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The Refined Calculation of the Band-gap Energy of Tetramethylammonium Pentaiodide

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The band-gap energy has been calculated by a tight-binding approximation in a previous report. Although the value thus calculated coincided rather well with the experimental value, it might yet be possible that the band-gap energy will change appreciably when the interactions of all the energy levels are considered at one time. It was, therefore, calculated by the following method, which considers in principle all the level interactions. A repeating unit is composed of 30 atomic orbitals. Each atomic wave function makes three-dimensional Bloch functions. The crystal wave function is set up in the form of a linear combination of these 30 Bloch functions. The energy is then calculated by applying the variation principle and by using the Hückel approximation. The band-gap energy thus calculated is 1.20 eV. This value is near the experimental value, 1.36 eV.; it was also close to the previous result, 1.26 eV., thus confirming the previous calculations. The consideration of the band-widths and the density of the state may interpret the experimental results on the sign of the carrier. The results offer additional support for our previous conclusion regarding the conduction mechanism.

In a previous paper,[1)] the band-gap energy of tetramethylammonium pentaiodide was calculated by a tight-binding approximation. The value thus calculated was 1.26 eV., which was satisfactorily near the experimental value, 1.36 eV., obtained from the conductivity measurements.[2)] The method used was, briefly, as follows: The iodine framework in the crystal was looked upon as being constructed by repeated translations of a group of two pentaiodide ions (the repeating unit). The wave function of a repeating unit was calculated by Hückel 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 were set up in the form of a Bloch function from the wave functions of the repeating unit. No mutual interactions of the Bloch functions of different energies were taken into consideration; thus, interactions between the levels with different energies were neglected.

Although the value thus calculated coincided rather well with the experimental value, it might yet be possible the band-gap energy will change appreciably when the interactions of all the energy levels are taken into consideration at one time.

We have, therefore, attempted in the present paper to calculate the band-gap energy of tetramethylammonium pentaiodide by another method, one which, in principle, takes all the level interactions into consideration (see Appendix).

Method

To solve the problem of the one-electron energy of a three-dimensional crystal from a general point of view, we have modified and extended the method which has previously been used to calculate the energy gap of one-dimensional macromolecules with conjugated double bonds[3)] and which has also been used in calculating the band structure of a one-dimensional polynucleotide model.[4)]

Primitive translations are denoted by $\boldsymbol{a}$, $\boldsymbol{b}$ and $\boldsymbol{c}$, and the numbering of the elementary cells, by N. It is assumed that one molecule composed of n atomic orbitals is contained in each elementary cell. The n atomic orbitals of a molecule are denoted by $\varphi_1, \varphi_2, \cdots, \varphi_l, \cdots, \varphi_n$, which make three-dimensional Bloch functions extending over the whole crystal.

$$\psi_{l\boldsymbol{k}}(\boldsymbol{r}) = \sum_{j=1}^{N} \exp(i\boldsymbol{k}\boldsymbol{R}_j)\varphi_l(\boldsymbol{r}-\boldsymbol{R}_j) \quad (l=1,2,\cdots,n)$$

where j is the numbering of the molecules and l, the numbering of the atomic orbitals in a molecule.

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1) S. Kusabayashi and H. Mikawa, This Bulletin, **39**, 736 (1966).

2) S. Kusabayashi, H. Mikawa, S. Kawai, M. Uchida and R. Kiriyama, ibid., **37**, 811 (1964); S. Kawai, R. Kiriyama, M. Uchida, S. Kusabayashi and H. Mikawa, ibid., **38**, 799 (1965).

3) J. Koutecký and R. Zahradník, *Collection Czech. Chem. Commun.*, **25**, 811 (1960).

4) J. Ladik and K. Appel, *J. Chem. Phys.*, **40**, 2470 (1964).

