Revista Brasileira de Física, Vol. 2, N.º 2, 1972

Optical Properties of a Four Layer Polytype of ZnS by the Empirical Pseudopotential Method

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Recebido em 5 de Novembro de 1971

The empirical pseudopotential method of Cohen and Bergstresser^{1,2,3} is used to show the linear decrease of the gap of polytypes with respect to the increasing portion of the cubic packing⁴. The method is also used to study the optical properties of a four layer polytype of ZnS.

O método do pseudopotencial empírico de Cohen e **Bergstresser^{1,2,3}** é usado para mostrar o decrescimento linear do *gap* dos politipos com relação ao crescimento da fração cúbica⁴. O método é **também** utilizado para estudar as propriedades ópticas dos politipos de *ZnS* de quatro camadas.

Introduction

A considerable amount of information with regard to the energy band structure of two and three layer crystals of ZnS has been obtained from various methods of band calculation. The empirical pseudo-potential method^{1,2,3} was used to calculate the band structure of a two layer hexagonal crystal of ZnS (wurtzite) from the optical spectrum of a three layer cubic crystal of ZnS (zincblende). An OPW calculation of the energy levels of wurtzite has been made⁵, where the crystal potential is formed by placing a self-consistent isolated atomic potential at each lattice site. The energy levels of wurtzite were also calculated using the Augmented Plane Wave Method (APW)⁶ at four symmetry points in the Brillouin Zone and at two points on the line A. A comparison between the energy levels of a two layer hexagonal and three layer cubic crystal of ZnS was made⁷ using the tight binding method. Experimental results of the reflectivity of some polytypes of ZnS are given by Baars⁴. Baars also shows the linear decrease of the gap ($\Gamma_6 - \Gamma_1$ transition) with respect to the increasing portion of the cubic packing in the polytypes.

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In this work, we calculated the energy band of a four layer polytype of ZnS and the energy at some symmetry points for higher order polytypes of ZnS using the empirical pseudo-potential method. We used the form factors determined by Cohen and Bergstresser² for a two layer to determine the energy for higher order polytypes.

The matrix elements of the pseudopotential can be shown to depend separately upon the ion positions (structure factors) and upon the ion potential (form factors)⁸. Consequently, the crystal potentials for two, four, six, etc. layer hexagonal polytypes were determined using the same form factors as in Ref. (2) with the structure factors calculated as shown in the text. This implies that any modification in the electronic distribution around each ion that may arise due to polytypism is neglected.

1. Polytypes

Certain crystals like ZnS, SiC, etc. crystalize in layers. These layers are stacked parallel to each other at constant intervals along a fixed direction (z-direction). When a group of layers repeats itself in such a way that it generates the whole crystal, this crystal is called a polytype. If the group which repeats itself contains two layers, the polytype is a two layer polytype, if it contains four layers it is a four layer polytype and so on. A useful terminology is to describe the layers by letters A, B, and C. With this notation a two layer polytype is described by the symbol AB/AB/AB... a three layer by ABC/ABC/ABC..., a four layer by ABAC/ABAC/... etc. When using this terminology for polytypes of ZnS, a layer A implies a layer A of Zn atoms and a layer A of S atoms, etc.

There is a simple rule to determine the symmetry of each layer of a polytype. A layer is an element of hexagonal packing (h) when it is neighbored by layers in equal positions, otherwise it is an element of cubic packing (c). In this way, the two, three, four, six, etc., layer polytypes can be expressed as AB/AB/AB, ABC/ABC/ABC, ABAC/ABAC/ABAC, ABACBC/ABACBC/Ahh ccc chch chcchc

..., respectively. The portion of the cubic packing is defined as the ratio between the number of layers of cubic symmetry in a period by the total number of layers, that is, $p = \frac{c}{c + h}$. The polytypes mentioned previously have p = 0, 1, 0.5, 0.6, respectively.

