

## One Dimensional Model for Polytypes

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The general expression for the dispersion relation for a polyatomic one dimensional crystal obtained by the Laplace Transform Method is applied to materials with the *fcc* and *hcp* structures, both consisting of close-packed planes of atoms with the stacking sequence of plane *ABC/ABC...* and *AB/AB...* respectively. The expression is also applied to polytypes, that is materials characterized by a stacking sequence with longer repeat unit. The effective mass is cast in a condensed form useful for further calculations. The results from this simple model are only qualitative.

A expressão geral para a relação de dispersão para um cristal unidimensional poliatômico, obtida pelo método da transformada de Laplace, é aplicada a materiais com estruturas *fcc* e *hcp*, ambas consistindo de planos densamente justapostos de átomos com a sequência de empilhamento de planos do tipo *ABC/ABC...* e *AB/AB...* respectivamente. A expressão é também aplicada a politipos, isto é, materiais caracterizados por uma sequência de empilhamento com unidade de repetição mais longa. A massa efetiva é posta em uma forma condensada, útil para cálculos adicionais. Os resultados deste modelo simples são apenas qualitativos.

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## 1. INTRODUCTION

The one dimensional representation of a periodic crystal has the advantage of allowing an exact solution of the Schrödinger equation, but the results obtained should be taken as a first insight into the problem, describing no more than the qualitative aspects of the crystals.

Seraphin<sup>1</sup> and Adawi<sup>2</sup> apply the one dimensional Kronig-Penney model to compound semiconductors having the zinblende structure. Along the (111) direction we find planes normal to this direction populated alternately by the two different types of atoms which constitute the compound. The model replaces these planes by Dirac delta functions located at the intersection of the line (111) with the plane and with strength proportional to the binding strength of the particular atom in the plane. The Schrödinger equation for the diatomic linear lattice which results from these assumptions is solved using one of the methods developed by Saxon and Hutner<sup>3</sup>. The results that they obtain in this way for the band structure and for the effective mass at the band edges are qualitatively good.

The zinblende structure, which is a face-centered cubic structure ( $fcc$ ) can be described as a close-packed plane of rigid spheres having the sequence  $\dots ABC/ABC\dots$  where  $A, B$  and  $C$ , in general, represent the position of the center of the spheres stacked in such a way that the arrangement is close-packed. The repeated unit which generates the whole structure is  $ABC$ . The hexagonal close-packed structure ( $hcp$ ) is a structure with the sequence of planes such as  $\dots/AB/AB\dots$  where the repeated unit is  $AB$ . There are variety of ways of close packing spheres, as mentioned above, each one differing by the number of planes in the repeated unit or by different sequence of planes. These arrangements receive the name of polytypes and they are characterized by a stacking sequence with a long period unit<sup>4</sup>.

In what follows we apply the model used by Seraphin and Adawi to polytypes of 2,3,4,6,8 and 10 layers, that is, polytypes with the structures  $\dots AB/AB\dots$ ,  $\dots ABC/ABC/\dots$ ,  $\dots ABAC/ABAC/\dots$  etc. having 2,3,4,6 and 10 layers in the repeated unit. We treat a polytype

as a one dimensional Kronig - Penney polyatomic crystal along the line of the stacking sequence and replace each plane that intercepts this line by a convenient Dirac delta function.

In order to accomplish this we need to know how to solve the Schrödinger equation for a linear lattice with many atoms per cell, that is we need the dispersion relation for a polyatomic crystal.