The crystal wave function is then set up in the form of a linear combination of these n Bloch functions;

$$\Psi_{\boldsymbol{k}}(\boldsymbol{r}) = \sum_{l=1}^{n} C_l \phi_{l\boldsymbol{k}}$$

By applying the variation principle and using the Hückel approximation, one arrives at a system of secular equations as usual. The following matrix eigenvalue problem for the determination of the possible energies of the electrons is obtained:

$$\boldsymbol{\gamma C} = \lambda \boldsymbol{C}$$

where an element of the matrix, $\boldsymbol{\gamma}$, is:

$$\begin{aligned}\gamma_{lm} = \beta_{lm} &+ \{\beta^{\overset{-}{a}}_{lm} \exp(-i\boldsymbol{ka}) + \beta^{\overset{+}{a}}_{lm} \exp(i\boldsymbol{ka})\} \\ &+ \{\beta^{\overset{-}{b}}_{lm} \exp(-i\boldsymbol{kb}) + \beta^{\overset{+}{b}}_{lm} \exp(i\boldsymbol{kb})\} \\ &+ \{\beta^{\overset{-}{c}}_{lm} \exp(-i\boldsymbol{kc}) + \beta^{\overset{+}{c}}_{lm} \exp(i\boldsymbol{kc})\}\end{aligned}$$

Here, β_{lm} is a resonance integral between atomic orbitals, l and m, in the same molecule, and β_{ll} in the diagonal element of the matrix, $\boldsymbol{\gamma}$, is the Coulomb integral of the atomic orbital, l; $\beta^{\overset{-}{a}}_{lm}$ is a resonance integral between the l atomic orbital of the $\boldsymbol{R}_j$ molecule and the m atomic orbital of the $\boldsymbol{R}_j-\boldsymbol{a}$ molecule; $\beta^{\overset{+}{a}}_{lm}$ is a resonance integral between the l atomic orbital of the $\boldsymbol{R}_j$ molecule and the m atomic orbital of the $\boldsymbol{R}_j+\boldsymbol{a}$ molecule, and $\beta^{\overset{-}{b}}_{lm}\cdots\beta^{\overset{+}{c}}_{lm}$ have similar meanings. The nearest neighboring molecules of a molecule $\boldsymbol{R}_j$ are assumed to be $\boldsymbol{R}_j\pm\boldsymbol{a}$, $\boldsymbol{R}_j\pm\boldsymbol{b}$, and $\boldsymbol{R}_j\pm\boldsymbol{c}$.

The matrix, $\boldsymbol{\gamma}$, is shown to be Hermitian. Column vector $\boldsymbol{C}$ is set equal to $\boldsymbol{u}+i\boldsymbol{v}$. Then, the $\gamma_{lm}C_m$ term of the secular equations is:

$$\gamma_{lm}C_m = (A_{lm}u_m - B_{lm}v_m) + i(B_{lm}u_m + A_{lm}v_m)$$

where:

$$\begin{aligned}A_{lm} &= \beta_{lm} + (\beta^{\overset{+}{a}}_{lm} + \beta^{\overset{-}{a}}_{lm}) \cos \boldsymbol{ka} \\ &\quad + (\beta^{\overset{+}{b}}_{lm} + \beta^{\overset{-}{b}}_{lm}) \cos \boldsymbol{kb} + (\beta^{\overset{+}{c}}_{lm} + \beta^{\overset{-}{c}}_{lm}) \cos \boldsymbol{kc} \\ B_{lm} &= (\beta^{\overset{+}{a}}_{lm} - \beta^{\overset{-}{a}}_{lm}) \sin \boldsymbol{ka} + (\beta^{\overset{+}{b}}_{lm} - \beta^{\overset{-}{b}}_{lm}) \sin \boldsymbol{kb} \\ &\quad + (\beta^{\overset{+}{c}}_{lm} - \beta^{\overset{-}{c}}_{lm}) \sin \boldsymbol{kc}\end{aligned}$$

By separating further the secular equation into the real part and the imaginary part, and by equating both to zero, one obtains secular equations of the $2n$ order.