2. Details of the Calculation

2.1. The Schrodinger equation for an electron in a crystal is

$$H\phi_k(\mathbf{r}) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V_c(\mathbf{r})\right]\phi_k(\mathbf{r}) = E(k)\phi_k(\mathbf{r}), \qquad (2-1)$$

where $V_c(\mathbf{r})$ is the self-consistent crystal potential. The pseudo-potential method for finding the energy levels in a crystal consists of solving the equation

$$H_p v_k(\mathbf{r}) = \left[- \mathbf{h} V^2 + V_{ps}(\mathbf{r}) \right] v_k(r) = E(k) v_k(\mathbf{r}), \qquad (2-2)$$

instead of Eq. (2-1).

In equation (2-2), $v_k(\mathbf{r})$ is the smooth part of $\phi_k(\mathbf{r})$ (Ref. 10) and can be represented by plane waves as

$$v_{k}(\mathbf{r}) = \sum_{\mathbf{B}} \alpha_{\mathbf{B}}(k) e^{i(\mathbf{k}-\mathbf{B})\cdot\mathbf{r}}$$
(2-3)

where B are reciprocal lattice vectors; $V_{ps}(\mathbf{r})$ is the small, non local pseudopotential. The energy eigenvalues are the same for Eqs. (2-1) and (2-2).

We assume that the pseudo wave function $v_k(\mathbf{r})$ is a slowly varying function of the position compared to the core wave function for distances of the order of the ion radius. For this case, the pseudo-potential $V_{ps}(\mathbf{r})$, in good aproximation, can be taken as a local potential^{11,12}. Since $V_{ps}(\mathbf{r})'$ has the periodicity of the lattice it can be expanded as

$$V_{ps}(\mathbf{r}) = \sum_{\mathbf{B}} W(\mathbf{B}) e^{i\mathbf{B}\cdot\mathbf{r}} .$$
(2-4)

Inserting Eqs. (2-4) and (2-3) into (2-2), we get

$$\sum_{\mathbf{B}} \alpha_{\mathbf{B}}(k) \left\{ \left[\frac{\hbar^2}{2m} (\mathbf{k} - \mathbf{B})^2 - E(k) \right] \delta_{\mathbf{B}, \mathbf{B}'} + W_{(\mathbf{B} - \mathbf{B}')} \right\} = 0.$$
(2-5)

The eigenvalues are given by the zeros of the

$$det\left[\left[\frac{\hbar^2}{2m}(\mathbf{k}-\mathbf{B})^2 - E\right]\delta_{\mathbf{B},\mathbf{B}'} + W_{(\mathbf{B}-\mathbf{B}')}\right] = 0, \qquad (2-6)$$

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which is a N x N determinant, where N is the number of plane waves in the expansion (2-3).

The Fourier coefficients of the pseudopotential $W(\mathbf{B})$ can be written as¹³

$$W(\mathbf{B}) = S^{S}(B)o^{S}(B) + iS^{A}(B)o^{A}(B), \qquad (2-7)$$

where

$$\omega^{S} = n \cdot \frac{1}{2} (W^{Zn} + W^{S}), \tag{2-8a}$$

$$\omega_{\perp}^{A} = n \cdot \frac{1}{2} (W^{Zn} - W^{S}), \qquad (2-8b)$$

$$S^{S} = \frac{1}{n} \sum_{i} [\exp\left(-i\mathbf{B}_{h} \cdot \mathbf{s}_{i}^{Zn}\right) + \exp\left(-i\mathbf{B}_{h} \cdot \mathbf{s}_{i}^{S}\right)], \qquad (2-9a)$$

$$S^{A} = -\frac{l}{n} \sum_{i} \left[\exp\left(-i\mathbf{B}_{h} \cdot \mathbf{s}_{i}^{Zn}\right) - \exp\left(-i\mathbf{B}_{h} \cdot \mathbf{s}_{i}^{S}\right) \right], \qquad (2-9b)$$

where *n* is the number of atoms per cell, W^{Z_n} and W^S are the Fourier coefficients of the pseudopotentials of the Zn and S atoms, respectively. The vectors \mathbf{s}_i^t characterize the atom t inside the unit cell and the index i runs over all atoms inside the cell.