## 2. DISPERSION RELATION FOR POLYATOMIC ONE DIMENSIONAL CRYSTALS

The one dimensional Schrödinger equation for a single electron moving in a potential represented by  $V(x)$  is

$$\left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} - eV(x) \right] \psi(x) = E\psi(x) \quad (1)$$

or

$$\left[ \frac{d^2}{dx^2} + \frac{2U(x)}{a^2} \right] \psi(x) = -K^2 \psi(x) , \quad (2)$$

where

$$K^2 \equiv \frac{2mE}{\hbar^2} , \quad (3)$$

$$U(x) = \frac{ma^2}{\hbar^2} eV , \quad (4)$$

and  $a$  is the lattice constant (length of the repeated unit),  $E$  is the electron energy and  $x$  is the direction of stacking sequence of planes. According to our model the potential  $U(x)$  is represented by Dirac delta functions, and for  $p$  different atoms per cell is

$$U(x) = a \sum_{n=-\infty}^{\infty} \sum_{i=1}^P P_i \delta(x - na - \beta_i a) \quad (5)$$

where  $P_i$  and  $\beta_i$  are the strength and the location of the Dirac delta functions inside the cell and  $0 < \beta_i < 1$ . Since the potential is periodic with period  $a$  the acceptable solutions of eq. (2) are of the form

$$\psi(x + la) = e^{ikla} \psi(x) \quad (6)$$

It has already been shown<sup>5</sup> that the dispersion relation for this case is

$$\begin{aligned}
 \cos ka = & \cos Ka - \sum_{i=1}^P \frac{P_i}{Ka} \sin Ka + 2 \sum_{i=1}^P \sum_{j>1}^P \frac{P_i P_j}{(Ka)^2} \sin [K(\beta_j - \beta_i) a] \cdot \\
 & \cdot \sin [K(1 - \beta_j + \beta_i) a] - \\
 & - 4 \sum_{i=1}^P \sum_{j>i}^P \sum_{s>j}^P \frac{P_i P_j P_s}{(Ka)^3} \sin [K(\beta_j - \beta_i) a] \sin [K(\beta_s - \beta_j) a] \sin [K(1 - \beta_s + \\
 & + \beta_i) a] + \dots (-1)^P (2)^{P-1} \frac{P_1 P_2 P_3 \dots P_P}{(Ka)^P} \sin [K(\beta_2 - \beta_1) a] \sin [K(\beta_3 - \beta_2) a] \\
 & \cdot \sin [K(\beta_p - \beta_{p-1}) a] \sin [K(1 - \beta_p + \beta_1) a] \quad (7)
 \end{aligned}$$

### The Effective Mass

In this one dimensional model the effective mass  $m^*$  is given by<sup>2</sup>

$$\frac{m^*}{m} = \hbar^2 \left( m \frac{\partial^2 E}{\partial k^2} \right)^{-1} = 2 \left( \frac{\partial^2 K^2}{\partial k^2} \right)^{-1} = \left[ K \frac{\partial^2 K}{\partial k^2} + \left( \frac{\partial K}{\partial k} \right)^2 \right]^{-1} \quad (8)$$

To calculate the derivatives that appear in eq.(8) we notice that we do not know  $K$  as a function of  $k$  but only  $\cos(ka)$  as a function of  $K$ , as stated in the dispersion relation eq.(7). So it seems necessary to replace the derivative  $\partial K / \partial k$  by  $\partial / \partial K (\cos ka)$  which can be calculated from eq.(7). This can be accomplished by noting that

$$\frac{\partial}{\partial k} (\cos ka) = \frac{\partial}{\partial K} (\cos ka) \frac{\partial K}{\partial k} = -a \sin ka \quad (9)$$

Taking the derivative with respect to  $k$  of the above expression we get

$$\frac{\partial}{\partial k} \left[ \frac{\partial}{\partial k} (\cos ka) \right] = \frac{\partial^2}{\partial k \partial K} (\cos ka) \frac{\partial K}{\partial k} + \frac{\partial}{\partial K} (\cos ka) \frac{\partial^2 K}{\partial k^2} = -a^2 \cos ka \quad (10)$$

A considerable simplification arises when one considers the effective mass at the band edges, that is, those states  $k$  such that  $ka = 0$  or  $\pi$ , since we can conclude from eq.(9) that  $\partial K/\partial k = 0$  everywhere, except at  $K = 0$ . Then, at the band edges eq.(10) becomes

$$\frac{\partial}{\partial K} (\cos ka) \frac{\partial^2 K}{\partial k^2} = \pm a^2 \quad (11)$$

where the plus or minus sign in for  $ka = \pi$  or  $ka = 0$ .

