (6), but using linear combinations of simplified, spherically symmetrical one-electron functions of the form

$$\psi_s^i(\rho_s^i) = \varphi(\rho_s^i) \chi(\rho_{n_s}^i), \quad (27)$$

TABLE IV. Locations and magnitudes of the absolute extremals in each band and the widths of the bands

No. of band	Location of maximum*			Location of minimum*			Maximum energy		Minimum energy		Width of band	
	$k_x$	$k_y$	$k_z$	$k_x$	$k_y$	$k_z$	in KCl	General form	in KCl	General form	in KCl	General form
	in KCl			in KCl			General form	General form	General form	General form	General form	General form
1	0	0	0	$\frac{\pi}{2}$	$\frac{\pi}{2}$	$\frac{\pi}{2}$	0.52	$4(E-2D)$	$\frac{\pi}{2}$	$-4(E+D)$	-1.0	$4(2E-D)$
2	0	$\alpha_2$	$\alpha_2$	0	0	0	0.551	$\frac{1}{4} \left\{ 2E \left( \frac{E}{D} + 1 \right) - D \left( \frac{E^2}{D^2} - 17 \right) \right\}$	$\frac{\pi}{2}$	$4D$	0.46	$\frac{1}{4} \left\{ 2E \left( \frac{E}{D} + 1 \right) - D \left( \frac{E^2}{D^2} - 1 \right) \right\}$
3	0	0	0	0	$\alpha_3$	$\alpha_3$	0.52	$4(E-2D)$	$\alpha_3$	$\frac{1}{4} \left\{ 9E \left( 1 - \frac{D^2}{E^2} \right) + 2D \left( 1 + 9 \frac{D}{E} \right) \right\}$	-0.513	$\frac{1}{4} \left\{ E \left( \frac{25 - 9 \frac{D^2}{E^2}}{E^2} \right) - 2D \left( 15 - 9 \frac{D}{E} \right) \right\}$
Sph. Sym.	$\frac{\pi}{8}$	$\frac{\pi}{8}$	$\frac{\pi}{8}$	0	0	0	1.159	-14.4811	$\frac{\pi}{2}$	$4I$	-0.32	-18.41

\*The notation  $\alpha_2$  and  $\alpha_3$  is the same as in Table III.

where  $\varphi$  is the  $\psi$  function of the five electrons of the halogen ion, which function is left undetermined, and  $\chi$  is the  $\psi$  function of the sixth electron of the Cl atom, given by

$$\chi(\rho_{n_s}^l) = R(\rho_{n_s}^l) + \gamma \sum_{l'=1}^{12} R(\rho_{n_s}^{l'}); \quad (28)$$

here  $R(\rho)$  is given by (4) and  $\gamma$  was chosen to satisfy orthogonality.<sup>1</sup>

For KCl the result was  $I_{ll'} = I = -0.08$ . The nondegenerate energy obtained in this approximation has a minimum at  $K\{0, 0, 2\pi/d\}$ , and the band width in the last line of Table IV is in good agreement with the width of the important band in the foregoing stricter approximation.

The present paper presents a relatively simple method of calculating the hole bands of all halogenous crystals as well as of others, such as oxides, with NaCl type lattices. The author is preparing to calculate the bands for LiCl, NaCl, RbCl and AgCl as well as for the fluorides.

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- <sup>1</sup>T. I. Kucher and K. B. Tolpygo, J. Exptl. Theoret. Phys. (U.S.S.R.) 31, 1002 (1956), Soviet Phys. JETP 4, 883 (1957).
- <sup>2</sup>T. I. Kucher, J. Exptl. Theoret. Phys. (U.S.S.R.) 30, 724 (1956), Soviet Phys. JETP 3, 580 (1956).
- <sup>3</sup>S. I. Pekar, J. Exptl. Theoret. Phys. (U.S.S.R.) 18, 525 (1948).
- <sup>4</sup>V. A. Fock, (Jubilee Volume for the 30th Anniversary of the Great Socialist October Revolution) Acad. Sci. Press, M.-L., 1947, Ch. 1, p. 255.
- <sup>5</sup>D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) A156, 45 (1936).
- <sup>6</sup>A. Sommerfeld and H. Bethe, Elektronentheorie der Metalle, Handb. Phys. 24/2, 2d Ed., Berlin, 1933.
- <sup>7</sup>M. Born and K. Huang, Dynamical Theory of Crystal Lattices, Oxford, 1954, p. 3.
- <sup>8</sup>G. G. Gell-Mann, Quantum Chemistry (Russ. Transl.) ONTI, NKTP SSSR, M.-L., 1937.
- <sup>9</sup>Bouckaert, Smoluchowski, and Wigner, Phys. Rev. 50, 58 (1936).
- <sup>10</sup>N. F. Mott and R. W. Gurney, Electronic Processes in Ionic Crystals, Oxford, 1950.