2.2. The structure factors are calculated for four and six layer polytypes of ZnS. For four layers (*ABAC*) there are four molecules of ZnS per cell.

The locations of Zn and S atoms in the unit cell are

$$s_{1}^{Zn} = (0, 0, 0); \ s_{2}^{Zn} = \left(\frac{\bar{1}}{3}, \frac{\bar{1}}{3}, \frac{1}{4}\right); \ s_{3}^{Zn} = \left(0, 0, \frac{2}{4}\right); \ s_{4}^{Zn} = \left(\frac{1}{3}, \frac{1}{3}, \frac{3}{4}\right);$$

$$s_{1}^{S} = (0, 0, u); \ s_{2}^{S} = \left(\frac{\bar{1}}{3}, \frac{\bar{1}}{3}, \frac{1}{4} + u\right); \ s_{3}^{S} = \left(0, 0, \frac{2}{4} + u\right);$$

$$s_{4}^{S} = \left(\frac{1}{3}, \frac{1}{3}, \frac{3}{4} + u\right), \qquad (2-10b)$$

where the coordinates are given in terms of the non orthogonal vectors **a**,, **a**,, and **a**,, which satisfy

$$|\mathbf{a}_1| = |\mathbf{a}_2| = a, \ \mathbf{a}_1 \cdot \mathbf{a}_3 = \mathbf{a}_2 \cdot \mathbf{a}_3 = 0, \ \mathbf{a}_1 \cdot \mathbf{a}_2 = -\frac{a^2}{2}, \ |\mathbf{a}_3| = pa \sqrt{\frac{2}{3}} = c.$$

(2-11)

Here, a is the lattice distance and p is the number of layers in the polytype.

When we say plane A of atoms, we mean plane A of Zn atoms and plane A of S atoms separated by the distance u. We take u = 3/8.

For six layers ABACBC, we have six molecules per cell. The vectors which characterize the atoms inside the cell are found in the same way as for four layers.

Inse	erting the	e vectors	s s _i in	ito e	expressions	(2-9a)	and	(2 - 9 <i>b</i>),	we	calculate
the	structure	e factors	for e	ach	reciprocal	lattice	vect	or.		

#	z	G	 G ²	ω^{A}	ω	S ^S	S ^A
1	1	000	0			1	0
2	2	001	.18692		_	0	0
3	2	002	.74770		-	0	0
4	2	003	1.68232		_	0	0
5	6	100	2.66667	-	24	.25 + 0.0i	0
6	12	101	2.85359	.23	22	.06 + .15i	.15 + .37i
7	2	004	2.99079	.23	-	0	i
8	12	102	3.41436	.19	19	.37 + .37i	.37 + .37i
9	12	103	4.34898	.12	15	.37 + .15i	.15 + .06i
10	2	005	4.67310		-	0	0
11	12	104	5.65745	.10	_	0	.25i
12	2	006	6.72927	_		0	0
13	12	105	7.33977	.05	.02	.37 + .15i	.15 + .06i
14	6	210	8.	-	.03	1	0
15	12	211	8.18692		-	0	0
16	12	212	8.74770		_	0	0
17	2	007	9.15928	-		0	0
18	12	106	9.39594	.03	.06	.37 + .37i	.37 + .37i
19	12	213	9.68322	-	—	0	0
20	6	200	10.66667	-	.07	.25	0
21	12	201	10.85359	.02	.07	.06 + .15i	.15 + .37i
22	12	214	10.99079	.02	-	0	i
23	12	202	11.41436	.02	.07	.37 + .37i	.37 + .37i
24	12	107	11.82595	.02	.06	.06 + .15i	.15 + .37i
25	2	008	11.96314	-	.06	1	0
26	12	203	12.34898	.02	.06	.37 + .15i	.15 + .06i
27	12	215	12.67310	-	-	0	0
28	12	204	13.65745		-	0	0
29	12	108	14 62981		.03	.25	0
30	12				-	0	0

TABLE I. Column 3 contains the coordinates of the vector G with respect to the primitive translation vectors of the reciprocal lattice, where the **first** two form an angle of 60°. Column 4 contains the magnitude of G where $c = 4a(2/3)^{1/2}$. Columns 5 and 6 contain the form factors for the four layer **polytype in** Ry. Columns 7 and 8 contain the structure factors for the four layer polytype. The number z in column 2 is the number of vectors G with the same magnitude.

