

HOLE BANDS IN NaCl

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IN a recent paper¹ the author presented, in general form, a calculation of hole bands and of effective masses in them for NaCl-type crystals. The many-electron problem was solved by the Hartree-Fock method, in the tight-binding approximation. Because of the threefold degeneracy of the p-state of the halogen, there are three hole bands; the principal band has four minima at the points $\{\pm \pi/d; \pm \pi/d; \pm \pi/d\}$. Expressions were given previously¹ for the energy $E(\mathbf{k})$, the width of the principal band, the effective masses etc., in terms of two exchange integrals D and \mathcal{G} . The latter was calculated for KCl only in reference 1.

Analogous calculations (see reference 1) have been made for NaCl. The expression for the energy $E(\mathbf{k})$ as a function of the wave number \mathbf{k} is:

$$E(\mathbf{k}) = \frac{2e^2}{d} \{B - 4D \sum_{x \neq y} \cos k_x \cos k_y + 2(\mathcal{G} + D) [\sum_{x \neq y} b^2 \cos k_x (\cos k_y + \cos k_z) - 2 \sum_{x \neq y} bc \sin k_x \sin k_y]\}, \quad (1)$$

where

$$B = \text{const};$$

$$D = \frac{d}{6} \iiint \{Q(\mathbf{r}'_s) + P(\mathbf{r}'_s)\} \psi_1^*(\mathbf{r}'_s) \psi_1(\mathbf{r}'_s) d\tau = 1.57 \cdot 10^{-2},$$

$$\mathcal{G} = -\frac{d}{6} \iiint \{Q(\mathbf{r}'_s) + P(\mathbf{r}'_s)\} \psi_3^*(\mathbf{r}'_s) \psi_3(\mathbf{r}'_s) d\tau = 6.7 \cdot 10^{-2},$$

$$Q = \frac{\hbar^2}{2me^2} \left\{ \alpha^2 - 2\alpha/|\mathbf{r}'_s| - 2/|\mathbf{r}'_s|^2 \right\}, \quad (2)$$

$$P(\mathbf{r}) = \frac{2\alpha}{5} \left\{ \frac{5}{\rho} + \frac{6}{\rho^3} \right\},$$

$$-8\rho^2 \text{Ei}(-2\rho) - e^{-2\rho} \left[4\rho + 13 + \frac{17}{\rho} + \frac{12}{\rho^2} + \frac{6}{\rho^3} \right],$$

$$\psi_1(\mathbf{r}) = (3\alpha^3/\pi \sqrt{2}) e^{-\alpha r} \sin \vartheta e^{i\varphi},$$

$$\psi_3(\mathbf{r}) = (3\alpha^3/\pi) e^{-\alpha r} \cos \vartheta, \quad \rho = \alpha r.$$

For NaCl, as for KCl, $\alpha = \alpha(\text{Cl}) = 1.54 \times 10^8 \text{ cm}^{-1}$, but $d(\text{NaCl}) = 5.64 \times 10^{-8} \text{ cm}$.

The coefficients $\{b, c, a\} \equiv \mathbf{a}$ appear in Eq. (1) through the ψ function of the crystal

$$\psi = A \sum_{l=1}^M e^{i\mathbf{k}\mathbf{r}_s^l} \{b\psi_{s1}^l + c\psi_{s2}^l + a\psi_{s3}^l\}, \quad (3)$$

and in the last equation through the ψ function of the chlorine atom which is in the s_l -th site, the ground state of which is threefold degenerate.

These coefficients are determined (to satisfy the normalization condition $b^2 + c^2 + a^2 = 1$) from the condition for minimizing the energy [Eq. (1)], which leads to a third-order secular equation.

On substituting the values of b, c and a , found in this way, into (1) we obtain (see reference 1):

1. The width of the principal band

$$(2e^2/d) 4(2\mathcal{G} - D) = 2.17 \text{ ev.} \quad (4)$$

2. The effective-mass tensor at the point $\{\pi/d; \pi/d; \pi/d\}$:

(a) parallel to the diagonal of the cube [111] — the longitudinal mass

$$\mu = \mu_{\text{min}} = 6.38 \cdot 10^{-2} / (2\mathcal{G} - D) = 0.539,$$

(b) perpendicular to the cube diagonal — the transverse mass

$$\mu = \mu_{\text{max}} = 6.38 \cdot 2 \cdot 10^{-2} / (4\mathcal{G} + D) = 0.98.$$

Some of the increase in width of the principal band in NaCl, compared with KCl, comes from the smaller lattice constant of NaCl; the exchange integrals increase exponentially and this leads to a broadening of the band. Since the radial wave function of the Cl^- ion in Eq. (3) agrees with the Hartree value² only at distances $R > 1 \text{ \AA}$,¹ the calculations are more accurate for NaCl than for KCl.

Casella³ obtained a qualitatively similar result for the properties of hole bands in NaCl within the framework of the one-electron problem. A spherically-symmetrical potential was built up, by Slater's method, from the atomic 3p wave functions of argon, which Casella substituted for the ψ function of chlorine. As he took into account the threefold p-degeneracy of argon, his band behavior is analogous to reference 1. He obtained $\sim 1.2 \text{ ev}$ for the width of the principal hole band in NaCl, which is smaller than the value of 1.5 ev obtained by the present author for KCl.¹ Mention should be made of the old work of Shockley,⁴ in which the Wigner-Seitz cellular method gave the hole band width of NaCl as 4.4 ev.

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