The equations can be considered as the partitioned forms of a real eigenvalue problem of twice the original size:

$$\begin{pmatrix} \boldsymbol{A} & -\boldsymbol{B} \\ \boldsymbol{B} & \boldsymbol{A} \end{pmatrix} \begin{pmatrix} \boldsymbol{u} \\ \boldsymbol{v} \end{pmatrix} = \lambda \begin{pmatrix} \boldsymbol{u} \\ \boldsymbol{v} \end{pmatrix}$$

This matrix is also Hermitian. In solving this problem, each eigenvalue appears twice.

In the actual calculation of tetramethylammonium pentaiodide, the same parameter values as in the previous paper were used. Each resonance integral was estimated on the basis of the relation:

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

where β' and S' are resonance and overlap integrals respectively between the interesting orbitals, and β and S are the resonance and overlap integrals respectively for a standard. The values of β and S are those for (5pσ, 5pσ) at the interatomic distance, 2.68 Å, of an iodine molecule. The appropriate overlap integrals between the interesting orbitals were calculated by Mulliken's formulas⁵⁾ for Slater-AO overlap integrals for $t=0$, taking the geometry of the atomic orbitals in crystal into consideration.

As has been stated before, the iodine framework in the crystal can be looked upon as being constructed simply by repeated translations of a group of two pentaiodide ions; this repeating unit is looked upon as a molecule. There are 30 Slater-type 5p atomic orbitals belonging to the 10 iodine atoms in a repeating unit. The nearest neighboring repeating units are located in the five directions, $\boldsymbol{a}$, $\boldsymbol{b}$, $\boldsymbol{c}$, $\boldsymbol{a}-\boldsymbol{b}$ and $\boldsymbol{b}+\boldsymbol{c}$.

Therefore, in our case, a 60-order matrix must be set up for each parametric $\boldsymbol{k}$ value, and then solved for eigenvalues.

Results and Discussion

A special computer program was set up, and the calculations of the eigenvalues for nearly one hundred different $\boldsymbol{k}$ values were performed with an IBM 7044 electronic computer. The maximum

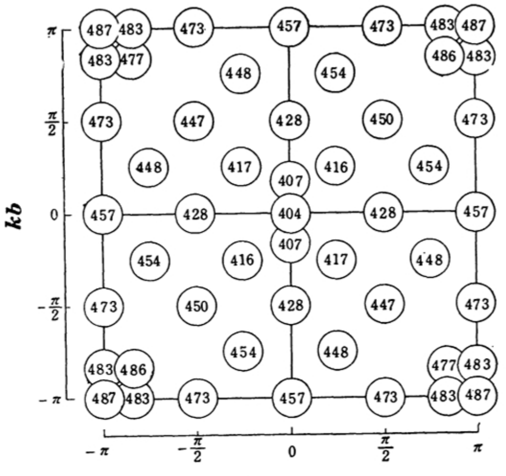

Fig. 1. Maximum energy value of filled band at $\boldsymbol{kc}=0$. ($-10^{-3}\beta$ unit).

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

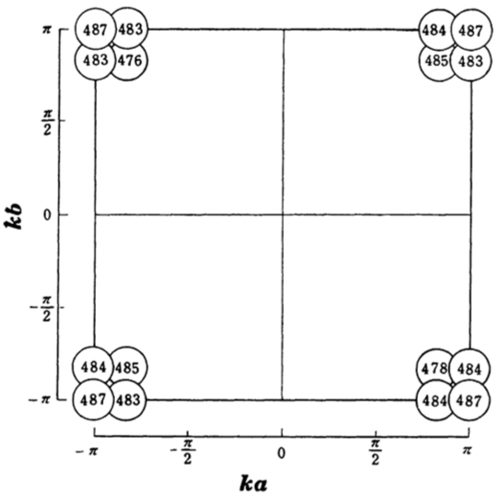

Fig. 2. Maximum energy value of filled band at $kc=\pi/6$. ($-10^{-3}\beta$ unit)