Substituting the value of  $\partial^2 K/\partial k^2$  of eq.(11) into eq. (8) we get

$$\frac{m^*}{m} = \pm \frac{1}{a^2 K} \frac{\partial}{\partial K} (\cos ka) \quad (12)$$

and having in mind eq. (7) we obtain

$$s \frac{m^*}{m} = -\frac{\sin ka}{Ka} + \sum_{1 \leq \ell \leq p} \frac{(-1)^{\ell_2} \ell_2 (\ell_2 - 1)}{(Ka)^{\ell_2 + 1}} \sum_{i \in C_p} \left\{ -\frac{\ell}{Ka} \frac{\ell}{t+1} P_{f_i}(t) \sin \right. \\ \left. \sin \left[ K(\beta_{f_i}(t+1) - \beta_{f_i}(t)) a \right] + \sum_{h=1}^{\ell} (\beta_{f_i}(h+1) - \beta_{f_i}(h)) P_{f_i}(h) \right. \\ \left. \cos \left[ K(\beta_{f_i}(h+1) - \beta_{f_i}(h)) a \right] \cdot \sum_{\substack{q=1 \\ q \neq h}}^{\ell} \pi P_{f_i}(q) \sin \left[ K(\beta_{f_i}(q+1) - \beta_{f_i}(q)) a \right] \right\} \quad (13)$$

This expression, as mentioned before, is valid at the band edges only, where  $s=1$  for  $ka=\pi$  and  $s=-1$  for  $ka=0$ , with the restriction  $K \neq 0$ . See the appendix for further details.

The right hand side of eq.(7) crosses the line  $\cos(ka) = -1$ , that is  $ka = \pi$ , twice. The first value of  $K$  for which this happens can be called the top of the valence band and the corresponding effective mass is the hole effective mass. The other value is the bottom of the conduction band and the effective mass there is the electron effective mass.

### 3. APPLICATION TO POLYTYPES AND RESULTS

A polytype made up of two types of atoms  $X$  and  $Y$  can be considered as consisting of a stacking sequence of interleaved close-packed double layers of  $X$  atoms and  $Y$  atoms. These layers are stacked along the (111) direction and one layer, say the layer of  $X$  atoms, can be differentiated from the next layer of  $X$  atoms by a rotation of  $60^\circ$  degree about the (111) direction. There are only three possibilities for the layers, and if we follow the current notation, the layers can be of types  $A$ ,  $B$  and  $C$ , and the corresponding polytypes could be  $\dots/A\alpha BB/\dots$ , or  $\dots/A\alpha BB\alpha C/\dots$ , or  $\dots/A\alpha BB\alpha C\alpha C/\dots$  etc., which are respectively a two, three or four layer polytypes, etc., where  $A$  means a close-packed layer of  $X$  atoms,  $\alpha$  is a similar layer of  $Y$  atoms, and so on<sup>6</sup>.

In order to represent a polytype by a one dimensional model we choose the packing direction (111) as the  $x$  axis of eq. (1) and the electrostatic potential of any layer of the structure we represent by a Dirac delta function whose position is the intersection of that layer with the (111) direction and whose strength is proportional to the binding strength of the type of atoms lying in the layer in question.

In fig. (1) we show some polytypes structures in three dimensions<sup>7</sup> and in fig. (2) the corresponding one dimensional structure as considered in this paper. Atoms of the  $X$  type are located in the  $A$  position and they are represented by a Dirac delta function of strength  $P_X$  and atoms of the  $Y$  type are located at the  $\alpha$  positions and are represented by Dirac delta function of strength  $P_Y$ . With this, eq.(5) has only two different values for  $P_i$ , which are the values  $P_X$  and  $P_Y$ , but for each value of  $n$  in that equation, that is, in each cell we may have several peaks  $P_i$  of potential, the number depending, of course, upon the polytype considered.

