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The Band Structure of Tetramethylammonium Pentaiodide*

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The iodine framework in the crystal is constructed by repeated translations of a group of two pentaiodide ions (repeating unit). The wave function of a repeating unit is calculated by Hückel's approximation, the resonance integrals between iodine 5 p orbitals being estimated empirically from the data for the gaseous iodine molecule. The wave functions of the crystal are set up in the form of Bloch functions from the wave functions of the repeating unit. The energy is calculated by a tight-binding approximation, the values of the resonance integrals between nearest neighboring repeating units being estimated from the wave functions of the repeating unit. The band-gap energy thus calculated is 1.26 eV., satisfactorily near the experimental value of 1.36 eV. This finding supports our conclusion (This Bulletin, **37**, 811 (1964)) that the iodine framework is primarily important in the electrical conductivity. It is also supposed that the band model may satisfactorily be applied to the conduction mechanism. The interactions of the Bloch functions of different energies being very slight, the band-gap energy is influenced at most in the order of 10^{-2} eV. even when level interactions are taken.

In previous papers,1) it was shown that the specific resistivities (20°C) and the band-gap energies of organic polyiodides decreased with the number of iodine atoms in the polyiodide anion. It was also shown that the iodine framework in the crystal structure was of primary importance in determining the electrical conductivity of polyiodides.

On the basis of the above discussion, we will now attempt to calculate the band structure of the tetramethylammonium pentaiodide crystal by the so-called tight-binding approximation, in order to see whether the band theory is applicable to the conduction mechanism of tetramethylammonium pentaiodide.

According to the X-ray analyses,2,3) the tetramethylammonium pentaiodide crystal is end-centered monoclinic with a space group C2/c and with $a_0=13.34$, $b_0=13.59$, $c_0=8.90$ Å, $\beta=107°50'$, and $Z=4$. The coordinates of the iodine atoms and the tetramethylammonium cations are also reported. Five iodine atoms as a group form a planar V-shaped pentaiodide ion. Pentaiodide anions are arranged nearly parallel to (001). Thus, the layer structure of iodine atoms exists in the crystal, as is shown in Figs. 1 and 2.

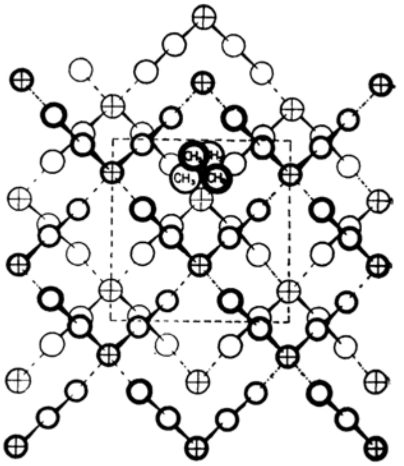

Fig. 1. Projection of the structure of tatramethylammonium pentaiodide along the c_0-axis onto the plane (001), showing the nets of iodine atoms in the upper plane and that in the lower plane. Nets are stacked so as to leave large holes for the cations. Only one is shown, upper center, though every hole is filled. The dashed line outlines the unit cell. (From Ref. 2)

The iodine framework in the crystal can be looked upon as being constructed simply by repeated translations of a group of two pentaiodide ions, as in Fig. 2. In order to calculate the band structure by tight-binding approximation, this repeating unit is first looked upon as a molecule and the wave function of the repeating unit is calculated as usual by the method of simple LCAO MO, the values of the resonance integrals between iodine atoms being estimated empirically from the data reported for the gaseous iodine molecule.

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1) a) S. Kusabayashi, H. Mikawa, S. Kawai, M. Uchida and R. Kiriyama, This Bulletin, **37**, 811 (1964); b) S. Kawai, R. Kiriyama, M. Uchida, S. Kusabayashi and H. Mikawa, ibid., **38**, 799 (1965); c) S. Kusabayashi and H. Mikawa, ibid., **38**, 1410 (1965).

2) R. J. Hach and R. E. Rundle, *J. Am. Chem. Soc.*, **73**, 4321 (1951).

3) J. Broekema, E. E. Havinga and E. H. Wiebenga, *Acta Cryst.*, **10**, 596 (1957).

