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MATRICES OF LCAO-HAMILTONIAN IN SPECIAL POINTS

Semiconductors of $A_3^{II}B_2^V$ group have the structures very near to cubic close packed lattices. Their cation's vacancies might be either in positional disorder or vice versa. This detail directly affects on so-called "structural factors" of the matrix elements of the Hamiltonian. The matrix elements change itself just depending on supposition about the degree of vacancies ordering. These investigations show that the part of energy levels is straightly depending on the degree of vacancies ordering, whereas other part of them is independent.

Key words: $A_3^{II}B_2^V$ *compounds, Hamiltonian matrix, energy bands, cation's vacancies.*

Introduction. Zinc phosphide (Zn_3P_2) has been intensively investigated as one of the promising high-efficiency semiconductors for solar-cell applications [1]. It is seems to bee an interesting compound not only from the point of view of its possible applications but also because of its basic properties, especially band-structure parameters. The crystal structure of phosphide-type compounds is very near to cubic close packed lattices. The tight-binding-structure calculations for $A_3^{II}B_2^V$ semiconducting compounds including the real crystal structures requires diagonalization of the matrix Hamiltonian [2]:

$$\begin{pmatrix}
\varepsilon_s^c & E_{ss}g_0 & 0 & 0 & 0 & E_{sp}g_1 & E_{sp}g_2 & E_{sp}g_3 \\
E_{ss}g_0^* & \varepsilon_s^a & -E_{sp}g_1^* & -E_{sp}g_2^* & -E_{sp}g_3^* & 0 & 0 & 0 \\
0 & -E_{sp}g_1 & \varepsilon_p^c & 0 & 0 & E_{xx}g_0 & E_{xy}g_3 & E_{xy}g_2 \\
0 & -E_{sp}g_2 & 0 & \varepsilon_p^c & 0 & E_{xy}g_3 & E_{xx}g_0 & E_{xy}g_1 \\
0 & -E_{sp}g_3 & 0 & 0 & \varepsilon_p^c & E_{xy}g_2 & E_{xy}g_1 & E_{xx}g_0 \\
E_{sp}g_1^* & 0 & E_{xx}g_0^* & E_{xy}g_3^* & E_{xy}g_2^* & \varepsilon_p^a & 0 & 0 \\
E_{sp}g_2^* & 0 & E_{xy}g_3^* & E_{xx}g_0^* & E_{xy}g_1^* & 0 & \varepsilon_p^a & 0 \\
E_{sp}g_3^* & 0 & E_{xy}g_2^* & E_{xy}g_1^* & E_{xx}g_0^* & 0 & 0 & \varepsilon_p^a
\end{pmatrix} \quad (1)$$

Such a Hamiltonian has been written down for these materials for the real symmetry of cubic modifications with $Fm3m - O_h^5$ space group. The matrix elements change itself just depending on supposition about the de-

gree of vacancies ordering. They depend on eight individual material parameters thereto: $E_{sa}, E_{pa}, E_{sc}, E_{pc}, E_{ss}, E_{sp}, E_{xx}, E_{xy}$ [3].

Theory. The calculations have been made by the program created in a comprehensive computer system Maple 8.

Let us assume that the origin is located on a site of the anionic sublattice which is almost close packed. So it is useful to list first all 8 possible cation positions:

$$\left.\begin{aligned} d_1 &= [\ 1 \quad 1 \quad 1]1/4 \\ d_2 &= [\ 1 \quad -1 \quad -1]1/4 \\ d_3 &= [-1 \quad 1 \quad -1]1/4 \\ d_4 &= [-1 \quad -1 \quad 1]1/4 \\ d_5 &= [-1 \quad 1 \quad 1]1/4 \\ d_6 &= [\ 1 \quad -1 \quad 1]1/4 \\ d_7 &= [\ 1 \quad 1 \quad -1]1/4 \\ d_8 &= [-1 \quad -1 \quad -1]1/4 \end{aligned}\right\} \tag{2}$$

Here each positional vector is given up in the units of the lattice constant. This allows us to define a wave vector without this constant into its denominator. Therefore our definition of a wave vector has a form:

$$k = [2\pi a \quad 2\pi b \quad 2\pi c]. \tag{3}$$

It is possible now to build an 8-vector with complex exponential functions as components. Thereto each of functions has the scalar product between a wave vector and a positional vector as its argument.