The values  $P_X$  and  $P_Y$  can be determined in a way similar to Seraphin<sup>1</sup> and Adawi<sup>2</sup>. In reference 1 it was found empirically that the covalent binding energy of the elements of the column IV of the periodic table could be represented by a Dirac delta function of strength  $P = 3$ . In reference 2 it was assumed that compounds like GaAs, ZnSe, CuBr, etc., made up of atoms symmetrically located with respect to the element in column

IV have, besides the covalent term  $P \approx 3$ , anionic component in the chemical bond, represented by  $\Delta P$ , which was proportional to the charge difference between the symmetrical element and the element in the column IV.

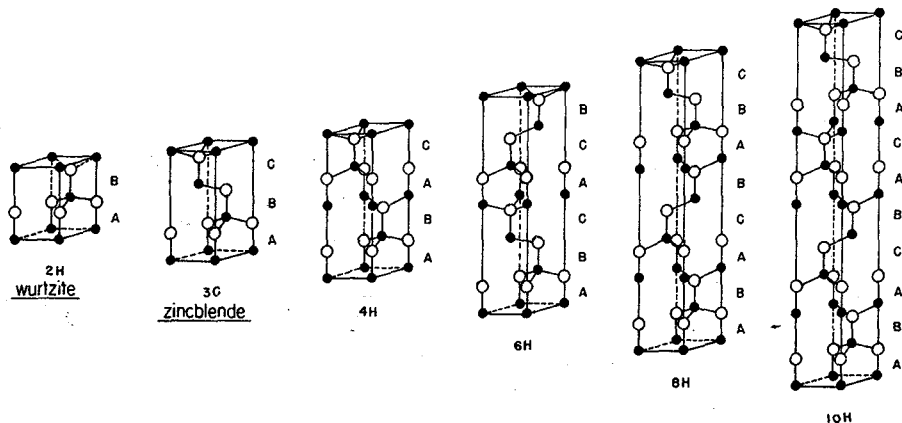


Fig.1 - Three dimensional polytypic modifications of ZnS. The small filled circles are the Zn atoms and the large open ones are the S atoms.

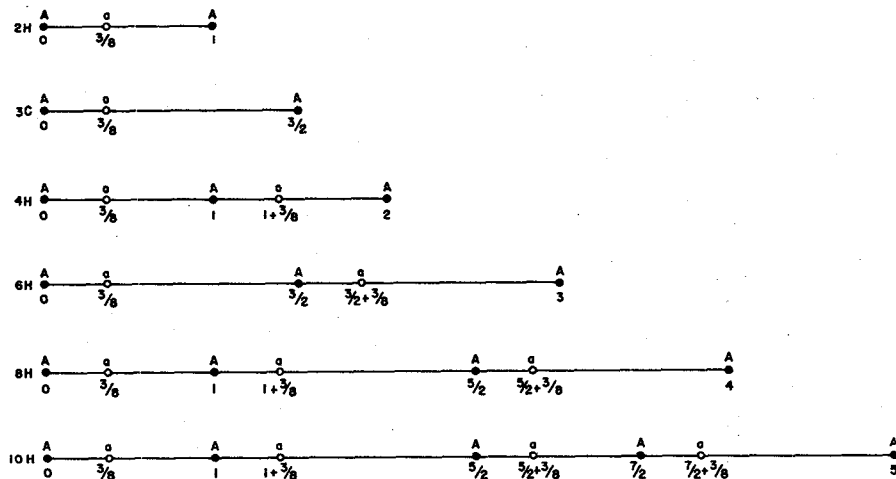


Fig.2 - One dimensional representation of the unit cell of the first six polytypes shown in fig.1 in the (111) direction. The intersections of the layers made up of distinct atoms, with the (111) direction, are called A and  $\alpha$  respectively. Once we fix the (111) direction these are the only layers which intercept the (111) direction with one atom at the intersection.

In this way the dispersion relation could be obtained, for the polytypic modifications of the compounds mentioned above, especially those which obey the structures shown in fig. (2), considering in eq.(7)  $P_X = P - \Delta P$  and  $P_Y = P + \Delta P$  where  $P=3$  and  $\Delta P = 1, 2, 3, \dots$  respectively and the location  $\beta_z$  of these peaks is as shown in fig. (2).