#	Z	G	 G ²	ω^{A}	ω^{s}	S ^s	S ^A
1	1	000	0			1	0
2	2	001	.08308	_	_	0	0
3	2	002	.33231	_	<u> </u> .	0	0
4	2	003	.74770	_	_	0	0
5	2	004	1.32924	-	-	0	0
6	2	005	2.07693	_	_	0	0
7	6	100	2.66667	-	24	.50 + .29i	0
8	12	101	2.74974	.23	24	1411i	.035 + .26i
9	14	102	2.99079	.22	22	.50 + .50i	.50 + .50i
10	12	103	3.41436	.19	19	.32 + .32i	.42 + .13i
11	12	104	3.99590	.14		0	50i
12	2	007	4.07079	·	-	0	0
13	12	105	4.74360	.11	12	.16 + .21i	24 + .04i
14	2	008	5.31695	_	_	0	0
15	12	106	5.65745	.10	06	.29 + .29i	2929i
16	2	009	6.72927		_	0	0
17	12	107	6.73746	.06	01	.10 + .04i	2510i
18	12	108	7.98262		.03	.25 + .14i	0
19	6	210	8.	_	.03	.50 + .29i	0
20	12	211	8.08308	.04	.03	1004i	.25 + .10i
21	2	0010	8.30774		-	0	0
22	12	212	8.33231	.03	.03	.14 – .14i	.14 – .14i
23	12	213	8.74770	.03	.04	.53 + .07i	2203i
24	12	214	9.32924	.03		0	.29
25	12	109	9.39594	.03	.06	.18 + .13i	.42 + .32i
26	2	0011	10.05236	—	_	0	0
27	12	215	10.07693	.02	.06	.16 + .21i	.07 + .09i
28	6	200	10.6667		.07	.50 + .29i	0
29	12	201	10.74974			0	0
30	12	1010	10.97441	.02	.07	.29 – .29i	.29 – .29i
31	12	216	10.99079	.02	.07	.11 – .39i	11 + .39i
32	12	202	10.99898	.02	.07	–.29 + .29i	28 + .28i
33	12	203	11.41436	-	-	0	0
34	22	0012	11.96314	.02	_	0	i
35	12	204	11.99590	.02	_	0	.29 + .50i
36	12	217	12.07079	.02	.07	.09 + .07i	.21 + .16i
31	12	1011	12./1903	.01	.05	.26031	$.1101_1$
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TABLE II. Column 3 contains the coordinates of the vector G with respect to the primitive translation vectors \mathbf{b}_1 , \mathbf{b}_2 , \mathbf{b}_3 where b, $\mathbf{b}_2 = \mathbf{b}^2/2$. Column 4 contains the magnitude of G where $c = 4a(2/3)^{1/2}$. Columns 5 and 6 contain the form factors in Ry. In columns 7 and 8, we have the structure factors. In column 2, z is the number of vectors G with the same magnitude.

The form factors are taken from Ref. 2, where they were calculated for a two layer (AB) ZnS, as explained in the introduction. The form factors are functions of the magnitude of the reciprocal lattice vectors. Since the reciprocal space for higher order polytypes are not the same as the two

layer polytype, we had to interpolate the form factors. In table I, we show the structure factors, the form factors, the vector **G** and the magnitude of the vector $|\mathbf{G}|$ for four layers, where

$$\mathbf{B} = \frac{\pi \sqrt{2}}{a} \mathbf{G}.$$
 (2-12)

Table II shows the same quantities for six layers.

2.3. Replacing the values of the structure factors and form factors so obtained in Eq. (2-7), we can determine the potential. Next, the matrix (2-6) can be formed for two, four and six layer polytypes of ZnS. The four layer polytype has four molecules of ZnS per cell. Each molecule has 8 valence electrons. Consequently, we have 32 valence electrons per cell. We need to solve Eq. (2-6) for 16 occupied valence bands and 16 empty conduction bands.