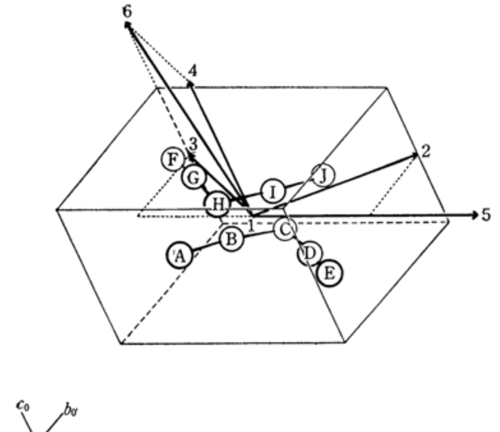

Fig. 2. Repeating unit consisting of two pentaiodide anions. Five vectors 2—6 connecting nearest neighboring repeating unit.

As the whole crystal is made up of simple repetitions of the three-dimensional translations of the repeating unit with the "molecular" wave functions thus calculated, the wave functions of the crystal can easily be set up in the form of Bloch functions from the "molecular" wave functions of the repeating unit. The energy band structure is next calculated by a tight-binding approximation as usual, the values of the resonance integrals between nearest neighboring repeating units needed for calculation being estimated from the "molecular" wave functions of the repeating unit.

The band structure thus calculated is shown in Fig. 4, the lower band being occupied and the upper vacant. The estimated band-gap energy is 0.455 β or 1.26 eV. This value is satisfactorily near to the experimental value of 1.36 eV.

Calculation

The Use of Only p Orbitals.—Several previous attempts have been made to explain the bonds in polyhalides by assuming the spd hybridization of the iodine atomic orbitals, the delocalization of the outer p orbital of the iodine atoms and so on.[4]

Pimentel[5] and Hach and Rundle[2] suggested the use of only the 5p orbitals; they based their argument on the linear form of triiodide ions. Havinga and Wiebenga[4] reviewed the structure of polyiodide ions and explained the observed configurations of atoms by means of the delocalization of the 5p orbitals, the valency angles being very close to 90° or 180° in all cases. Bersohn[6] and Rosenberg[7] have worked out the band structure of iodine on the assumption that only p orbitals are involved.

In such circumstances, only the 5p orbitals were used in the present calculation of the pentaiodide ion.

The Coordinates of the Iodine Atoms.—In our calculation of the band structure, the coordinates of the iodine atoms were estimated by the parameter reported in Ref. 3.

In order to set up the Bloch functions of an electron in a periodic field of the crystal, the repeating unit, which consists of two neighboring anions in a direction parallel to the c_0-axis, as has been stated before, must be examined first. The relation between neighboring repeating units in the crystal is drawn in Fig. 2; the numbers, 1, 2, ...,6, denote the nearest neighboring repeating units in the crystal. The ten iodine atoms in a repeating unit were named A, B, C,.., I and J. The distances between each two atomic centers were estimated as follows:

(a) Distances within the 1 repeating unit:
$A_1B_1=D_1E_1=F_1G_1=I_1J_1=2.81$ Å, $B_1C_1=C_1D_1=G_1H_1=H_1I_1=3.17$ Å, $B_1D_1=G_1I_1=4.67$ Å, $A_1G_1=D_1J_1=4.40$ Å, $A_1H_1=C_1J_1=4.73$ Å, $B_1G_1=D_1I_1=4.48$ Å, $B_1H_1=C_1I_1=4.74$ Å, $B_1I_1=4.68$ Å.

(b) Distances between the 1 and 2 repeating units:
$C_1A_2=J_1H_2=3.62$ Å, $D_1A_2=J_1G_2=4.91$ Å, $J_1A_2=4.59$ Å.

(c) Distances between 1 and 3:
$B_1E_3=F_1I_3=4.91$ Å, $C_1E_3=F_1H_3=3.62$ Å.

(d) Distances between 1 and 4:
$F_1B_4=I_1E_4=4.40$ Å, $F_1C_4=H_1E_4=4.73$ Å, $G_1B_4=I_1D_4=4.48$ Å, $G_1C_4=H_1D_4=4.74$ Å, $G_1D_4=4.68$ Å.