Unfortunately the model does not give a perfect differentiation among some polytypes, for instance there is no way to differentiate the two layer polytype (2H) from the four layer (4H), the six layer (6H) from the cubic three layer (3C). For the other polytypes which are uniquely characterized by the one dimensional model, we are interested in comparing the energy bands and the effective mass in such a way that the difference among the calculated bands are due only to polytypism. To accomplish this, we choose the 2H polytype for reference. Then in eq. (5)  $P = P_X(2H)$  and this peak is located at  $\beta = 0$ , and  $P_2 = P_Y(2H)$  and is located at  $\beta_2 = 3/8$ . The size of the unit cell is taken as  $a_{2H}$  and it is used as reference for other polytypes. The average potential per cell,  $\bar{V}_{2H}$ , is

$$\bar{V}_{2H} = \frac{\hbar}{m a_{2H}} \frac{1}{a_{2H}} \int_0^{a_{2H}} U(x) dx = \frac{\hbar}{m a_{2H}} \{P_X(2H) + P_Y(2H)\} \quad (14)$$

As we mentioned before, the 2H and the 4H polytypes can not be distinguished in this model, so they should present the same band structure. In order to accomplish this, we see from eq. (7) that we have to consider the strength of the Dirac delta function of each atom of the 4H as double the value for 2H, that is  $P_X(4H) = 2P_X(2H)$ . This is due to the fact that the length of the cell  $a_{4H} = 2a_{2H}$ , and we must keep the average potential per cell the same for all polytypes. In this way we get

$$\begin{aligned} P_X(6H) &= 3P_X(2H) & a_{6H} &= 3a_{2H} \\ P_X(8H) &= 4P_X(2H) & a_{8H} &= 4a_{2H} \\ P_X(10H) &= 5P_X(2H) & a_{10H} &= 5a_{2H} \\ P_X(3C) &= (3/2)P_X(2H) & a_{3C} &= (3/2)a_{2H} \end{aligned}$$

the same relations hold for the strength  $P_Y$  of the atoms of type Y.



It can be shown<sup>8</sup> that if the relations above connecting the strength of the potentials and the cell dimension were substituted in eq.(7) and if the atoms along the lines in fig.2 were placed in such a way that they were all located along the same vertical line<sup>9</sup> then we would get the same band structure and the same effective mass for all polytypes. The difference between them comes from the displacement of the atoms from this vertical line and that is the effect of the polytypism in our model.

We must remember that eq.(7) give us a relation between the states  $k$  and the wave number  $K$  and since  $K$  is the energy we get from eq.(7) a relation between the states and their respective energies. The allowed quantum states are those for which the wave function in eq.(6) are travelling waves, that is,  $k$  is real. If  $k$  is not real the corresponding state is a forbidden state. From eq.(7) we see that  $k$  is real for all values of  $K$  for which the right hand side of the expression is limited by  $\pm 1$ . These values of  $K$  gives us the allowed energy levels of the electron. Outside this range, the values of  $K$  correspond to forbidden energy levels because to satisfy the equation  $|\cos ka| > 1$ ,  $k$  can not be real.

We plot the right-hand side of eq.(7) in a vertical axis against  $(Ka)^2$  and we look for the intersections of this curve with the horizontal lines  $+1$  and  $-1$ . It is observed that for  $(Ka)^2 < 0$ , that is, for negative energies, the right hand side of eq.(7) contains hyperbolic functions and this means that once it crosses the line  $+1$  it will never cross it again for decreasing energy. The point  $(Ka)^2$  of the intersection mentioned above correspond to the first line in the bottom of fig.3. The next intersection for increasing energies, will give us the other lines shown in fig.3 and in this way we get the band structure for each polytype mentioned in fig.1.