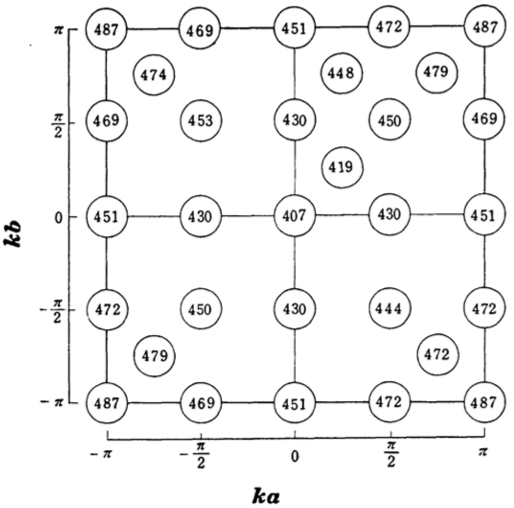

Fig. 3. Maximum energy value of filled band at $kc=\pi/2$. ($-10^{-3}\beta$ unit).

energy values of the filled bands are shown in Figs. 1—4, while the minimum energy values of the unfilled band are shown in Figs. 5—8. It seems that the energy values do not change much with the variation in $\boldsymbol{kc}$ value, and that the point of ($\boldsymbol{ka}=\pi$, $\boldsymbol{kb}=\pi$, $\boldsymbol{kc}=0$) or some points closed to (π, π, 0) give the lower limit of the unfilled band and the upper limit of the filled band.

The band-gap energy is found to be 0.434β by using the value of (π, π, 0). The substitution of the $\beta=-2.76$ eV. from a previous assumption[1] into 0.434β gives 1.20 eV. This value is near the experimental value of 1.36 eV., and it is also close to 1.26 eV., the value obtained in the previous calculation.

The present method gives information about

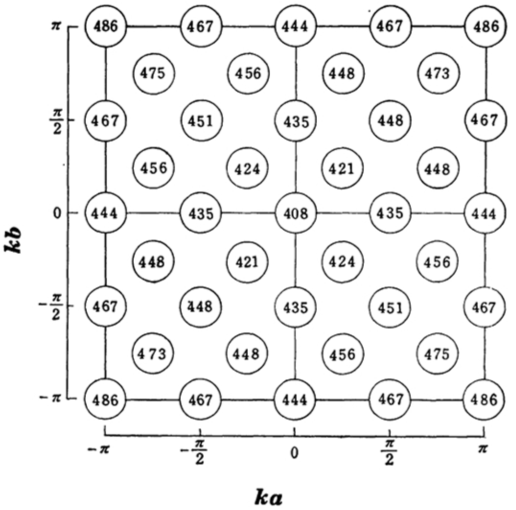

Fig. 4. Maximum energy value of filled band at $kc=\pi$. ($-10^{-3}\beta$ unit)

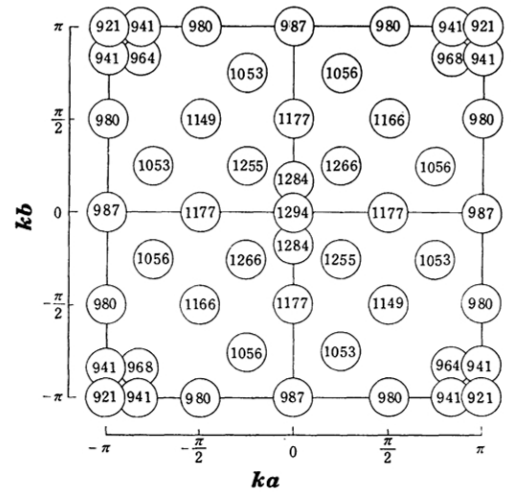

Fig. 5. Minimum energy value of unfilled band at $kc=0$. ($-10^{-3}\beta$ unit)