(e) Distances between 1 and 5:
$E_1A_5=J_1F_5=4.92$ Å.

(f) Distances between 1 and 6:
$F_1E_6=4.59$ Å.

Any distances between two atomic centers larger than 5.0 Å may be disregarded, for the overlap integrals decrease exponentially with the distance of two atomic centers.

The "Molecular Orbital" of a Repeating Unit.—The "molecular" orbital function of a repeating unit, φ, was approximated with a linear combination of 30 Slater-type 5p atomic orbitals, χ, belonging to the 10 iodine atoms in the unit. The energy and the coefficients of the "molecular" orbitals of the repeating unit were calculated by applying the variation principle and Hückel's approximation in the usual manner.

If χ_i is the wave function of the ith atomic orbital, the explicit parameters which enter the secular determinant are the Coulomb integral, $\alpha_i=\int\chi_i^*\boldsymbol{H}\chi_i\mathrm{d}\tau$, and the resonance integral between adjacent orbitals, $\beta_{ij}=\int\chi_i^*\boldsymbol{H}\chi_j\mathrm{d}\tau$, the overlap integrals being neglected. If all the orbitals are

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[4] E. E. Havinga and E. H. Wiebenga, *Rec. Trav. Chim.*, **78**, 724 (1959).

[5] G. C. Pimentel, *J. Chem. Phys.*, **19**, 446 (1951).

[6] R. Bersohn, ibid., **36**, 3445 (1962).

[7] J. L. Rosenberg, ibid., **40**, 1707 (1964).

equivalent, the Coulomb integral will become an additive constant. $\boldsymbol{H}$ is a one-electron Hamiltonian. It is, therefore, necessary to evaluate the resonance integrals.

The resonance integrals were estimated by the familiar relation:

$$\beta' = \beta \frac{S'/(1+S')}{S/(1+S)} \tag{1}$$

where β' and S' are, respectively, resonance and overlap integrals between the interesting orbitals, and β and S are, respectively, the resonance and overlap integrals for some standard. In our present calculation, β and S are the values for (5pσ, 5pσ) at the interatomic distance, 2.68 Å, of an iodine molecule. The estimation of the numerical value of the basic parameter of our calculation, β, will be discussed later in detail.

The values of $S(5\mathrm{p}\sigma,\ 5\mathrm{p}\sigma)$ and $S(5\mathrm{p}\pi,\ 5\mathrm{p}\pi)$ between two iodine 5p atomic orbitals were calculated by Mulliken's special formulas[8] for Slater-AO overlap integrals for $t=0$. The formulas may be given as follows:

$$\begin{aligned} S(5\mathrm{p}\sigma,\ 5\mathrm{p}\sigma) = \mathrm{e}^{-P}[&-1-p-(29/70)p^2-(17/210)p^3 \\ &-(1/735)p^4+(1/294)p^5+(67/66150)p^6 \\ &+(13/66150)p^7+(1/33075)p^8] \end{aligned}$$

$$\begin{aligned} S(5\mathrm{p}\pi,\ 5\mathrm{p}\pi) = \mathrm{e}^{-P}[&1+p+(33/70)p^2+(29/210)p^3 \\ &+(41/1470)p^4+(1/245)p^5 \\ &+(29/66150)p^6+(1/33075)p^7] \end{aligned}$$

where $p=(\mu_a+\mu_b)R/2a_{\mathrm{H}}$, $t=(\mu_a-\mu_b)/(\mu_a+\mu_b)$, R is the interatomic distance, a_{H} is the Bohr radius, and the $\mu_a=\mu_b$ value is 1.90 for the iodine-pair.