If we call the higher negative band the valence band (for the 2H polytype there is only one negative band) and the lowest positive one the conduction band, we can see from fig.3 that the general tendency as we go from the 2H to 3C polytype in the following - the top of the valence band shows encreasing negative energy and the bottom of the conduction band shows decreasing positive energy but the difference between these values (gap) keeps approximately constant.

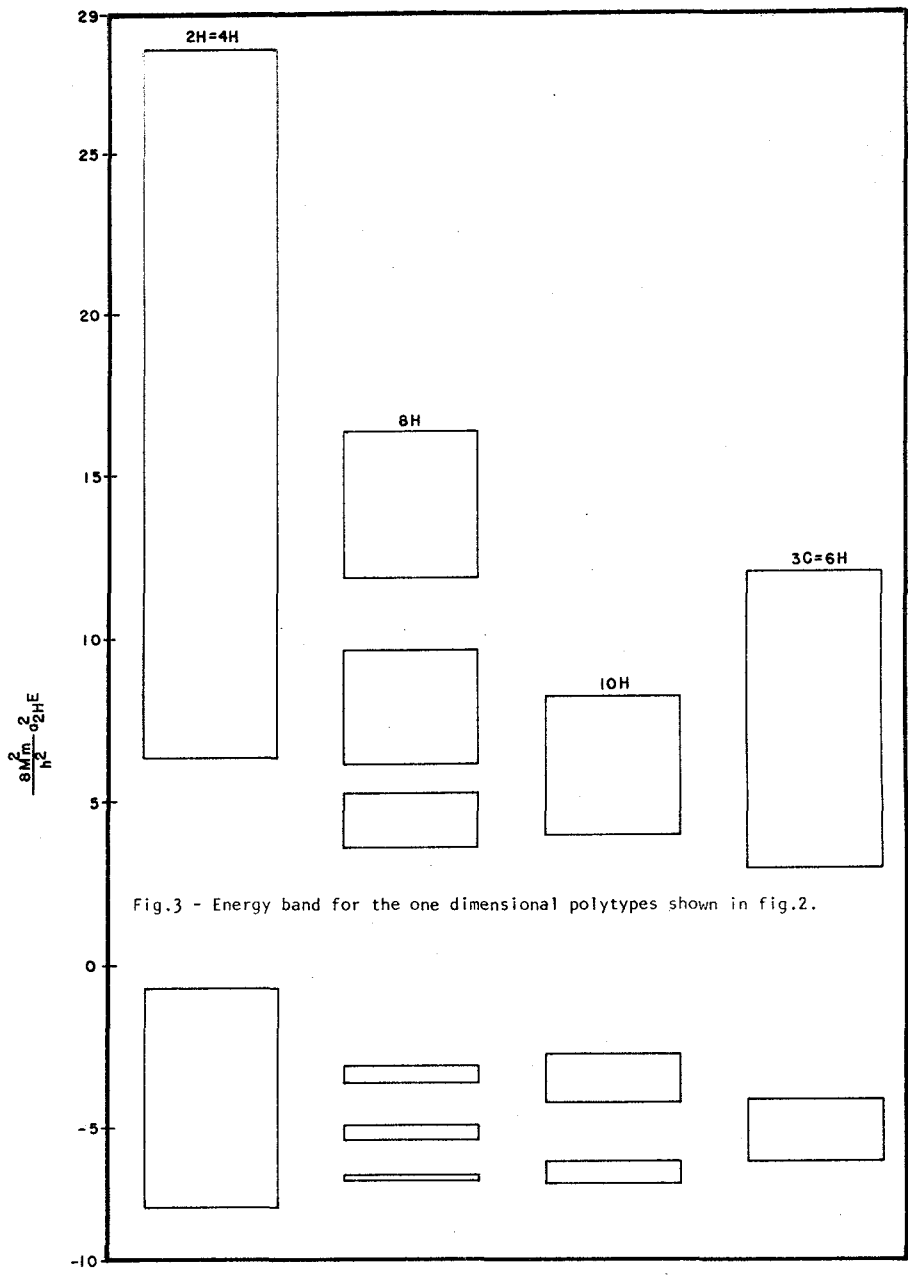


Fig.3 - Energy band for the one dimensional polytypes shown in fig.2.