$$E_x = \left[\begin{array}{cccc} e^{\frac{1}{2}i\cdot\pi(a+b+c)} & e^{\frac{1}{2}i\cdot\pi(a-b-c)} & e^{\frac{1}{2}i\cdot\pi(-a+b-c)} & e^{\frac{1}{2}i\cdot\pi(-a-b+c)} \\ e^{\frac{1}{2}i\cdot\pi(-a+b+c)} & e^{\frac{1}{2}i\cdot\pi(a-b+c)} & e^{\frac{1}{2}i\cdot\pi(a+b-c)} & e^{\frac{1}{2}i\cdot\pi(-a-b-c)} \end{array} \right]. \tag{4}$$

Now we need the set of vectors, which shall describe the probability of the occupation of a position (p_j, j = 0..6) as well as the magnitudes of so-called structural factors (g_j, j = 0..6). The probability distribution vectors are:

$$\begin{aligned} p_0 &= [\ w_1 \quad w_2 \quad w_3 \quad w_4 \quad w_5 \quad w_6 \quad w_7 \quad w_8\ ]; \\ p_1 &= [\ w_1 \quad w_2 \quad -w_3 \quad -w_4 \quad -w_5 \quad w_6 \quad w_7 \quad -w_8\ ]; \\ p_2 &= [\ w_1 \quad -w_2 \quad w_3 \quad -w_4 \quad w_5 \quad -w_6 \quad w_7 \quad -w_8\ ]; \\ p_3 &= [\ w_1 \quad -w_2 \quad -w_3 \quad w_4 \quad w_5 \quad w_6 \quad -w_7 \quad -w_8\ ]; \\ p_4 &= [\ w_1 \quad -w_2 \quad -w_3 \quad w_4 \quad -w_5 \quad -w_6 \quad w_7 \quad w_8\ ]; \\ p_5 &= [\ w_1 \quad -w_2 \quad w_3 \quad -w_4 \quad -w_5 \quad w_6 \quad -w_7 \quad w_8\ ]; \end{aligned}$$

$$p_6 = \begin{bmatrix} w_1 & w_2 & -w_3 & -w_4 & w_5 & -w_6 & -w_7 & w_8 \end{bmatrix}. \qquad (5)$$

Here the set of constants (w_i, $i = 1..8$, $0 \le w_i$ and $w_i \le 1$) describes the individual probabilities of the occupation of cation positions listed above.

It is good time now for the determination of so-called structural factors. Each of them will be presented as a function of three components of the wave vector (a, b, c) and depends thereto on the set of probabilities but only as on parameters.