Next, in order to ascertain the overlap integral, S'_{ab}, between any two 5p iodine orbitals, $\boldsymbol{A}_a$ and $\boldsymbol{A}_b$, new orthogonal coordinates (X, Y, Z), in which the Z axis is parallel to the direction of the internuclear vector, are set up, and the interesting overlap integral, S'_{ab}, is estimated as follows:

$$\begin{aligned} S'_{ab} = -\mathrm{A}_{az}\cdot\mathrm{A}_{bz}\cdot S(5\mathrm{p}\sigma,\ 5\mathrm{p}\sigma) + (&\mathrm{A}_{ax}\cdot\mathrm{A}_{bx} \\ &+\mathrm{A}_{ay}\cdot\mathrm{A}_{by})\cdot S(5\mathrm{p}\pi,\ 5\mathrm{p}\pi) \end{aligned}$$

where A_{ax}, A_{ay}, .., A_{bz} are the X, Y and Z components of the vectors of the atomic orbitals, $\boldsymbol{A}_a$ and $\boldsymbol{A}_b$.

In order to calculate the energy of the repeating unit, it is first assumed that the V-shaped pentaiodide ion is planar, that the $\mathrm{I_B}$–$\mathrm{I_C}$–$\mathrm{I_D}$ angle is 90° and that the arms are linear, the pentaiodide ion reported in Ref. 3 being planar within ±0.09 Å, the $\mathrm{I_B}$–$\mathrm{I_C}$–$\mathrm{I_D}$ angle, 95°, and the angle of arms, 174.5°.

The sign and the numbering of the atomic p orbitals are as shown in Fig. 3. Thus, all the resonance integrals between any pairs of iodine atoms from A to J were estimated in β untis. Using these resonance integrals, a 30-order secular determinant was set up and solved by a computor. The energy levels of a repeating unit and the orbital coefficients for some levels are shown in Fig. 4 and Table I. The levels from 1 to 26 are filled; the levels from 27 to 30, lying much higher, are vacant.

TABLE I. THE ORBITAL COEFFICIENTS FOR SOME LEVELS OF A REPEATING UNIT

Number of level	Coefficients*				
28	−0.009	0.025	−0.211	0.351	−0.287
	−0.008	0.028	−0.212	0.349	−0.286
	0.005	0.006	−0.002	−0.006	0.002
	−0.008	0.028	−0.212	0.349	−0.286
	−0.009	0.025	−0.211	0.351	−0.287
	−0.002	0.006	0.002	−0.006	−0.005
27	−0.006	0.029	−0.213	0.349	−0.287
	−0.007	0.026	−0.211	0.349	−0.287
	−0.004	−0.005	0.001	0.004	−0.001
	0.007	−0.026	0.211	−0.349	0.287
	0.006	−0.029	0.213	−0.349	0.287
	−0.001	0.004	0.001	−0.005	−0.004
26	−0.047	0.019	−0.002	−0.001	0.003
	−0.098	0.129	−0.014	−0.010	0.012
	0.272	−0.403	0.298	−0.304	0.231
	0.098	−0.129	0.014	0.010	−0.012
	0.047	−0.019	0.002	0.001	−0.003
	0.231	−0.304	0.298	−0.403	0.272
25	0.072	−0.041	0.013	0.004	−0.008
	0.102	−0.132	0.021	0.011	−0.013
	0.295	−0.299	0.288	−0.358	0.277
	0.102	−0.132	0.021	0.011	−0.013
	0.072	−0.041	0.013	0.004	−0.008
	−0.277	0.358	−0.288	0.299	−0.295

* Orbital number from left to right, up to down.

Band Structure. — The band structure is calculated by the tight-binding approximation. We denote the unit cell vector by $\boldsymbol{a}_0$, $\boldsymbol{b}_0$ and $\boldsymbol{c}_0$, and define the new vector by $\boldsymbol{a}=(\boldsymbol{a}_0+\boldsymbol{b}_0)/2$, $\boldsymbol{b}=(-\boldsymbol{a}_0+\boldsymbol{b}_0)/2$ and $\boldsymbol{c}=\boldsymbol{c}_0$; therefore, $\boldsymbol{a}$, $\boldsymbol{b}$ and $\boldsymbol{c}$ connect the centers of the nearest-neighbor repeating units (Fig. 2).

The one-electron crystal wave functions, Ψ_k, are constructed from the linear combination of one-electron wave functions of the repeating unit, φ_j; since we are dealing with an electron in a periodic field, the wave function must be a Bloch function:

$$\Psi_k(\boldsymbol{r}) = \sum_{j=1}^{N} \exp(i\boldsymbol{k}\boldsymbol{r}_j)\varphi_j(\boldsymbol{r}-\boldsymbol{r}_j)$$

Here $\boldsymbol{r}_j$ locates the center of a repeating unit, j, and the sum extends over N repeating units in the crystal.