In this respect the results from the model can be compared with the experimental results obtained by Baars<sup>10</sup> for polytypic modifications of zinc sulfite, ZnS. We consider the polytypes 2H, 8H, 10H and 3C, the only ones that can be differentiated by our model and from the band structure in fig.3 we plot the top of the valence band and the bottom of the conduction band against the fraction of the cubic packing<sup>11</sup> in each polytype. Proceeding in this way we obtain fig.4 which should be compared with the experimental results. Even though the ZnS compound should in our model have different values of  $P$  but the same asymmetry potential  $\Delta P = 2$  due to the localization of the elements Zn and S in the periodic table with respect to the column IV, the agreement is qualitatively good and the model seems to be able to show the general trend of the experimental results.

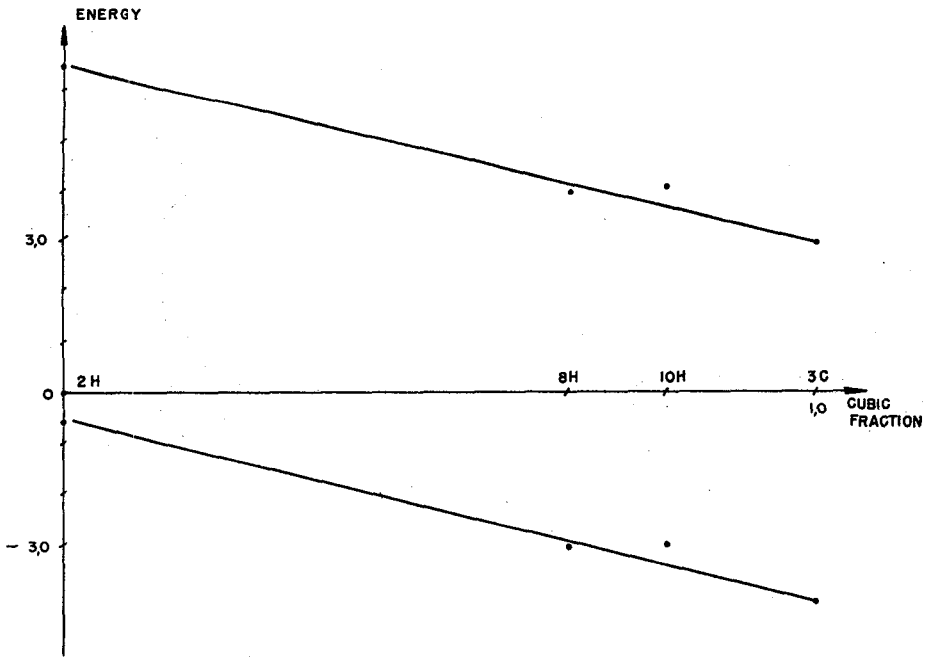


Fig.4 - Energy of the band edges of the polytypes versus fraction of the cubic packing.

## APPENDIX

It is possible to write the dispersion relations, eq. (7) in a condensed form. This will facilitate the handling of the equation and will help in obtaining numerical results. To accomplish this let us define  $P_p$  as the strength of the Dirac delta function corresponding to each atom,  $p$  as the number of Dirac delta function per cell,  $C_{p,\ell}$  the set of all the subsets of  $\{1,2,3\dots p\}$  with  $\ell$  elements each,  $f_i: J \rightarrow I$  is a strictly increasing function defined over the set  $J = \{1,2,\dots,\ell+1\}$  and taking values in the set  $I = iU\{p+1\}$ , that is,  $f_i(\ell+1) = p+1$ ,  $\beta_{f_i}(\ell+1) = 1 + \beta_{f_i}(1)$  and  $z = ka = \frac{a}{\hbar} (2mE)^{1/2}$ : with these definitions eq.(7) can be written as

$$\cos(ka) = \cos(z) + \sum_{\ell=1}^P (-1)^\ell 2^{(\ell-1)} \sum_{i \in C_{p,\ell}} \sum_{t=1}^{\ell} \pi P_{f_i}(t) \frac{1}{z} \sin \left[ (\beta_{f_i}(t+1) - \beta_{f_i}(t)) z \right] \quad (\text{A. 1})$$