the band-gap energy, but the characteristics of each level are still not clear, as it is not possible to know $E(\boldsymbol{k})$ in an analytical form nor the functional forms of wave functions. As is shown in Fig. 9, 22 levels are filled by electrons and as a whole form a hole band, while the upper 4 levels are all vacant and form an electron band. It is found that the width of the electron band is nearly the same as that obtained in the previous report, but the width of the hole band is about 5 times as large as the previous result. (In the previous paper, it was thought tentatively that the hole band was constructed by an overlap of the upper 8 filled bands.) After all, the width of the hole band is about 3 times as large as the width of the electron band.

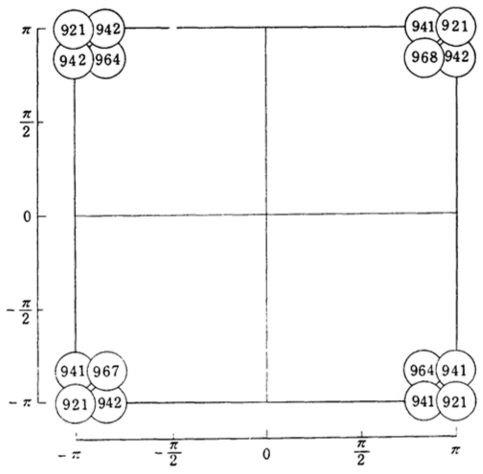

Fig. 6. Minimum energy value of unfilled band at $kc=\pi/6$. ($-10^{-3}\beta$ unit)

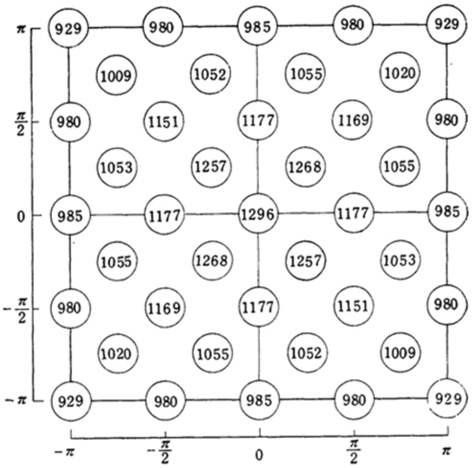

Fig. 8. Minimum energy value of unfilled band at $kc=\pi$. ($-10^{-3}\beta$ unit)

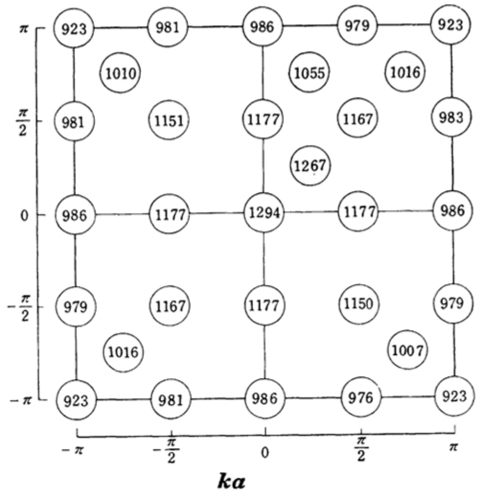

Fig. 7. Minimum energy value of unfilled band at $kc=\pi/2$. ($-10^{-3}\beta$ unit)