The application of periodic boundary conditions defines an elementary cell in $\boldsymbol{k}$ space, whose volume

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[8] R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

is given by the conditions:

$$-\pi < \boldsymbol{ka},\ \boldsymbol{kb},\ \boldsymbol{kc} \leq \pi$$

The energy of one-electron with the wave vector $\boldsymbol{k}$ is calculated by the following expression:

$$E(\boldsymbol{k})=\frac{\int \Psi_k{}^* \boldsymbol{H} \Psi_k \mathrm{d}\tau}{\int \Psi_k{}^* \Psi_k \mathrm{d}\tau}=E_0+2\sum E_s \cdot \cos \boldsymbol{kr}_s$$

where $\boldsymbol{H}$ is the Hamiltonian for one electron in the crystal; E_0 is the molecular orbital energy of a repeating unit, and $\boldsymbol{r}_s$ is the primitive translation vector. The structure of the band is determined by the resonance integrals between repeating units, E_s. Each resonance integral between repeating units is a sum of the interatomic resonance integrals. Of the two-center atomic integrals in each E_s, only those involving a small interatomic distance and a large Hückel coefficient of a repeating unit are important.

The resonance integrals fall off rapidly with the distance between repeating units; only five nearest-neighbor interactions are found to be important. They are E_a, E_b, E_c, E_{a-b} and E_{b+c}, corresponding to $\boldsymbol{r}_s=\boldsymbol{a}$, $\boldsymbol{b}$, $\boldsymbol{c}$, $\boldsymbol{a}-\boldsymbol{b}$ and $\boldsymbol{b}+\boldsymbol{c}$ respectively.

The one-electron energy for each band is, therefore, given by:

$$E(\boldsymbol{k})=E_0+2[E_a\cos\boldsymbol{ka}+E_b\cos\boldsymbol{kb}+E_c\cos\boldsymbol{kc}+E_{a-b}\cos\boldsymbol{k}(\boldsymbol{a}-\boldsymbol{b})+E_{b+c}\cos\boldsymbol{k}(\boldsymbol{b}+\boldsymbol{c})] \quad (2)$$

The values of E_a, E_b, ..., and E_{b+c} for the band corresponding to each nth "molecular" orbital are listed in Table II.

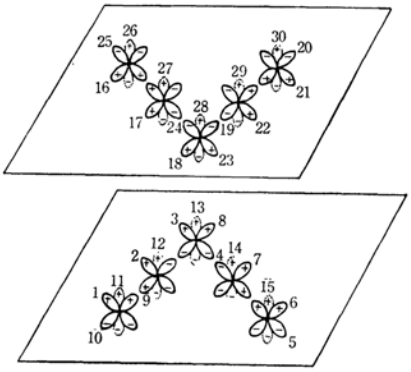

Fig. 3. The sign and the numbering of the atomic p-orbitals. 1—15 make a lower layer and 16—30 an upper layer. Lobes shown with dotted lines are perpendicular to each layer.