For instance, suppose we have three peaks per cell,  $P_1$ ,  $P_2$ , and  $P_3$  located at  $\beta_1 a$ ,  $\beta_2 a$  and  $\beta_3 a$ . The sets  $C_{3,\ell}$  for  $1 < \ell < 3$  are:

$$C_{3,1} = \{\{1\}, \{2\}, \{3\}\}$$

$$C_{3,2} = \{\{1,2\}, \{1,3\}, \{2,3\}\}$$

$$C_{3,3} = \{\{2,1,3\}\}.$$

For each  $\ell$  the sets  $i$  are:

$$i \subset C_{3,1} \rightarrow i = \{1\} \quad \text{or} \quad i = \{2\} \quad \text{or} \quad i = \{3\}$$

$$i \subset C_{3,2} \rightarrow i = \{1,2\} \quad \text{or} \quad i = \{1,3\} \quad \text{or} \quad i = \{2,3\}$$

$$i \subset C_{3,3} \rightarrow i = \{2,1,3\}$$

For each  $i$  the functions  $f_i = J \rightarrow I$  are

$$f_{\{1\}} : \{1,2\} \rightarrow \{1,4\} \quad \text{for } \ell = 1$$

$$f_{\{2\}} : \{1,2\} \rightarrow \{2,4\} \quad \text{for } \ell = 1$$

$$\begin{aligned}
f_{\{3\}} &: \{1,2\} + \{3,4\} && \text{for } \ell = 1 \\
f_{\{1,2\}} &: \{1,2,3\} + \{1,2,4\} && \text{for } \ell = 2 \\
f_{\{1,3\}} &: \{1,2,3\} + \{1,3,4\} && \text{for } \ell = 2 \\
f_{\{2,3\}} &: \{1,2,3\} + \{2,3,4\} && \text{for } \ell = 2 \\
f_{\{2,1,3\}} &: \{1,2,3,4\} + \{1,2,3,4\} && \text{for } \ell = 3
\end{aligned}$$

With these values eq. (A.1) becomes

$$\begin{aligned}
\cos(ka) = & \cos(z) - P_1 \frac{\sin z}{z} - P_2 \frac{\sin z}{z} - P_3 \frac{\sin z}{z} + 2 \frac{P_1 P_2}{z^2} \sin[(\beta_2 - \beta_1)z] \\
& \sin[(1 + \beta_1 - \beta_2)z] + 2 \frac{P_1 P_3}{z^2} \sin[(\beta_3 - \beta_1)z] \sin[(1 + \beta_1 - \beta_3)z] + \\
& + 2 \frac{P_2 P_3}{z^2} \sin[(\beta_3 - \beta_2)z] \sin[(1 + \beta_2 - \beta_3)z] - 4 \frac{P_1 P_2 P_3}{z^3} \sin[(\beta_2 - \beta_1)z] \\
& \sin[(\beta_3 - \beta_2)z] \sin[(1 + \beta_1 - \beta_3)z] .
\end{aligned}$$

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9. This would correspond to the trivial case of having the same array repeated in fig. (2) but considering the lattice distances as  $a_{2H}$ ,  $a_{4H}$ ,  $a_{6H}$  etc., respectively.

10. J.W. Baars, *International Conference on II-VI Semiconducting Compounds* (Benjamin, New York, 1976) pp.631.

11. One of the notation used to describe close packings is the one in which a symmetry is assigned to each layer the layer is hexagonal (*h*) if it is preceded and succeeded by layers in the same orientation, and it is a cubic (*c*) if the layers on either side are in different orientations. For instance, the 8H polytype *ABACBABC* of fig. 1 can be denoted by *chccchcc*, and the cubic percentage on it is  $6/8$ , that is, the number of *c* layer divided by the total number of layer.