The number of terms in the expansion (2-3) which determines the size of the matrix is related to the convergence that we are looking for. Using the Lowdin-Brust scheme^{14,15}, it is possible to include more terms in the expansion (2-3) without increasing the size of the matrix to be diagonalized. This is done in the following way. The set of N plane waves, considered in (2-3) is divided into two sets: the basic set, which is treated exactly, contains M plane waves whose reciprocal lattice vectors go from

$$|\mathbf{k} - \mathbf{B}_1|^2 = E_1$$
 to $|\mathbf{k} - \mathbf{B}_M|^2 = E_M$. (2-13)

The set of N-M plane waves, whose reciprocal lattice vectors satisfy

$$|\mathbf{E}_{M}|^{2} \leq |\mathbf{k} - \mathbf{B}_{\lambda}|^{2} \leq E_{N}, \qquad (2-14)$$

enter the calculation through perturbation theory.

For four layers, if we choose $E_M = 8$ and $E_1 = 18$, we have to diagonalize an approximate 80 x 80 matrix with approximately 300 more plane waves added as perturbation. The convergence is of the order of 0.1 eV. For six layers, however, we did not increase the cut off energy due to practical computational difficulties. As a consequence, the convergence for six layers is worse than 0.1 eV.

2.4. If we neglect life-time broadening effects, such as those resulting from phonons and impurity scattering, and consider only vertical band to band transitions, the imaginary part of the dielectric constant $\varepsilon_2(\omega)$ is given by^{15,16,17}

$$\varepsilon_2(\omega) = \frac{2\pi e^2 h}{3m^2 \omega^2} \sum_{n,m} \int_{B \cdot \mathbb{Z}} \frac{2}{(2\pi)^3} \left[\hat{e} \cdot \mathbf{S}_{m,n} \right]^2 \delta \left[E_n(k) - E_m(k) - \hbar \omega \right] d\mathbf{k}, \quad (2-15)$$

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where \hat{e} is the polarization of the light, m and n the valence and conduction band indices and

$$\mathbf{S}_{n,m} = \int v_{n,k}^*(\mathbf{r}) \nabla v_{m,k}(\mathbf{r}) d\mathbf{r}.$$
 (2-16)

The imaginary part of the dieletric constant was calculated for four layers only. It was done in a way similar to that used by Collins, Euwema *et al.*¹⁷. A mesh of 112 equally spaced points is constructed inside a section of 1/24 of the Brillouin Zone, Fig. 1.



Fig. 1. Brillouin zone for he:cagonal lattice, with symmetry points and section of the zone where the matrix is diagonalized.

The eigenvectors and eigenvalues of Eq. 2-6 are calculated for all points of the crude mesh mentioned above. A fine mesh of 1000 points is placed around each point of the crude mesh. The energy at each point in the fine mesh, $E_p(\mathbf{k}_i + 6)$ is given by

$$E_p(\mathbf{k}_i + \boldsymbol{\delta}) = E_p(\mathbf{k}_i) + \boldsymbol{\delta} \cdot \nabla E_p|_{\boldsymbol{\delta}=0}, \qquad (2-17)$$

where $E_p(\mathbf{k}_i)$ is the eigenvalue of Eq. (2-6) at the crude mesh point \mathbf{k}_i , and

$$\nabla_k E_p(\mathbf{k}) = \frac{\hbar^2}{m} \sum_j \alpha_j^{(p)*} \alpha_j^{(p)} \mathbf{k}_j, \qquad (2-18)$$

where the a's are the eigenvectors of Eq. (2-5).

The imaginary part of the dielectric constant, $\varepsilon_2(\omega)$, is calculated for energies going from 0 to 12 eV. This range of energy is divided in bins of size 0.04 eV. The energies are calculated at points $\mathbf{k} + 6$. Then $E(\mathbf{k} + 6)$ is divided by 0.04 to see which bin the contribution

$$\frac{S_{n,m}^2}{|E_n - E_m|^2}$$
(2-19)

goes to, where $E_{,-}E_{m} \simeq \hbar\omega$, as in Eq. (2-15).