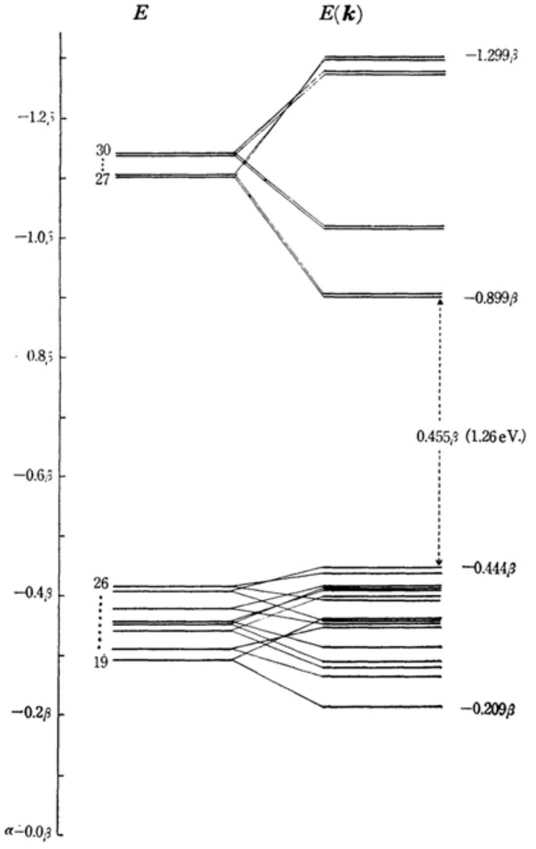

Fig. 4. Energy levels of a repeating unit, E, and energy bands of solid pentaiodide, $E(\boldsymbol{k})$. (Among 30 energy levels of a repeating unit only the levels 19—30 are shown.)

TABLE II. RESONANCE INTEGRALS BETWEEN REPEATING UNITS (β UNIT)

Number of level	E_a	E_b	E_c	E_{a-b}	E_{b+c}
30	−0.032	−0.031	0.000	−0.003	−0.001
29	−0.031	−0.032	0.000	−0.003	0.001
28	−0.048	−0.049	0.000	0.003	0.001
27	−0.050	−0.049	0.000	0.003	−0.001
26	0.005	0.006	0.000	0.000	0.000
25	0.009	0.008	0.006	0.000	0.003
24	0.008	0.007	−0.004	−0.002	−0.004
23	0.009	0.009	0.006	−0.002	0.000
22	−0.001	0.010	−0.017	0.004	−0.003
21	0.010	0.009	−0.011	0.002	0.000
20	0.008	0.008	0.005	0.002	0.001
19	0.015	0.005	0.013	0.004	0.004

Results and Discussion

Using Eq. 2, the total width of each band was calculated. The energy levels of a repeating unit and the total width of each band are represented in Fig. 4.

As is shown in Fig. 4, the bands from 19 to 26 are all occupied by electrons and as a whole form a hole band, while the bands from 27 to 30 are all vacant and form an electron band. The band-gap energy is found to be 0.455 β.

In order to estimate the numerical value of β, as Rosenberg suggested,[7] the following assumption was made:

$$\beta(5p\sigma,\ 5p\sigma)-\beta(5p\pi,\ 5p\pi)=-1.71\ \text{eV}. \qquad (3)$$

where β is the value for the interatomic distance, 2.68 Å, for the iodine molecule. This is the average value of T_e,[9] the pure electronic excitation, of the first two excited states, A and B, relative to the ground state, X, in the gaseous iodine molecule. The $X\rightarrow A$ and $X\rightarrow B$ transitions are the two spectroscopically-observed transitions of the vapor phase iodine corresponding to the orbital jump from π-antibonding to σ-antibonding orbitals.

The substitution of $\beta(5p\pi,\ 5p\pi)=0.381\beta$ from Eq. 1 into Eq. 3 gives $\beta=-2.76$ eV.

The band-gap energy is, therefore, calculated to be 1.26 eV. This value is in good agreement with the experimental value of 1.36 eV., reported in the previous papers,[1a,1b] for the band-gap energy of tetramethylammonium pentaiodide from the conductivity measurements.

As described before, the calculations have been performed on the assumptions that the V-shaped pentaiodide ion is planar, the I_B–I_C–I_D angle is rectangular, and the arms are linear. The calculations were also carried out with the pentaiodide ion, which has a more complicated geometry; the band gap energy thus calculated was found, however, to be almost the same as the above value (the difference was within 0.1 eV).

Although the treatment of the calculation is semiquantitative, this result may offer additional evidence in support of our previous conclusion that the iodine framework in the tetramethylammonium pentaiodide crystal structure is of primary importance in determining the electrical conductivity. It may also be supposed that the band model is satisfactorily applied for the conduction mechanism. Thereby, the experimental energy gap may be supposed to be the one of intrinsic conduction.