$$\begin{aligned}
g_0 &= w_1 e^{\frac{1}{2} i\cdot\pi(a+b+c)} + w_2 e^{\frac{1}{2} i\cdot\pi(a-b-c)} + w_3 e^{\frac{1}{2} i\cdot\pi(-a+b-c)} + w_4 e^{\frac{1}{2} i\cdot\pi(-a-b+c)} + \\
&+ w_5 e^{\frac{1}{2} i\cdot\pi(-a+b+c)} + w_6 e^{\frac{1}{2} i\cdot\pi(a-b+c)} + w_7 e^{\frac{1}{2} i\cdot\pi(a+b-c)} + w_8 e^{\frac{1}{2} i\cdot\pi(-a-b-c)}; \\
g_1 &= w_1 e^{\frac{1}{2} i\cdot\pi(a+b+c)} + w_2 e^{\frac{1}{2} i\cdot\pi(a-b-c)} - w_3 e^{\frac{1}{2} i\cdot\pi(-a+b-c)} - w_4 e^{\frac{1}{2} i\cdot\pi(-a-b+c)} - \\
&- w_5 e^{\frac{1}{2} i\cdot\pi(-a+b+c)} + w_6 e^{\frac{1}{2} i\cdot\pi(a-b+c)} + w_7 e^{\frac{1}{2} i\cdot\pi(a+b-c)} - w_8 e^{\frac{1}{2} i\cdot\pi(-a-b-c)}; \\
g_2 &= w_1 e^{\frac{1}{2} i\cdot\pi(a+b+c)} - w_2 e^{\frac{1}{2} i\cdot\pi(a-b-c)} + w_3 e^{\frac{1}{2} i\cdot\pi(-a+b-c)} - w_4 e^{\frac{1}{2} i\cdot\pi(-a-b+c)} + \\
&+ w_5 e^{\frac{1}{2} i\cdot\pi(-a+b+c)} - w_6 e^{\frac{1}{2} i\cdot\pi(a-b+c)} + w_7 e^{\frac{1}{2} i\cdot\pi(a+b-c)} - w_8 e^{\frac{1}{2} i\cdot\pi(-a-b-c)}; \\
g_3 &= w_1 e^{\frac{1}{2} i\cdot\pi(a+b+c)} - w_2 e^{\frac{1}{2} i\cdot\pi(a-b-c)} - w_3 e^{\frac{1}{2} i\cdot\pi(-a+b-c)} + w_4 e^{\frac{1}{2} i\cdot\pi(-a-b+c)} + \\
&+ w_5 e^{\frac{1}{2} i\cdot\pi(-a+b+c)} + w_6 e^{\frac{1}{2} i\cdot\pi(a-b+c)} - w_7 e^{\frac{1}{2} i\cdot\pi(a+b-c)} - w_8 e^{\frac{1}{2} i\cdot\pi(-a-b-c)}; \\
g_4 &= w_1 e^{\frac{1}{2} i\cdot\pi(a+b+c)} - w_2 e^{\frac{1}{2} i\cdot\pi(a-b-c)} - w_3 e^{\frac{1}{2} i\cdot\pi(-a+b-c)} + w_4 e^{\frac{1}{2} i\cdot\pi(-a-b+c)} - \\
&- w_5 e^{\frac{1}{2} i\cdot\pi(-a+b+c)} - w_6 e^{\frac{1}{2} i\cdot\pi(a-b+c)} + w_7 e^{\frac{1}{2} i\cdot\pi(a+b-c)} + w_8 e^{\frac{1}{2} i\cdot\pi(-a-b-c)}; \\
g_5 &= w_1 e^{\frac{1}{2} i\cdot\pi(a+b+c)} - w_2 e^{\frac{1}{2} i\cdot\pi(a-b-c)} + w_3 e^{\frac{1}{2} i\cdot\pi(-a+b-c)} - w_4 e^{\frac{1}{2} i\cdot\pi(-a-b+c)} - \\
&- w_5 e^{\frac{1}{2} i\cdot\pi(-a+b+c)} + w_6 e^{\frac{1}{2} i\cdot\pi(a-b+c)} - w_7 e^{\frac{1}{2} i\cdot\pi(a+b-c)} + w_8 e^{\frac{1}{2} i\cdot\pi(-a-b-c)}; \\
g_6 &= w_1 e^{\frac{1}{2} i\cdot\pi(a+b+c)} + w_2 e^{\frac{1}{2} i\cdot\pi(a-b-c)} - w_3 e^{\frac{1}{2} i\cdot\pi(-a+b-c)} - w_4 e^{\frac{1}{2} i\cdot\pi(-a-b+c)} + \\
&+ w_5 e^{\frac{1}{2} i\cdot\pi(-a+b+c)} - w_6 e^{\frac{1}{2} i\cdot\pi(a-b+c)} - w_7 e^{\frac{1}{2} i\cdot\pi(a+b-c)} + w_8 e^{\frac{1}{2} i\cdot\pi(-a-b-c)}.
\end{aligned} \qquad (6)$$

The Hamiltonian has more simple form with the following basis function: $(s, p_x, p_y, p_z)_a, (s, p_x, p_y, p_z)_c$, here the indicators "*a, c*" pointed out whose functions (anion's or cation's) are presented.

Let us to define few matrices, which will be used as blocks of the Hamiltonian Matrix.

$$Ha = \begin{bmatrix} E_{sa} & 0 & 0 & 0 \\ 0 & E_{pa} & 0 & 0 \\ 0 & 0 & E_{pa} & 0 \\ 0 & 0 & 0 & E_{pa} \end{bmatrix}; \tag{7}$$

$$Hc = \begin{bmatrix} E_{sc} & 0 & 0 & 0 \\ 0 & E_{pc} & 0 & 0 \\ 0 & 0 & E_{pc} & 0 \\ 0 & 0 & 0 & E_{pc} \end{bmatrix}; \tag{8}$$

$$Hac = \begin{bmatrix} E_{ss}g_0 & E_{sp}g_1 & E_{sp}g_2 & E_{sp}g_3 \\ -E_{sp}g_1 & E_{xx}g_0 & E_{xy}g_4 & E_{xy}g_5 \\ -E_{sp}g_2 & E_{xy}g_4 & -E_{xx}g_0 & E_{xy}g_6 \\ -E_{sp}g_3 & E_{xy}g_5 & E_{xy}g_6 & E_{xx}g_0 \end{bmatrix}. \tag{9}$$

Finally we can to construct the complete Hamiltonian in the form of a blocked (8*8) Matrix:

$$H = \begin{bmatrix} Ha & Hac \\ HermitianTranspose(Hac) & Hc \end{bmatrix} = \begin{bmatrix} Ha & Hac \\ Hac^{+} & Hc \end{bmatrix}. \tag{10}$$