From $\varepsilon_2(\omega)$, we calculated the real part of the dielectric constant $\varepsilon_1(\omega)$. The real part of the dielectric constant and the reflectivity $R(\omega)$ are given by the relations

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\xi \varepsilon_2(\xi)}{\xi^2 - \omega^2} d\xi, \qquad (2-20)$$

$$R(\omega) = \frac{[n(\omega) - 1]^2 + k(\omega)^2}{[n(\omega) + 1]^2 + k(\omega)^2},$$
 (2-21)

where $n(\omega)$ and $k(\omega)$ are given by

$$\varepsilon_1(\mathbf{0}) = \mathbf{n}^{\mathbf{Z}} - \mathbf{k}^2, \tag{2-22}$$

$$\varepsilon_2(0) = 2\mathbf{n}\mathbf{k}.\tag{2-23}$$



Fig. 2. Variation of the band-gap with the structure of ZnS.

Fig. 2 shows the gap decrease of the polytypes with respect to the increasing portion of the cubic packing. We can see the increase in the uncertainty in the results as we increase the order of the polytype. For six layers we kept approximately the same number of plane waves in the expansion of the wave function as for four layers. The six layer unit cell is more crowded than the four layer one. The wave function should oscillate more in the six layer unit cell. So we need more terms in expansion (2-3) to get a better representation of the wave function.

To obtain convergence of the order of 0.1 eV for six layers we would have to use such a large matrix that we would exceed the memory of the computer (CDC 6600).

Fig. 3 shows the imaginary part of the dielectric constant. Fig. 4 shows the real part of the dielectric constant and in Fig. 5 we have the reflectivity as calculated theoretically. We also present the experimental reflectivity determined by Baars. We notice that our results agree with the experimental one with respect to the location of the peaks of reflectivity but not with respect to the ntensity of the peaks. In our calculation, the maximum intensity occurs at energies around 9.5 eV which corresponds to peak no. 4 in Fig. 6. 11 addition, the intensity of peak number 1 is less than 100. What we plot in Fig. 3 is $\overline{\epsilon}_2(\omega)$ given by

$$\bar{\varepsilon}_2(\omega) = \frac{\varepsilon_2(\omega)}{|\varepsilon_2(\omega)|_{Max}} \times 100, \qquad (2-24)$$

where $\varepsilon_2(\omega)$ is the contribution found in each bin after the calculation is over.



Fig. 3. Imaginary part the dielectric constant for a four layer polytype of ZnS



Fig. 4. Real part of the dielectric constant for a four layer polytype of ZnS.

We can have a rough idea of the perturbation caused by the polytypism by comparing the energy levels (along the A line, in particular at the point A) of the four layer polytype, with wurtzite, but considering the Brillouin zone of wurtzite divided in half along the \mathbf{b}_3 direction and folding the energies of the second half into the first half. This is shown on table III where the first column represents the energies at point A as calculated by Cohen and Bergstresser for the two layer polytype ABAB.... The second column gives the values of the energy at the middle point between Γ and A for the two layer polytype, as obtained by Cohen and Bergstresser. The third column shows the energies at the same point as the second column, but for the four layer polytype ABACABAC....



Fig. 6. Reflectivity spectra of 4H ZnS as determined experimentally in Baars.

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CB (two layers)	Zone divided	four layers
- 2.5	- 3.5 - 3.5	- 3.8 - 3.5
- 2.5	7 7	1.0 9
3	4 4	3 2
3	2 2	2 1
5.3	4.8 4.8	4.0 4.0
5.3	5.3 5.3	5.7 5.7
8.3	8.4 8.4	8.6 8.6
8.3	8.6 8.6	8.6 8.7

TABLE III. The first column shows the energies (in eV) for wurtzite as calculated by Cohen and Bergstresser for the symmetry point A. The second column shows the same energies but with the Brillouin zone divided in half. The third column is the result for four layers for the same point A.

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