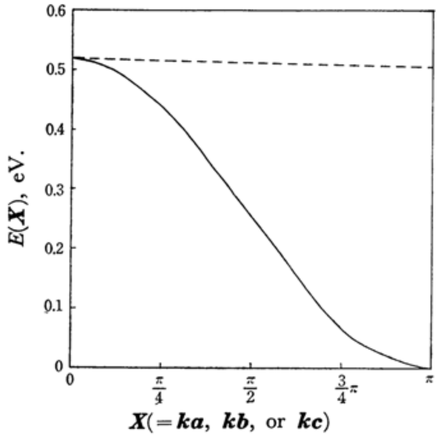

Fig. 5. The 27 band structure in the a^{-1} (solid line), b^{-1} (the same line as a^{-1}) and c^{-1} (dashed line) directions.

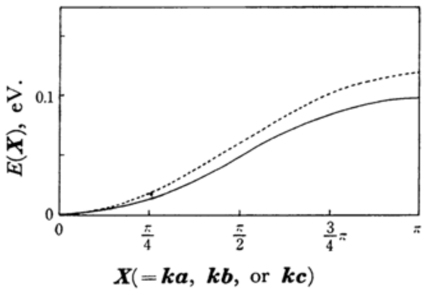

Fig. 6. The 25 band structure in the a^{-1} (solid line), b^{-1} (dotted line) and c^{-1} (the same line as a^{-1}) directions.

On examining the Hückel coefficients of the wave functions of the repeating unit, one finds that the electron band is mainly σ in character. No. 25 and 26 bands located at the top of the hole band are mainly π in character, perpendicular to the planar V-shaped pentaiodide ion.

In the reduced zone scheme given by $-\pi<\boldsymbol{ka}$, $\boldsymbol{kb}$, $\boldsymbol{kc}\leq\pi$, the 27 and 25 band structures in the reciprocal crystal axis direction are as shown in Figs. 5 and 6. The origins of the energy scales are arbitrarily taken in both figures. The values of the bandwidths in the $\boldsymbol{a}^{-1}$, $\boldsymbol{b}^{-1}$, and $\boldsymbol{c}^{-1}$ directions are shown in Table III.

TABLE III. BANDWIDTHS OF 27 AND 25 (eV.)

	27	25
$\boldsymbol{a}^{-1}$	0.519	0.099
$\boldsymbol{b}^{-1}$	0.519	0.121
$\boldsymbol{c}^{-1}$	0.011	0.099

So far no mutual interactions of the Bloch functions of different energy have been taken into consideration; the interactions between the levels with different energies have thus been neglected.

In order to calculate the electron band, it is desirable to mix four vacant levels 27—30. The usual way to do this is to make a linear combination of these four functions and, next, set up a 4th order secular determinant by variation. It is, however, very difficult to solve the determinant thus obtained. To calculate the hole band in this way, it is desirable to interact eight levels at one time, leading to the 8th order secular determinant; these interactions are, however, impossible to solve.

We therefore attempted to see if there were pairs of levels which interact so strongly that the value of the energy gap estimated hitherto without level interactions must be changed. As will be shown below the level interactions were found to be so slight that the value of the energy gap changes at most in the order of 10^{-2} eV.

The interaction between two different Bloch functions, Ψ_p and Ψ_t, has been examined on the basis of a linear combination;

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[9] L. Mathieson and A. L. G. Rees, *J. Chem. Phys.*, **25**, 753 (1956).

TABLE IV. E_s' FROM A PAIR OF DIFFERENT BLOCH FUNCTIONS

p, t	E_a'	E_b'	E_c'	E'_{a-b}	E_{b+c}'	cos or sin
27, 30	0.082	−0.080	0.000	0.000	−0.002	cos
27, 29	0.018	−0.016	0.000	−0.006	−0.002	sin
27, 28	0.000	0.000	0.000	0.000	0.002	sin
25, 26	0.000	0.000	0.004	−0.002	0.002	sin
24, 25	0.014	0.012	0.000	−0.002	0.008	sin
19, 25	0.014	−0.010	−0.014	−0.002	−0.008	cos

$$\Phi = c_1\Psi_p + c_2\Psi_t$$

By applying the variation principle, the secular determinant of the following form is obtained:

$$\begin{vmatrix} \int\Psi_p{}^*\boldsymbol{H}\Psi_p\mathrm{d}\tau - E & \int\Psi_p{}^*\boldsymbol{H}\Psi_t\mathrm{d}\tau \\ \int\Psi_t{}^*\boldsymbol{H}\Psi_p\mathrm{d}\tau & \int\Psi_t\boldsymbol{H}\Psi_t\mathrm{d}\tau - E \end{vmatrix} = 0$$