So, the Hamiltonian Matrix is obtained. Let it to be below:

$$\begin{aligned} &Ha = H_1; \qquad Hc = H_2; \\ &Hac = H_{12}; \qquad Hac^{+} = H_{21}; \\ &Ham = H. \end{aligned} \tag{11}$$

Then we can to rewrite the Hamiltonian Matrix in the form:

$$Ham = \begin{bmatrix} H_1 + \begin{bmatrix} -\varepsilon & 0 \\ 0 & -\varepsilon \end{bmatrix} & H_{12} \\ H_{21} & H_2 + \begin{bmatrix} -\varepsilon & 0 \\ 0 & -\varepsilon \end{bmatrix} \end{bmatrix}. \tag{12}$$

Let us to multiply *Ham* on the left with the matrix:

$$A = \begin{bmatrix} 1 & -\left(H_{12} \cdot \left(\dfrac{1}{H_2 + \begin{bmatrix} -\varepsilon & 0 \\ 0 & -\varepsilon \end{bmatrix}} \right) \right) \\ 0 & 1 \end{bmatrix}. \tag{13}$$

Because the determinant A is equal to one, we have that determinant of matrix $A\cdot(Ham\text{-}eE)$ is equal to determinant of matrix $Ham\text{-}eE$, here $E=\begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix}$.

Because matrix $A\cdot(Ham\text{-}eE)$ is Upper Triangle Matrix with upper diagonal block

$$H_1+\begin{bmatrix}-\varepsilon & 0\\ 0 & -\varepsilon\end{bmatrix}-\left(H_{12}\cdot\left(\frac{1}{H_2+\begin{bmatrix}-\varepsilon & 0\\ 0 & -\varepsilon\end{bmatrix}}\right)\right)H_{21}. \qquad (14)$$

The final secular equation for the eigenvalues problem might be rewritten in the form:

$$\det\left(A\cdot Ham\right)_{1,1}=0. \qquad (15)$$

The last equation has twice lower order as for starting 8*8 equation $\det(Ham)=0$.

Let us to find the reduced secular matrix S and the corresponding secular equation.

$$E=\begin{bmatrix}\varepsilon & 0 & 0 & 0\\ 0 & \varepsilon & 0 & 0\\ 0 & 0 & \varepsilon & 0\\ 0 & 0 & 0 & \varepsilon\end{bmatrix} \qquad (16)$$

$$S=Ha-E-Hac\cdot\left(Hc-E\right)^{-1}\cdot Hac^{+}. \qquad (17)$$

The eigenvalues problem should be solved from such equation:

$$\det\left(S\right)=0. \qquad (18)$$

Discussions. It should be noted first that diagonal blocks of Hamiltonian Matrix are independent on the both set of parameters: (a, b, c) and (w_1, w_2, w_3, w_4, w_5, w_6, w_7, w_8). Thus our analysis will be in touching just with the interaction (4*4) block of Hamiltonian Hac.

Disordered crystals

Let us consider a complete disordered crystal:

$$w_1=w_2=w_3=w_4=w_5=w_6=w_7=w_8=3/4. \qquad (19)$$

Let us to consider the point $a=0$, $b=0$, $c=0$ (or Γ-point). Then from (18)

$$\varepsilon_{\Gamma}=\frac{E_{sa}+E_{sc}}{2}\pm\frac{\sqrt{\left(E_{sa}-E_{sc}\right)^2+144E_{ss}^2}}{2}; \qquad (20)$$

$$\varepsilon_{\Gamma} = \frac{E_{pa} + E_{pc}}{2} \pm \frac{\sqrt{\left(E_{pa} - E_{pc}\right)^2 + 144E_{xx}^2}}{2}. \quad (21)$$

Let us consider the point $a = 1/2$, $b = 0$, $c = 0$ (or X-point):

$$\varepsilon_{X} = \frac{E_{pa} + E_{pc}}{2} \pm \frac{\sqrt{\left(E_{pa} - E_{pc}\right)^2 + 72E_{xx}^2}}{2}. \quad (22)$$

Let us consider the point $a = 1/2$, $b = 1/2$, $c = 1/2$ (or L-point):

$$\varepsilon_{L} = \frac{E_{pa} + E_{pc}}{2} \pm \frac{\sqrt{\left(E_{pa} - E_{pc}\right)^2 + 18E_{xx}^2 + 36E_{xx}E_{xy} + 18E_{xy}^2}}{2}. \quad (23)$$