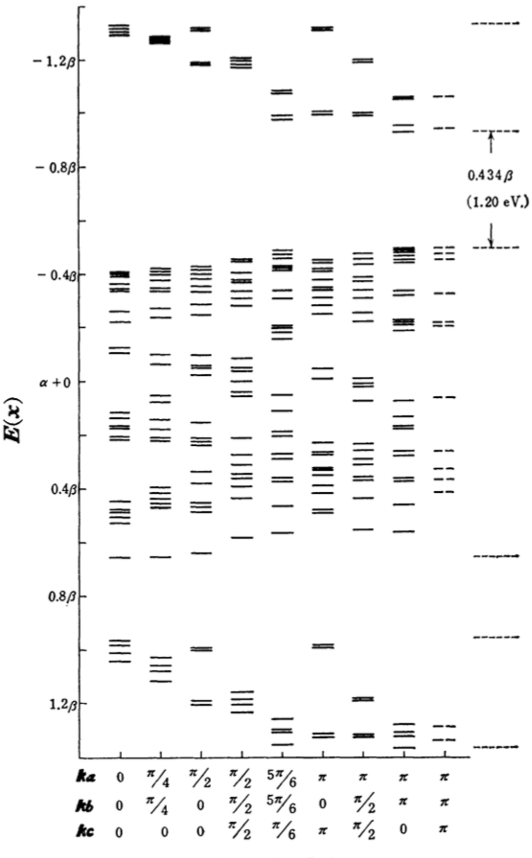

Fig. 9. Energy bands of pentaiodide. (α is the coulomb energy of the iodine 5p atomic orbital.)

As for mobility, no experimental data has yet been obtained. Preliminary thermoelectric power measurements showed that the sign of the carrier was positive.[2] The fact that the width and the density of states in the hole band are much larger than those in the electron band might explain the experimental finding on the sign of the carrier.

Although the method used in the present calculations is more reliable than the previous method, the results are very near the previous results. This tends to confirm the prevoius calculation. Moreover, the results presented here are in agreement with the experimental results. They support our previous conclusion that the iodine framework in the crystal structure is of primary importance in determining the conductivity. They also offer additional support for the idea that the band model is applicable to the conduction mechanism of tetramethylammonium pentaiodide.

Appendix

The molecular orbital function, Φ^t, is approximated with a linear combination of atomic orbitals, φ_l;

$$\Phi^t = \sum_{l=1}^{n} a_l^t \varphi_l \tag{1}$$

where a_l^t is the coefficient of the lth atomic orbital of the tth level in the jth molecule. By multiplying both sides of (1) with $\exp(i\boldsymbol{kR}_j)$, and by summing them up with respect to j,

$$\sum_{j=1}^{N} \Phi_{j\boldsymbol{k}}^t = \sum_{l=1}^{n} a_l^t \Big(\sum_{j=1}^{N} \varphi_{l\boldsymbol{k}}\Big) \tag{2}$$

where $\sum_{j=1}^{N} \Phi_{j\boldsymbol{k}}^t$ and $\sum_{j=1}^{N} \varphi_{l\boldsymbol{k}}$ are Bloch functions derived from the tth molecular orbital and from the atomic orbital respectively. In order to take all the level interactions into consideration, both sides of (2) are multiplied with an arbitrary coefficient, c^t, and the values from 1 to n are summed up with respect to t; hence,

$$\sum_{t=1}^{n} c^t \Big(\sum_{j=1}^{N} \Phi_{j\boldsymbol{k}}^t\Big) = \sum_{t=1}^{n} \sum_{l=1}^{n} c^t a_l^t \Big(\sum_{j=1}^{N} \varphi_{l\boldsymbol{k}}\Big)$$

As $\sum_{t=1}^{n} c^t a_l^t$ is an arbitrary parameter, one obtains:

$$\sum_{t=1}^{n} c^t \Big(\sum_{j=1}^{N} \Phi_{j\boldsymbol{k}}^t\Big) = \sum_{l=1}^{n} c'_l \Big(\sum_{j=1}^{N} \varphi_{l\boldsymbol{k}}\Big)$$

This formula indicates that the linear combination of the Bloch functions derived from each atomic orbital is equivalent to the case of the linear combination of the Bloch functions derived from each molecular orbital (level), i.e., to the case where all level interactions are taken into consideration.

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