In solving the determinant, the band energy is written in explicit form as:

$$E_{p,t}(\boldsymbol{k}) = \frac{E_p(\boldsymbol{k}) + E_t(\boldsymbol{k})}{2} \pm \sqrt{\left(\frac{E_p(\boldsymbol{k}) - E_t(\boldsymbol{k})}{2}\right)^2 + |B|^2}$$

where

$$E_p(\boldsymbol{k}) = \int\Psi_p{}^*\boldsymbol{H}\Psi_p\mathrm{d}\tau,\ E_t(\boldsymbol{k}) = \int\Psi_t{}^*\boldsymbol{H}\Psi_t\mathrm{d}\tau,$$

$$B = \int\Psi_p{}^*\boldsymbol{H}\Psi_t\mathrm{d}\tau = \int\varphi_p(\boldsymbol{r})\boldsymbol{H}\varphi_t(\boldsymbol{r})\mathrm{d}\tau$$
$$+\sum\{\exp(-i\boldsymbol{k}\boldsymbol{r}_s)\int\varphi_p{}^*(\boldsymbol{r})\boldsymbol{H}\varphi_t(\boldsymbol{r}-\boldsymbol{r}_s)\mathrm{d}\tau$$
$$-\exp(i\boldsymbol{k}\boldsymbol{r}_s)\int\varphi_p{}^*(\boldsymbol{r})\boldsymbol{H}\varphi_t(\boldsymbol{r}+\boldsymbol{r}_s)\mathrm{d}\tau\}$$

$$B^* = \int\Psi_t{}^*\boldsymbol{H}\Psi_p\mathrm{d}\tau,\ |B|^2 = (\sum E_s'\cos\boldsymbol{k}\boldsymbol{r})^2$$
$$\text{or } (\sum E_s'\sin\boldsymbol{k}\boldsymbol{r})^2$$

Since $\varphi_p(\boldsymbol{r})$ and $\varphi_t(\boldsymbol{r})$ are orthogonal, $\int\varphi_p(\boldsymbol{r})\boldsymbol{H}\cdot\varphi_t(\boldsymbol{r})\mathrm{d}\tau$ vanishes. The sum, $\sum$, is taken over the nearest-neighboring repeating units located in the five directions, $\boldsymbol{a}$, $\boldsymbol{b}$, $\boldsymbol{c}$, $\boldsymbol{a}-\boldsymbol{b}$ and $\boldsymbol{b}+\boldsymbol{c}$. One finds that, for some p, t pairs, $|B|^2$ contains only sine terms, $(\sum E_s'\sin\boldsymbol{k}\boldsymbol{r}_s)^2$ and for some other pairs, only cosine terms, $(\sum E_s'\cos\boldsymbol{k}\boldsymbol{r}_s)^2$. The E_s' values are listed in Table IV for several p, t pairs.

E_a' and E_b' in cosine terms are large but are opposite in sign. E_a and E_b are large and have the same sign. Hence, it is clear that when $\cos\boldsymbol{k}\boldsymbol{a} \fallingdotseq \cos\boldsymbol{k}\boldsymbol{b} \fallingdotseq \pm 1$, i. e., near the top and bottom of these bands, $|B|^2$ must be small, the interaction between p and t levels being very small for these $\boldsymbol{k}$ values. For the $E_{p,t}(\boldsymbol{k})$ bands with only sine terms in $|B|^2$, $|B|^2$ remains very small, irrespective of $\boldsymbol{k}$, very small interactions existing between p and t levels here also.

It may, therefore, be inferred that the position of the bottom of the electron band, as well as the position of the top of the hole band, will not change very much even when corrected for the interactions of the levels with different energies. Consequently, the band-gap energy will also remain unchanged, or will change at most in the order of 10^{-2} eV.

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