Ordered crystals

Let us to consider a complete ordered crystal:

$$w_1 = 0,\ w_2 = 1,\ w_3 = 1,\ w_4 = 1,\ w_5 = 1,\ w_6 = 1,\ w_7 = 1,\ w_8 = 0. \quad (24)$$

Let us to consider the Γ-point:

$$\varepsilon_{\Gamma} = \frac{E_{sa} + E_{sc}}{2} \pm \frac{\sqrt{\left(E_{sa} - E_{sc}\right)^2 + 144E_{ss}^2}}{2}; \quad (25)$$

$$\varepsilon_{\Gamma} = \frac{E_{pa} + E_{pc}}{2} \pm \frac{\sqrt{\left(E_{pa} - E_{pc}\right)^2 + 144E_{xx}^2 - 192E_{xx}E_{xy} + 64E_{xy}^2}}{2}; \quad (26)$$

$$\varepsilon_{\Gamma} = \frac{E_{pa} + E_{pc}}{2} \pm \frac{\sqrt{\left(E_{pa} - E_{pc}\right)^2 + 144E_{xx}^2 - 96E_{xx}E_{xy} + 16E_{xy}^2}}{2}. \quad (27)$$

Let us to consider the X-point:

$$\varepsilon_{X} = \frac{E_{pa} + E_{pc}}{2} \pm \frac{\sqrt{\left(E_{pa} - E_{pc}\right)^2 + 72E_{xx}^2 + 48E_{xx}E_{xy} + 8E_{xy}^2}}{2}. \quad (28)$$

Let us to consider the L-point:

$$\varepsilon_{L} = \frac{E_{pa} + E_{pc}}{2} \pm \frac{\sqrt{\left(E_{pa} - E_{pc}\right)^2 + 72E_{xx}^2 + 48E_{xx}E_{xy} + 8E_{xy}^2}}{2}. \quad (29)$$

The investigations show that the part of energy levels is straightly depending on the degree of vacancies ordering, whereas other part of them is independent. Here may be illustrated an example of a couple of the depending levels for Γ-point (see Eqs. (26) and (21)) for ordered and disordered crystals respectively.

It would be noted that expressions (26) and (21) are describing one and the same couple of levels, and a constant is never equal to zero generally speaking (i.e. $E_{xy} \neq 0$). Therefore the difference between energy levels is caused itself by structural factors and thus is the reflection of the status of the vacancies organization (i.e. of their ordering).

References:

1. Pawlikowski J. M., Appl J. Phys. 53, 5 (1982).
2. Sieranski K., Szatkowski J., and Misiewicz J. Phys. Rev. B 50, 11 (1994).
3. Harrison A. W. Electronic structure and the Properties of Solids // The Physics of the Chemical Bond. – San Francisco: W.H. Freeman and Co., 1980.

Напівпровідники групи $A_3^{II}B_2^{V}$ мають структури, сильно наближені до кубічних щільно упакованих кристалічних ґраток. Їхні катіонні вакансії можуть знаходитися у відносному безладі і навпаки. Ця деталь безпосередньо впливає на так звані "структурні фактори" елементів матриці гамільтоніана. Елементи матриці змінюються в залежності від припущення про ступінь впорядкування вакансій. Дослідження показують, що частина енергетичних рівнів знаходяться в прямій залежності від ступеню впорядкування вакансій, тоді як друга їхня частина незалежна.

Ключові слова: *$A_3^{II}B_2^{V}$ сполуки, матриця гамільтоніана, енергетичні зони, катіонні вакансії.*

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ЧИСЕЛЬНЕ ЗНАХОДЖЕННЯ ОПТИМАЛЬНОГО РОЗПОДІЛУ ГРАНИЧНИХ ПОТЕНЦІАЛІВ ТА ГЕОМЕТРІЇ ГРАНИЧНИХ ПОВЕРХОНЬ В ЗАДАЧАХ ТЕОРІЇ ПОТЕНЦІАЛУ

Розглядається обернена задача теорії потенціалу знаходження оптимальної геометрії граничних поверхонь та оптимального розподілу граничних потенціалів в осесиметричному випадку. Методика рішення оберненої задачі зводиться до мінімізації деякого функціоналу та розв'язуванні системи інтегральних рівнянь Фредгольма першого роду з логарифмічною особливістю.

Ключові слова: *обернена задача, інтегральні рівняння, сплайн-функції, метод колокації, функціонал.*

Постановка проблеми. Крайові задачі математичної фізики поділяються на прямі та обернені.

У прямих задачах потрібно знайти характеристики поля при відомих геометрії граничних поверхонь та крайових умовах. В оберне-

